BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1927.

General, Physical, and Inorganic Chemistry.

Infra-red spectrum of hydrogen. A. H. Poetker (Nature, 1927, **119**, 123—124).—The secondary spectrum of hydrogen has been extended to 9300 Å., about 170 lines being measured in addition to those observed by Allibone (A., 1926, 873). In a practically pure monatomic spectrum, the fourth, fifth, sixth, seventh, and eighth members of the Paschen series were obtained, the wave-lengths agreeing with those calculated from the Bohr formula.
A. A. Eldridge.

Fine structure of the Balmer lines of hydrogen. N. A. Kent, L. B. Taylor, and H. Pearson (Nature, 1927, **119**, 163).—Values of $\Delta\lambda$ were obtained as follows: (25 milliamp./cm.^{2}) H_α 0·1370, H_β 0·0791, H_γ 0·0669 Å.; (13 milliamp./cm.^{2}) H_α 0·1391 Å. A third component on the longer wave-length side of λ' is also present.
A. A. Eldridge.

Continuous spectrum of hydrogen. O. Oldenberg (Z. Physik, 1927, **41**, 1—7).—The continuous spectrum obtained from a discharge tube filled with hydrogen is shown to be due to hydrogen, and not to water vapour. The addition of argon suppresses this continuous spectrum while simplifying the bands in the Schumann region, thus showing the two spectra to be independent. Pressure variation, addition of helium and neon, variation of current density, and effect of a magnetic field show the spectrum to be homogeneous and probably due to a homogeneous elementary process. A minimum intensity at 4000° Å. is observed in canal rays and is explained as being due to the superposition of the limit of the series spectrum of the atom.
W. E. Downey.

Absorption coefficient of helium for its own radiation. A. Wolf and B. B. Weatherby (Physical Rev., 1927, [ii], **29**, 135—140).—The mass absorption coefficient of helium for its own radiation in the extreme ultra-violet is $1{\cdot}24(\pm0{\cdot}02)\times10^7$ in the pressure range 0·016—0·040 mm. Below 0·016 mm., the coefficient increases rapidly with decrease in pressure.
A. A. Eldridge.

Structure of the third order spectra of oxygen (O III). C. Mihul (Compt. rend., 1927, **184**, 89—91).—Four multiplets of the same system of triplets and four multiplets of a system of quintuplets are added to those previously found for the third order spectrum of oxygen (this vol., 3). The wave-lengths and intensities of the various combinations are given in full.
J. Grant.

Hyperfine structure in the neon spectrum. G. Hansen (Nature, 1927, **119**, 237).—All neon lines which arise from an *s*-term have a component of shorter wave-length, of separation varying according to the term concerned, apparently due to a multiplicity in the *s*-levels. There are also evidences of a fine structure in the *pd* series lines.

The mercury line 4916 Å. consists of five components of separation +0·098 cm.$^{-1}$ (2), +0·056 (4), ±0 (10), −0·066 (3), −0·121 (5).

The components $^3P_2$ and $^3P_1$ of the helium line 5876 Å. have been resolved; the frequency differences are: $^3P_2-^3P_1$ 0·075 cm.$^{-1}$; $^3P_1-^3P_0$ 0·98 cm.$^{-1}$
A. A. Eldridge.

Electric field near the surface of the atoms of certain elements as deduced from the doublet separations of their spectra. N. R. Sen (Phil. Mag., 1927, [vii], **3**, 209—213).—By an extension of the results of Landé (A., 1924, ii, 711) to the doublet series of aluminium, gallium, indium, and thallium and to the triplet series of zinc and cadmium, it has been shown that the effective charge influencing the electron orbits near the aphelion is practically the same for all six elements. With zinc and cadmium, the aphelion of the *p*-orbit must be under the influence of the one electron moving in the *s*-orbit. From the constancy of the results and the agreement with the other four elements, it is concluded that in their cases the first *p*-orbit is influenced by only one of the two electrons moving in the *s*-orbits.
A. E. Mitchell.

Series of the argon spectrum. K. W. Meissner (Z. Physik, 1927, **40**, 839—875; cf. A., 1926, 766, 1186).—A continuation of the former work, giving wave-lengths and combinations from the extreme ultra-violet, 797·68, down to 9766·58 Å.
E. B. Ludlam.

Extension of doublet laws in the first long period to chromium and manganese. R. C. Gibbs and H. E. White (Proc. Nat. Acad. Sci., 1926, **12**, 675—677).—The regular and irregular doublet laws of stripped atoms have been shown (A., 1926, 874) to hold for the *N*-doublets for K I, Ca II, Sc III, Ti IV, and V V. Recent data on chromium and manganese in the extreme ultra-violet have made it possible to extend these laws to include Cr VI and Mn VII. Further measurements confirm the choice of lines for the V V doublet.
J. S. Carter.

Arc and spark spectra of iron in the extreme ultra-violet. L. Bloch and E. Bloch (Ann. Physique, 1926, [x], **6**, 409—451).—A more detailed account of work already published (A., 1926, 650).

Resonance radiation of zinc. P. Soleillet (Compt. rend., 1927, **184**, 149).—It has been shown

that each of the resonance radiations of zinc 3076 ($1S-2p_2$) and 2139 ($1S-2P$) excites only radiations of the same wave-length (cf. A., 1926, 766). Similar confirmatory results have been obtained for cadmium.
J. Grant.

Spark spectra of bromine. L. Bloch and E. Bloch (Compt. rend., 1927, **184**, 193—195).—The method previously described (A., 1925, ii, 611) has been applied to the analysis of the spark spectra of bromine between the red and extreme ultra-violet regions. A few are rays of long wave-length and numerous spark rays extending into the extreme ultra-violet region were observed. The latter fall into two distinct groups (the wave-lengths and intensities of which are given in full), and are attributed to the ionised atoms Br II and Br III. A few of the rays observed in the same region are due to a higher degree of excitation.
J. Grant.

Spectrum of krypton in the extreme ultra-violet. L. B. Taylor (Proc. Nat. Acad. Sci., 1926, **12**, 658—659).—The following wave-lengths are recorded: 1235·87, 1164·90, 1074·52, 1067·11, 1051·97, 1041·38, and 1003·46 Å., the first two being resonance lines. The frequency difference for the resonance pair is 4930, a value repeated in other parts of the spectrum.
J. S. Carter.

Flash arc spectrum of rubidium. F. H. Newman (Phil. Mag., 1927, [vii], **3**, 229—235).—With an applied voltage of 120 volts and at a pressure below 10^{-3} mm., an intermittent arc could be struck between an iron anode and a rubidium cathode. The radiation from this arc comprised 69 lines from 6517 to 3081·6 Å., and included most of the enhanced lines of rubidium as well as the ordinary arc lines. All the spark lines, with the exception of those at 3851·9, 3833·94, 3492·5, 3321·61, and 3286·6 Å., noted by Exner and Haschek, and all the induction spectral lines noted by Dunoyer (A., 1922, ii, 729), appear in the flash arc spectrum. A bright line at 4763 Å. has not been reported by previous experimenters. The optical centre of the group of enhanced lines developed in the flash arc is in the neighbourhood of 4070 Å. The spectrum is analogous to the red krypton arc spectrum and points to a similarity in structure between the ionised rubidium and the normal krypton atoms.
A. E. Mitchell.

Intensity-ratio for the doublets in the principal series of the alkali metals. H. Kohn and H. Jakob (Physikal. Z., 1926, **27**, 819—825).—The relative intensities of the components of doublets in the principal series of rubidium and cæsium have been measured when the lines are excited in a flame. The results do not agree with the values expected on the basis of the Burger–Dorgelo relationships between intensity and inner quantum numbers. The question is discussed as to whether the number of centres concerned in line emission from the flame is so small that the relative intensity of the doublet components is unaffected by the characteristic absorption. The "line absorption" has been investigated for the components at the same time as the brightness of the line. When the line absorption becomes very small, the observed intensity ratio of the doublet components corresponds with the "true" ratio for a very small number of centres. The line absorption does not, however, become zero, and the Gouy–Ladenburg–Reiche relations between line absorption and number of centres can be compared with experiment. The intensity ratio is not constant at 2 : 1, but increases with increasing term number in the principal series (cf. A., 1922, ii, 6, 194, 242).
R. A. Morton.

Intensity-ratio for the doublets in the principal series of the alkali metals. C. Füchtbauer and H. Meier (Physikal. Z., 1926, **27**, 853—856).—Both in respect of the shape of the curve and the ratio of half-breadths, the broadening of the *D*-lines of sodium through the presence of foreign gases (hydrogen, argon, nitrogen) resembles the broadening for the 2537 line of mercury under similar conditions. It is shown by experiments on the broadening of absorption lines in the principal series of cæsium by foreign gases that the intensity ratio of the doublets does not conform with the expected 2 : 1 value. The ratio actually increases to 5·6 : 1 for the third pair in the series.
R. A. Morton.

$1s-md$ Series of cæsium and the other alkali metals. G. M. Shrum, N. M. Carter, and H. W. Fowler (Phil. Mag., 1927, [vii], **3**, 27—31).—It has been shown that the $1s-md$ combination lines of the alkali metals can be excited directly by means of a direct-current arc between carbon electrodes well coated with a salt of the alkali metal. By this means, six members of the $1s-md$ series of cæsium between 6894·7 and 3391 Å., not previously observed in emission, have been obtained. The measurements are in good agreement with the values calculated from Fowler's "Report on Series Spectra." The observed wave-lengths are approximately the same as those obtained by Sowerby and Barratt (A., 1926, 213) in absorption experiments. It is suggested that the great differences, found by Sowerby and Barratt, between observed and calculated values have arisen from the omission by these authors of the ordinary vacuum correction for their calculated wave-lengths.
A. E. Mitchell.

Regularities in the arc spectrum of lanthanum. W. F. Meggers (J. Washington Acad. Sci., 1927, **17**, 25—35).—The relative terms, comprising 48 levels in the La I spectrum, the corresponding energies, level separations, and term combinations have been tabulated from data, shortly to be published by the author and by King and Carter, relating to the arc spectrum of lanthanum. The spectrum of lanthanum is compared with the spectra of scandium and of yttrium.
R. W. Lunt.

Arc spectrum of europium. Measurements made at normal pressure between 3100 and 2200 I.Å. S. Piña de Rubies (Compt. rend., 1927, **184**, 87—89; cf. A., 1926, 986).—A list of rays belonging to europium and their intensities is given for wave-lengths of range 3100—2200 I.Å. Urbain's pure europium gave more lines than Auer's mixed europium. Lines obtained by previous investigators which were not found by the author are enumerated and attributed to impurities, particularly iron.
J. Grant.

Continuous spectrum of mercury. H. Volkringer (Compt. rend., 1927, **184**, 150—151).—A relation between the intensity of radiation of the continuous spectrum of mercury and the frequency is deduced mathematically from the author's hypothesis of the distribution of energy in the visible portion of the continuous spectrum of mercury vapour. The curve obtained is in satisfactory agreement with that given by the experimental results. The theory postulates the existence of vibrators composed of groups of atoms, formed as a result of atomic excitation by the spectral rays, and subsequent production of a dipole capable of uniting with a neutral or other excited atom. J. GRANT.

Line spectra of the isotopes of mercury and chlorine. F. A. JENKINS (Physical Rev., 1927, [ii], 29, 50—58).—The lines 5461, 4359, 4078, and 4047 Å. of two sample-pairs of mercury of at.-wt. differences 0·124 and 0·180, respectively, showed no shift greater than 3×10^{-4} Å., and the first two showed no differences in the relative intensities of the satellites. With chlorine, shifts of the order of 0·001 Å. were obtained, the at.-wt. difference of the sample-pair being 0·097. For chlorine, the discharge tube was provided with a trough-shaped platinum cathode on which silver chloride was fused; the tube was then highly evacuated and filled with hydrogen at 1 mm. pressure. A. A. ELDRIDGE.

Intensity changes in the lines of a mercury triplet. S. ESKELAND (Physikal. Z., 1927, 28, 89—92).—The triplet 5461 ($2p_3-2s$), 4358 ($2p_2-2s$), 4047 ($2p_1-2s$) has been investigated. The relative intensities of the lines are not changed when the applied voltage is changed from 120 to 460. On the other hand, at temperatures of 37° and 83°, which correspond with pressures of mercury in the ratio 1 : 25, the intensities are affected as follows: at 37°, 4·9, 24·4, 3·0; at 83°, 5·8, 18·4, 3·3, for λ 5461, 4358, and 4047, respectively. The middle component decreases in intensity, whilst the extreme lines increase as the temperature is increased. R. A. MORTON.

[Intensity changes of the lines of a mercury triplet.] L. VEGARD (Physikal. Z., 1927, 28, 92—93; cf. preceding abstract).—The significance of Eskeland's results is pointed out. The intensity-distribution within the triplet certainly varies, but whether the effect of pressure is to be ascribed to collisions or to absorption is not yet clear. R. A. MORTON.

Magnetic separation of the mercury line 5770 into a nonet of special type. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1926, 2, 479—480).—When resolved in a field of 27,000 gauss, the *p*-components consist of a triplet in which the separation amounts to ±0·083 Å., and in which the *n*-components are symmetrically situated about the initial position of the line, and consist each of three components separated from the initial line by ±1·0, ±1·083, and ±1·66 Å. R. W. LUNT.

Auroral green line 5577 A. D. A. KEYS (Nature, 1927, 119, 162).—The results of McLennan, McLeod, and McQuarrie (A., 1926, 985), indicating that the line is primarily due to oxygen, are confirmed. A. A. ELDRIDGE.

Intensity and width of spectral lines. B. TRUMPY (Z. Physik, 1926, 40, 594—617; cf. A., 1926, 101; Holtsmark, *ibid.*, 102).—Results with mercury vapour instead of sodium, as in the earlier experiments, lead to the same conclusions. Different foreign gases were introduced, the total pressure being kept constant whilst the pressure of mercury vapour was varied. The total widening is satisfactorily accounted for as the sum of the effects due to collisions and the coupling of the electric fields of the molecules. E. B. LUDLAM.

Spectral series of bismuth. V. THORSEN (Z. Physik, 1926, 40, 642—647).—With the help of some new lines, the terms and combinations of the spectrum are worked out and a scheme is constructed. E. B. LUDLAM.

Wave-length of ruthenium $K\beta_1$. F. H. LORING (Chem. News, 1927, 134, 49).—The wave-length of this line has been determined from the values assigned by Auger and Dauvillier to the *K* lines, from the exact values of $K\alpha_1$ and $K\alpha_2$, and from the values of $(\nu R^{-1})^{\frac{1}{2}}$ of the *K* series. The mean of these and of the author's experimental value (cf. this vol., 87) is 0·57158 Å. R. W. LUNT.

Satellites of lines of *X*-rays. D. COSTER and M. J. DRUYVESTEYN (Z. Physik, 1927, 40, 765—774).—A new *X*-ray tube is described for fluorescence observations, with which satellites could be observed on the hard side of the lines, although the intensity was less than that obtained by cathode-ray excitation. The existence of these satellites indicates the simultaneous ejection of two electrons from the inner ring of the atom. The satellites on the soft side of the lines possessed normal intensity. Their interpretation is discussed. E. B. LUDLAM.

Absorption in the region of soft *X*-rays. E. R. LAIRD (Physical Rev., 1927, [ii], 29, 41—49).—The energy of soft *X*-rays from a tungsten-coated nickel target varies approximately as the square of the potential from 40 to 610 volts. Experiments with thin celluloid films support the view that the absorption varies as the cube of the wave-length, and that *K*-absorption discontinuities in celluloid occur between 300 and 600 volts. Values of μ/ρ for air are corrected (cf. Laird and Barton, *ibid.*, 1920, [ii], 15, 303) to 6·0, 6·25, 7·0, $7·6 \times 10^3$ at 600, 500, 400, 300 volts, respectively; for hydrogen, μ/ρ is about $1·8 \times 10^4$. A. A. ELDRIDGE.

Anomalous Zeeman effect of the mercury line 5791 and its satellite 0·124. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1926, 2, 383—386).—The behaviour of the line 5791 and its satellite 0·124 has been examined by an interferential spectroscope in fields up to 32,000 gauss. R. W. LUNT.

Stark patterns observed in helium. J. S. FOSTER (Proc. Roy. Soc., 1927, A, 114, 47—65; cf. A., 1924, ii, 511, 798; 1925, ii, 831).—Four Stark patterns, each constant within its appropriate spectral series, have been found in parhelium and orthohelium. A detailed analysis of these effects supports the Bohr perturbation theory of the Stark effect as developed by Kramers, which predicts corrections between the fine structure of the hydrogen lines and the components observed in high fields. The general characteristics of the Stark effect in both hydrogen and helium are reviewed, and found to differ mainly in the range of field strength at which the more interesting features appear. The work may be regarded as an extension to the observations of Stark and Nyquist, but definite reasons are advanced for an extensive revision of the analyses reported by Takamine and Kokubu (A., 1919, ii, 379). A modified Lo Surdo discharge tube is described.

L. L. Bircumshaw.

Dielectric constant and Stark effect for polyatomic dipolar gases with symmetrical molecules according to the wave-mechanics. C. Manneback (Physikal. Z., 1927, 28, 72—84).—Mathematical. The wave-mechanics and the matrix mechanics lead equally to the conclusion that the dielectric constant of an ideal polyatomic gas with two equal principal moments of inertia approaches the values indicated for high temperatures by the classical theory of Langevin and Debye.

R. A. Morton.

Stark–Lunelund effect. A. Weigl (Ann. Physik, 1927, [iv], 82, 1—15).—The light emitted by hydrogen canal rays is polarised so that the component vibrating in a direction parallel to the direction of motion is 30% stronger than the component at right angles. The polarisation is due to the moving atoms. An increased potential or pressure causes a changed intensity of the polarisation induced in this way. The polarisation persists in spite of collisions between moving and stationary atoms. Canal rays in nitrogen and in oxygen exhibit no polarisation.

R. A. Morton.

Polarisation of canal-ray light. R. Döpel and R. von Hirsch (Ann. Physik, 1927, [iv], 82, 16—24).—Hydrogen canal rays in air exhibit a polarisation of 1·12 for H_β which is independent of pressure, whilst for the nitrogen 4709 band the value is 1·00.

For air canal rays in hydrogen, there is no polarisation. For atomic hydrogen in molecular hydrogen the value falls from 1·37 at 3600 volts to 1·11 at 32,000 volts. For hydrogen in oxygen, the value 1·16±0·01 is independent of pressure and voltage. These and other results indicate that the polarisation of the emitted light depends on the nature of both the gases present and is in general absent in the absence of an exciting gas. R. A. Morton.

Intensities in the Stark effect of helium. J. M. Dewey (Physical Rev., 1926, [ii], 28, 1108—1124).—The observed intensities of the helium lines $2P-nM$, $2P-nm$, and $2S-4M$, where $n=4, 5, 6, 7$; $M=P, D, F$, etc., are in agreement with values calculated by application of the quantum theory of dispersion to the Stark effect. A. A. Eldridge.

Critical potentials and the heat of dissociation of hydrogen as determined from its ultra-violet band spectrum. E. W. Witmer (Physical Rev., 1926, [ii], 28, 1223—1241).—See A., 1926, 552.

Electron collisions in carbon monoxide. F. L. Mohler and P. D. Foote (Physical Rev., 1927, [ii], 29, 141—144).—The authors' values of the critical potentials for electron impact in carbon monoxide ("Origin of Spectra," 1922, 188) are correlated with recent analyses of the carbon monoxide band spectrum. The resemblance of carbon monoxide to metals of the second periodic group is in accord with the spectral classification which makes the 6-volt level a ^3P state and the 8-volt level a ^1P state. A. A. Eldridge.

Photo-electric electron emission and the optical absorptive power of potassium in relation to the gas content of the metal. R. Fleischer (Ann. Physik, 1927, [iv], 82, 75—86).—The selective photo-electric emission of electrons is connected with the use of light so polarised that the electric vector is parallel to the plane of incidence of the component. Outgassed potassium exhibits a maximum of selective absorption and of photo-electric emission at 313 $\mu\mu$ under these conditions, whereas if the metal is allowed to absorb hydrogen, the selective emission and absorption occur near 436 $\mu\mu$. When the photo-electric emission is plotted against the absorption at different wave-lengths, there is no selectivity for the outgassed metal, but with the hydrogen containing potassium, the maximum is enhanced. When the electric vector is perpendicular to the plane of incidence, both the photo-electric electron emission and the light absorption show no selectivity. If instead of a plane mirror a black body-cell is used, the outgassed metal exhibits the normal photo-electric emission, whereas if hydrogen is present, the maximum occurs at 436 $\mu\mu$. This selective effect also occurs with unpolarised light if hydrogen is present. R. A. Morton.

Experimental evidence of the thermal ionisation of elements. M. N. Saha, N. K. Sur, and K. Mazumdar (Z. Physik, 1926, 40, 648—651).—Metal vapour was distilled from a small silica furnace into a graphite vacuum furnace which could be maintained at 2000°. A potential of 1 volt across two graphite plates in the latter furnace produced no current for mercury, zinc, or cadmium, but for sodium or potassium a current was obtained large enough to be measured with a milliammeter.

E. B. Ludlam.

Thermionic experiments with a new source of positive ions. C. H. Kunsman (Proc. Nat. Acad. Sci., 1926, 12, 659—662; cf. A., 1926, 218, 685, 769).—A further study of the positive ion and the electron emission from reduced iron oxide–alkali or alkaline-earth oxide mixtures. Both types of emission satisfy Richardson's equation over a considerable temperature range. As before, the surface is defined in terms of ϕ_+ and ϕ_-, the equivalent voltages of the work function for the vaporisation of a positive ion and an electron, respectively. For cæsium and potassium, the values of ϕ_+ are 1·96 and 2·10 volts, respectively. Measurements with thoroughly reduced iron–barium mixtures show that the hot surface is a constant source of positive ions when used as anode, and of electrons when used as cathode, the values of ϕ_+ and ϕ_- being 2·12 and 3·49 volts, respectively. Somewhat similar results were obtained with calcium and strontium. Whenever it was found possible to measure both positive ion and electron currents for the same surface, ϕ_- was found to be greater than ϕ_+. At high temperatures, an appreciable vaporisation of iron occurs, but only in the form of neutral atoms. It is concluded that when an element is vaporised from a surface, the vaporisation will be in the form of positive ions if the electron work function ϕ_- of the surface is greater than the potential tending to hold the outer electron to the atom vaporised. With barium–iron mixtures, ϕ_- is not sufficient to remove both outer electrons, since no doubly-charged ions were observed in mass-spectrograph studies. Positive ion emission is largely an interface phenomenon and confined to a small part of the total surface. J. S. Carter.

Continuity of existence [of electrons]. D. B. Mair (Nature, 1927, **119**, 199).—The theory of relativity indicates that the existence of electrons is discontinuous. A. A. Eldridge.

Orbits and radiations of hydrogen electrons. T. Engset (Ann. Physik, 1927, [iv], 82, 143—154, 184—190).—Theoretical. R. A. Morton.

Deformation of electronic orbits in crystalline salts. K. Fajans (Rocz. Chem., 1926, **6**, 396—403).—Examples are given where measurements of the refraction of alkaline-earth fluorides indicate various degrees of deformation of electronic orbits.
R. Truszkowski.

Electrical discharge and the radiations emitted by gases and solids bombarded by slow electrons. A. Dauvillier (J. Phys. Radium, 1926, [vi], 7, 369—389).—A detailed account of work published earlier (cf. A., 1926, 330, 1196), to which is added a section on the bombardment of solids. Slow electrons give rise to a spectrum showing a feeble continuous background and intense characteristic lines, as found in the region of short-wave *X*-rays. The continuous spectrum appears to be governed by a different law. Various precautions are outlined which increase the accuracy of measurements of critical emission potentials, so that a new method is available for determining the principal levels of low energy for both light and heavy elements. Seven elements from boron to thorium have been studied in this way.
R. A. Morton.

Attribution to the secondary electrons of the action of *X*-rays on micro-organisms. J. J. Trillat (Compt. rend., 1927, **184**, 170—172).—Results of experiments show that the bactericidal action of secondary *X*-rays is due almost entirely to the bombardment of the microbes by the electrons arising from the radiator. W. Robson.

Cross-sectional curve of hydrogen chloride for slow electrons and its comparison with the argon curve. E. Brüche (Ann. Physik, 1927, [iv], 27, 25—38).—The curve cross-sectional area–electron velocity in volt$^{1/2}$ for hydrogen chloride shows a maximum at 3 volt$^{1/2}$. A special apparatus has been devised and a new source of error in the change of cross-section with time is disclosed. In general character, the curves for hydrogen chloride and argon are closely similar and show maxima at velocities of 3 volt$^{1/2}$ and 3·5 volt$^{1/2}$, respectively. Hydrogen shows a maximum at 1 volt$^{1/2}$, and it does not appear to affect the curve for hydrogen chloride. The argon curve corresponds with that due to the other rare gases, and the effect is ascribed to the completed outer shell of eight electrons. The comparison of argon with hydrogen chloride with its similarly completed octet supports this view if the resemblance between the curves is not fortuitous.
R. A. Morton.

Ionic mobilities in ammonia–hydrogen mixtures and an anomalous effect of ammonia. L. B. Loeb (Proc. Nat. Acad. Sci., 1926, **12**, 677—684; cf. A., 1925, ii, 7; 1926, 219; this vol., 86; Erikson, A., 1925, ii, 6).—Traces of ammonia in hydrogen and air attach themselves to positive ions to form a protective cluster of one or more molecules, which prevents the attachment of other bulky molecules and raises the mobility of the positive ion by as much as 30% without affecting the negative ion. In the presence of ether, however, the ether molecule is preferentially attached, and the observed mobility is that due to the superposed retarding effect of ether and ammonia molecules in hydrogen or air on a positive ion carrying an ether molecule (or molecules). The mobilities of both ions in ammonia–hydrogen mixtures decrease with increasing concentration of ammonia, the decrease following no simple law. The results are discussed and the importance of minute traces of foreign gases in work of this type is emphasised. J. S. Carter.

Ionisation of gases and the Saha equation. G. Homès (Bull. Acad. roy. Belg., 1926, [v], 12, 422—428).—Mathematical. The application of the Saha equation to the ionisation and excitation of gas molecules is considered. C. H. D. Clark.

Phenomenon of ionisation of mercury vapour at low pressures. R. Moens (Bull. Acad. roy. Belg., 1926, [v], 12, 429—436).—Experiments have been conducted on the ionisation currents set up when mercury ions, produced by the impact of electrons from a heated filament, fall on suitably placed anodes, the relation between applied *P.D.* and current being determined. It is found that no appreciable currents are detected until the ionisation potential is reached, after which the current increases rapidly with increasing *P.D.* If a primary stage of increasing *P.D.* is followed by a second stage of decreasing *P.D.*, a marked hysteresis occurs, the current being always stronger for a given *P.D.* during the second than during the primary stage. A subsequent temporary increase of current is generally observed during the second stage.
C. H. D. Clark.

Distribution of intensity in a positive-ray spectral line. I. M. C. Johnson (Ann. Physik, 1926, [iv], 81, 666—680; Proc. Physical Soc., 1926, 38, 324—334).—The extreme faintness of the light emitted by positive rays has hitherto required the use of instruments of low resolving power, so that the Stark and Döppler effects have been difficult to investigate for positive rays.

A technique has been developed employing interference analysis, the Merton wedge method for determining intensity distribution, and a relatively intense light source. The design of the tube and cathode necessary for an intense positive-ray light and the control of the intensity ratio of the Balmer and many-lined spectra are discussed in detail. The new technique discloses a line structure differing from that observed in ordinary discharge tube spectra.

The explanation of the structure in terms of Döppler and Stark components is compared with the theory of broadened lines in ordinary discharge tube spectra.
R. A. MORTON.

Distribution of intensity in a positive-ray spectral line. II. M. C. JOHNSON (Proc. Physical Soc., 1926, 39, 26—38; cf. preceding abstract).—Work is continued with the apparatus described previously. The direction of observation is here longitudinal, in order to isolate the Döppler effect in the "moving" spectrum; accordingly, a 6-prism spectrograph is substituted for the échelon previously used. The results are added to those of Stark, Paschen, Wilsar, and Krefft on the same spectrum, and the uncertainties in identifying atomic and molecular carriers are analysed. The distribution of velocities among the particles contributing to the "moving" spectrum is compared with the distribution of velocity in positive rays measured by the electromagnetic method. The appearance of the many-lined spectrum of hydrogen in the positive rays and the ratio of intensity of the "moving" and "resting" spectra are considered. The inverse square law of probability of electron capture, and some consequences of the work of Wien and Rüchart, are the most likely controlling factors in the several phenomena. C. J. SMITHELLS.

Scattering-absorption of hydrogen positive rays on passage through hydrogen. G. P. THOMSON (Z. Physik, 1926, 40, 652; cf. Conrad, A., 1926, 990).—Conrad's criticisms are answered and the improbability that his results are accurate is indicated. E. B. LUDLAM.

Passage of positively-charged particles through helium. A. J. DEMPSTER (Phil. Mag., 1927, [vii], 3, 115—127).—A study of the passage of very slow positively-charged particles through helium has shown that protons having velocities corresponding with *P.D.* between 14 and 900 volts pass through a large number of helium atoms without neutralisation and with only slight changes in velocity or direction. The loss of energy in penetrating the atom is probably less than that corresponding with 0·5 volt per collision. When hydrogen is mixed with helium, hydrogen-molecule ions are dissociated with a free path for dissociation about nine times the free path calculated on the kinetic theory for 900-volt protons. Helium ions are neutralised after about the first collision.
A. E. MITCHELL.

Mobility of ions in solution with particular reference to the separation of isotopes. E. R. JETTE (Phil. Mag., 1927, [vii], 3, 258—269).—Available theoretical and experimental material on the possibility of separating isotopes by methods depending on an assumed influence of the different masses of isotopic ions on their mobilities in solution, is examined. It is concluded that an experimental detection of a difference in the mobility of isotopic ions in solution is impossible by any method at present available.
A. E. MITCHELL.

Seventh report of the German committee on the determination of atomic weights. M. BODENSTEIN, O. HAHN, O. HÖNIGSCHMID, and R. J. MEYER (Ber., 1927, 60, [*B*], 1—20).—The report comprises a criticism of measurements of atomic weight by physico-chemical methods [mainly a reply to Moles (A., 1926, 654)] and by chemical gravimetric processes, and discussion of the progress in the isotope question as far as ordinary, non-radioactive elements are concerned. Alterations in the German atomic weight table of 1926 are not suggested. H. WREN.

Weight of the litre and atomic weight of argon. E. MOLES (Ber., 1927, 60, [*B*], 134—138).—The atomic weight, $A=39{\cdot}88$, adopted by the German Commission (1923) is based on the weight of the litre of crude argon, and is certainly low. The most probable weight of the litre of pure gas is 1·7833± 0·0001 g., from which the atomic weight $A=39{\cdot}94$ is deduced; this is regarded as a minimal value.
H. WREN.

Density, compressibility, and atomic weight of nitrogen. G. P. BAXTER and H. W. STARKWEATHER.—See this vol., 194.

Determination of the half-value period of polonium. M. A. DA SILVA (Compt. rend., 1927, 184, 197—199; cf. A., 1926, 877).—A constant saturation-current in pure argon ionised by the α-particles from polonium is obtained at 50 volts. The polonium is best deposited on a silver plate and covered with a thin mica leaf. Measurements of the rate of fall of the saturation-current during 8 months gave a value for the half-value period of polonium of 140·2 days. This agrees with most recent determinations. J. GRANT.

Heat of radiation of radium. (MLLE.) A. DORABIALSKA and D. K. YOVANOVITCH (Rocz. Chem., 1926, 6, 569—577).—The heat produced by the absorption of β- and γ-rays of radium by aluminium, copper, and lead is measured calorimetrically. The mean coefficient of absorption (μ/ρ) for β-rays in aluminium is 51·02, the values for the two different groups of β-particles, the heats of radiation of which are 10·4 and 3·0 g.-cal. per g. radium per hr., respectively, being 73·8 and 19·5. The heat of radiation due to α-particles is 129 g.-cal. R. TRUSZKOWSKI.

Comparison of the spectra of radon with those of uranium and thorium. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1926, 2, 390—394).—A table of the spectra of these substances from 6204 to 3089 Å. compiled from the data of Rutherford and Royds, Royds, Watson, and Nyswander, Lind and Moore. The results show that in the published spectra of uranium and of thorium, lines due to actinon and thoron have been included.
R. W. LUNT.

Joachimstal pitchblende residues and their capacity for emanating. J. MARKL (Physikal. Z., 1927, 28, 10—12).—Direct determinations of the radium content and of the evolution of radon in Joachimstal pitchblende residues are in agreement with those calculated from the uranium content and the known radium–uranium ratio. R. W. LUNT.

Anomalies associated with the γ-radiation of radium-*C*. K. W. F. KOHLRAUSCH (Physikal. Z., 1927, 28, 1—10).—A review of the literature dealing with the γ-radiation of radium-*C* in which the photoelectric computation of the energy distribution in the line spectrum of this radiation is discussed at length. It is shown that this distribution is in general agreement with observations on electron scattering; but the application of the Compton–Debye theory to the data relating to absorption and scattered radiation leads to considerable discrepancies. R. W. Lunt.

Scattering of gamma rays. L. H. Clark (Nature, 1927, **119**, 121—122).—Confirmatory experiments show that a comparatively soft radiation is produced from air penetrated by gamma rays. The effect on numerical results of lining the electroscope is considered. A. A. Eldridge.

Method of making H-particles audible. G. Ortner and G. Stetter (Physikal. Z., 1927, **28**, 70—72).—A new arrangement, comprising an ionisation chamber, a system of valve amplification connected to a loud speaker, and devices to reduce acoustical and mechanical disturbances is described. The noises caused by the entry of α- and H-particles can be distinguished, and the method appears to possess advantages over the scintillation method and the ordinary ionisation chamber.

R. A. Morton.

Synthesis and disintegration of atoms as revealed by the photography of Wilson cloud tracks. W. D. Harkins and H. A. Shadduck (Proc. Nat. Acad. Sci., 1926, **12**, 707—714; cf. A., 1923, ii, 720; Blackett, *ibid.*, 1925, ii, 256).—A more detailed account of work previously published (this vol., 87).

Breakdown of atoms at high pressures. P. W. Bridgman (Physical Rev., 1927, [ii], **29**, 188—191).—Thermodynamic evidence tends to indicate that in addition to atomic dissociation at high temperatures and comparatively low pressures, sufficiently high pressures are also capable at the ordinary temperature of reducing matter to an electrical gas of electrons and protons. A. A. Eldridge.

Chemistry of lightning. J. Estalella (Anal. Fís. Quím., 1926, **24**, 587—599).—The author discusses the chemistry of thunderbolts and lightning, and suggests that during the passage of the electric discharge the elements present in the air may suffer ultrachemical change, leading to the transitory formation of unstable atomic groupings.

G. W. Robinson.

Structure of nickel. H. Collins (Chem. News, 1927, **134**, 81—85).—Speculative.

Relation between the reciprocal impenetrability of matter and Pauli's exclusion principle. P. Ehrenfest (Nature, 1927, **119**, 196).—Mathematical. A. A. Eldridge.

Spinning electrons and protons. H. S. Allen (Nature, 1927, **119**, 237—238).—It is postulated that the proton, as well as the electron, may be capable of a quantised spin. A spinning electron is one example of a magneton; a quantised magneton was first described by McLaren (*ibid.*, 1913, **92**, 165).

A. A. Eldridge.

Theory of the spectra of diatomic molecules. L. Landau (Z. Physik, 1926, **40**, 621—627).—Formulæ are obtained, using the new quantum mechanics, for the frequencies of the band spectrum, for the intensities, and for the Stark and Zeeman effects.

E. B. Ludlam.

Electronic states and band-spectrum structure in diatomic molecules. II. Spectra involving terms essentially of the form $B(j^2-\sigma^2)$. R. S. Mulliken (Physical Rev., 1926, [ii], **28**, 1202—1222).—Evidence is adduced to show that the AlH, He_2, and certain other bands involve rotational terms essentially of the form $B(j^2-\sigma^2)$, the chief empirical properties of which are discussed. Additional confirmation is afforded of Kratzer's interpretation of the violet CN bands. The AlH bands fall under the classification $^1S-^1P$; it is predicted that the fourth positive CO bands, designated $^1S-^1P$ by Birge, will have the corresponding structure and missing lines. The three-branch " series " bands of helium are of the $^1S-^1P$ type, the three-branch bands 6400 and 4546 of the $^1P-^1S$ type and the six-branch band 5733 of the $^1P-^1D$ type. Revised values are given of various constants of molecular helium in its different electronic states. The band spectra of the alkalis and the halogens are considered; the Na_2 absorption bands in the green, and probably most alkali metal bands, are probably $^1S-^1P$. The red CN, BO-α, and CO^+ comet tail bands probably have a structure essentially the same as that of the ZnH, CdH, and HgH bands, and characteristic of the transition $^2S-^2P_{1,2}$. The " combination " bands of BO and CO^+, the NO third positive bands, and presumably Jevons' SnCl bands probably have a similar structure characteristic of $^2P_{1,2}-^2S$ transitions. The OH, CH, and MgH bands are discussed. A. A. Eldridge.

Interpretation of molecular spectra. F. Hund (Z. Physik, 1927, **40**, 742—764).—A qualitative expression for those features of band spectra which are due to the motions of the electrons is obtained. A system with one degree of freedom is examined, by the aid of quantum mechanics, of which the potential energy has several minima. The conditions for stationary states of such systems are considered, and an adiabatic correspondence is established between the states of two separated atoms or ions, of a diatomic molecule, and of a composite atom formed by the union of two atomic cores. These ideas are applied to the positively-charged hydrogen molecule, the neutral hydrogen molecule, and to polar molecules such as sodium chloride, of which the spectrum indicates dissociation into two oppositely-charged ions. E. B. Ludlam.

Measurement of absorptive power. E. C. C. Baly and R. W. Riding (Proc. Roy. Soc., 1927, **A**, **113**, 709—716).—The relative merits of the Hilger rotating sector photometric method and the Judd Lewis sector spectrophotometric method (J.C.S., 1919, **105**, 312) for the determination of extinction coefficients are discussed. The methods are compared by measuring, with both instruments, the absorptive powers of a thin glass plate, transmitting to about 254 μμ, of a neutral-tinted glass plate, and of standard solutions of potassium chromate and potassium and barium nitrates. The results given between 436 and 254 μμ agree well within the limits of experimental error (±2%). In the visible region, the photographic and von Halban's photo-electric methods (cf. A., 1921, ii, 145) agree with the visual methods. The error of the photographic method, which is ±2% in this region with the dispersion of a Hilger E_3 spectrograph, is probably greater than that shown by the photo-electric method and less than that of the visual method. In the region 240—330 μμ, the photo-electric method gives values which are uniformly smaller than those given by the two photometers. It is suggested that von Halban's results are subject to a wave-length error in this region. With solutions of barium and potassium nitrates, a new discrepancy is superimposed in the short-wave ultra-violet. L. L. Bircumshaw.

Oxygen bands in the ultra-violet. V. M. Ellsworth and J. J. Hopfield (Physical Rev., 1927, [ii], 29, 79—84).—A number of new bands have been observed, some of which have been measured and found to represent the $(n'-n'')$ 7—0, 8—0, 9—0, 10—0, 9—1, and 0—9 transitions as given by Birge's formula (*ibid.*, 1925, [ii], 25, 240).

A. A. Eldridge.

Absorption of light by ozone between 3050 and 3400 Å. J. Dutheil and (Mme.) M. Dutheil (J. Phys. Radium, 1926, [vi], 7, 414—416).—Ozone exhibits about 23 bands of low persistence in the region 3050—3400 Å. (Huggins' bands). The wave-lengths of maximum and minimum absorption and the corresponding absorption coefficients have been redetermined. The new data, when applied to the absorption of the atmosphere, yield results for the thickness of the ozone layer which are in agreement with results based on the great ultra-violet band (2550 Å.) of ozone. R. A. Morton.

Band spectra associated with silicon. W. H. B. Cameron (Phil. Mag., 1927, [vii], 3, 110—115).—When an arc was burned between silicon poles in air or oxygen at atmospheric pressure, the silicon oxide bands observed by de Gramont and de Watteville (A., 1908, ii, 909) were obtained. When the silicon arc was burned in a slow stream of oxygen at about 10 mm. pressure, the character of the radiation changed to an intense blue, and showed, in addition to the silicon oxide bands, a system of five or six bands with heads between 4393·4 and 4648·2 Å. It is suggested that this new band system has its origin also in the silicon oxide molecule. When an uncondensed discharge was passed through the vapour of silicon tetrachloride at very low pressures and oxygen was added in slight excess, the colour of the discharge was dark green, and was found to comprise a series of bands with heads extending from 3960·2 to 5677·6 Å. Most of the bands were degraded towards the red, and in many cases the fine structure was clearly visible at a considerable distance from the head. It is suggested that this system is the analogue of the comet-tail and associated bands of carbon monoxide. A. E. Mitchell.

Spectrographic identification of certain elements and the possibility of determination by means of the arc spectrum. II. Uranium. C. Porlezza and A. Donati (Annali Chim. Appl., 1926, 16, 622—636).—The spectrum obtained when a small quantity of the oxide U_3O_8 is placed on the positive carbon of an arc exhibits an intense continuous foundation, especially in the green region, where also the density of the spectral lines is the greatest; all the possible lines cannot therefore be identified. The spectrum may be simplified and the continuous basis rendered less pronounced by mixing the oxide with a diluent. When mixed with silica, which forms the predominating gangue in various uraniferous minerals, uranium is detectable by its arc spectrum when present to the extent of 0·05%, whilst with tricalcium phosphate as diluent, 0·5% of uranium, and with silicates of calcium. aluminium, alkali metals, etc., intermediate proportions of the metal may be detected. By mixing a mineral such as autunite or carnotite with definite proportions of silica and comparing the spark spectrum with those of mixtures of the oxide with silica, the percentage of uranium in the mineral may be determined very approximately. (Cf. this vol., 124.)

T. H. Pope.

Band spectra of carbon monoxide. R. T. Birge (Physical Rev., 1926, [ii], 28, 1157—1181).—A critical discussion. The known band spectra of neutral carbon monoxide comprise the fourth positive group of carbon, the Ångström CO bands, the Cameron bands, and the third positive group of carbon; those of ionised carbon monoxide are the comet-tail bands, the first negative group of carbon, and the Baldet–Johnson combination bands. The relation of the various systems is shown in diagrammatic and tabular form, and possible correlation with magnesium is considered. An analysis of the fourth positive group of carbon is tabulated, and data on the Ångström bands are collected. There is probably a triple electronic level common to the third positive group and the Cameron bands. A. A. Eldridge.

Effect of water on the infra-red emission from the flame and explosion of carbon monoxide and oxygen. W. E. Garner and C. H. Johnson (Phil. Mag., 1927, [vii], 3, 97—110).—The infra-red spectrum of carbon monoxide burning in oxygen has been mapped for the flame and for the explosion between 1·3 and 6·1 μ. Small quantities of water vapour depress the infra-red emission from the explosion, whilst at the same time they increase the rate of reaction. It is suggested that the reduction in the intensity of the infra-red emission, brought about by the addition of water, is due to collisions of water molecules with the freshly-formed molecules of carbon dioxide, which are known to emit infra-red radiation at 2·8 and 4·4 μ. In the absence of water, the carbon dioxide molecules give up their excess of internal energy as infra-red radiation, whilst in the presence of water they lose part or all of this energy by collision. The result is then that more energy is retained in the system, and leads to the observed increase in the rate of reaction. In this case, water vapour is only a special example of a number of substances which are known to depress or to accelerate infra-red emission. The term "energo-thermic catalysis" is proposed for the action of those substances which retard or accelerate the rate of attainment of thermal equilibrium in a reacting gaseous system.

A. E. Mitchell.

Spectra of NH compounds. E. HULTHÈN and S. NAKAMURA (Nature, 1927, **119**, 235—236).—The origin of the β-group of ammonia bands is referred to the NH dipole; new bands observed by Gleu (A., 1926, 992) are similarly referred. A *ν–m* diagram of the β-group is given. The initial state contains an electronic triplet, whilst the final state is a singulet; the final state, however, includes a rotational triplet of unknown nature. The nuclear spacing of the molecule in its final state is $r_0 = 1{\cdot}10 \times 10^{-8}$ cm. A ${}^3P \longrightarrow {}^1S$ transition is assigned to the β-group of the NH spectrum, where ${}^3P$ separations should agree in magnitude with those of carbon.

A. A. ELDRIDGE.

β Bands of nitric oxide. F. A. JENKINS, H. A. BARTON, and R. S. MULLIKEN (Nature, 1927, **119**, 118—119).—A comprehensive analysis of the β bands of nitric oxide has been made, and an interpretation put forward which is in agreement with theory. The internuclear distance in nitric oxide is computed to be, for the initial states, 1·44 and $1{\cdot}40 \times 10^{-8}$ cm., and for the final (normal) states 1·16 and $1{\cdot}14 \times 10^{-8}$ cm. A detailed account is promised.

A. A. ELDRIDGE.

Many-lined spectrum of sodium hydride. E. H. JOHNSON (Physical Rev., 1927, [ii], **29**, 85—96).—Several bands and branches between 3900 and 5100 Å. were identified in a many-lined spectrum; data are tabulated for bands at 4333 and 4655 Å. It is concluded that the carrier of the bands is the NaH dipole. There is evidence that several of the bands are members of the same system.

A. A. ELDRIDGE.

Quantum analysis of the band spectrum of aluminium oxide (5200—4650 Å.). W. C. POMEROY (Physical Rev., 1927, [ii], **29**, 59—78).—The frequencies and combination differences of all measured lines of the 0,0, 0,1, and 1,0 bands of AlO are tabulated. Numerical formulæ are given for the frequencies of individual band lines and for doublet separations. A direct method of locating band origins and verifying the combination principle is described. The moments of inertia of the AlO molecule for infinitely small vibration are $46{\cdot}02 \pm 0{\cdot}02 \times 10^{-40}$ and $43{\cdot}38 \pm 0{\cdot}02 \times 10^{-40}$ g. cm.^{2} for the initial and final states, respectively, the corresponding distances of nuclear separation being 1·665 and 1·617 Å. A. A. ELDRIDGE.

Absorption spectra of alkali halides in aqueous solution and in the vapour state. L. A. MÜLLER (Ann. Physik, 1927, [iv], **82**, 39—66).—4*N*-Solutions of alkali halides show characteristic absorption maxima at 3567 Å. for iodides, 2800 Å. for bromides, and 2680 Å. for chlorides (Macbeth and Brannigan, J.C.S., 1916, **109**, 1277). The existence of these bands is not indicated in the dispersion. A series of 0·5*N*-solutions has now been investigated by means of an aluminium spark under water as light source, Hansen's step arrangement for intensity measurements, followed by photometric registration of the darkening of negatives. Sodium iodide shows a band $\lambda_{\max.}$ 3153, $e_{\max.}$ 0·07, and rubidium iodide exhibits somewhat more persistent absorption, $\lambda_{\max.}$ 3245, $e_{\max.}$ 0·07. Potassium iodide absorbs strongly, owing possibly to a trace of the tri-iodide. Cæsium chloride has a weak band at 2945 Å., but the remaining alkali halides examined all exhibit general absorption under the conditions: concentration 0·5*N*, range of extinction coefficient 0—0·26. The absorption increases in the order F⟶Cl⟶Br⟶I and Na⟶K⟶Cs⟶Rb except for potassium iodide.

It was hoped to determine electron affinity from measurements of the absorption spectra of the vapours, since this constant can be calculated from the long-wave limit of the continuous emission spectrum. Selective absorption became apparent at 700—800°, at which temperature the partial pressures, NaCl 3×10^{-4} atm., C 3×10^{-11} atm., Cl^- 5×10^{-14} atm., express the condition of the vapour.

The observed maxima due to undissociated alkali halide molecules are tabulated. The vapour bands are in all cases persistent and well defined.

The bands due to the halogens are shifted towards the red as the at. wt. of the metal increases, but cæsium is definitely anomalous in this respect. (Cf. Getman, A., 1925, ii, 837.) R. A. MORTON.

Band spectrum of calcium hydride. E. HULTHÈN (Physical Rev., 1927, [ii], **29**, 97—111).—The spectrum of a calcium arc in hydrogen at low pressure contains many bands between 6000 and 7000 Å.; the *A*-group has heads at 7035, 7028, 6921, 6903 Å., and the *B*-group at 6389, 6382 Å. The *C*-group is a single band at 3533·6 Å. The lines of the bands *A*, *B*, *A'*, *B'* (the overlapping faint bands in *A* and *B*) are tabulated in series. Values of the final and initial terms of rotation are also tabulated. The nuclear spacings in the CaH molecule are not in correlation with their vibration frequencies.

A. A. ELDRIDGE.

Constitution and absorption spectra of the nitrososulphides of iron. L. CAMBI and L. SZEGÖ (Atti R. Accad. Lincei, 1926, [vi], **4**, 491—497).—Compounds containing the grouping $\cdot S\cdot Fe\cdot N_2O_2$ or $\cdot S_2O_3\cdot Fe\cdot N_2O_2$ give absorption spectra exhibiting certain analogies to those of the ferric compounds, $Fe(N_2O_2Ph)_3$ and $Fe(CNS)_3$. Just as is the case with the compound $FeSO_4\cdot NO$, the absorption spectrum of the salt $KS_3Fe_4(NO)_7$ at great dilutions indicates the presence of ferrous iron. The absorption of light by solutions of the above nitrososulphides presents no characteristic justifying the hypothesis that they contain univalent iron. T. H. POPE.

Possible cause of the changes of colour in vapours. (MRS.) F. LANGWORTHY (Chem. News, 1927, **134**, 20—21).—When illuminated by a spark, the vapour of mercuric chloride appears green, that of mercuric bromide blue, and that of the iodide violet. This is accounted for on the supposition that, as the halogen atom becomes more positive with increasing at. wt., the violet or more negative rays are more likely to be attracted to its vicinity. Elements in the same group of the periodic table become more positive with increasing at. wt., and the conclusion is reached that this increase of positivity is acquired in stages.

W. J. POWELL.

Bohr's model and the supposed coloration of the ions. G. MAGNANINI (Atti R. Accad. Lincei, 1926, [vi], **4**, 530—532; cf. A., 1912, ii, 142).—That the dissociated part of a coloured electrolyte has always the same absorption spectrum as the non-dissociated part follows both from experimental data and also from deductions based on the theory of Arrhenius. Since this is not in accord with Bohr's theory, it follows that either electrolytic dissociation is a spontaneous process having nothing in common with true dissociation, such as is caused by the spark discharge, or the explanations of the intimate structure of matter furnished by Bohr's theory require modification. T. H. Pope.

Coloration of alkaline-earth sulphides under the influence of pressure. J. Stalony-Dobrzański (Rocz. Chem., 1926, 6, 633—640).—The colours observed in compressed alkaline-earth sulphides correspond with those given by the respective element in the Bunsen flame, with the difference that the absorption bands are more diffuse. Absolutely pure sulphides prepared by reduction of sulphates also become coloured under pressure, showing that the presence of an activator is not essential for this phenomenon. If very great pressure is used, the sulphides are less intensely coloured than with lower pressures; this is shown to be due to the greater homogeneity of these specimens, so that the light passing through suffers less internal reflexion, and consequently travels through the mass by a shorter path. R. Truszkowski.

Infra-red absorption of coloured glasses and salt solutions. T. Dreisch (Z. Physik, 1927, 40, 714—724).—The infra-red absorption spectra of the following metal glasses and metallic solutions have been examined in the range 0·75—2·0 μ: green and greyish-violet ferrous oxide glasses, ferrous sulphate, ferrous ammonium sulphate, and ferric chloride solutions; green and blue copper glasses, cupric sulphate, and cupric chloride solutions; yellowish-green chromium glass and chromic sulphate solution; blue cobalt glass and cobalt chloride solution; violet and yellowish-brown nickel glass and nickel chloride solution; uranium glass and uranyl nitrate solution. Marked similarities are to be found between the absorption of these metal salts in aqueous and vitreous solution, so that the compound to which the colour of a glass is due may be identified from the absorption spectrum of the glass. R. W. Lunt.

Infra-red absorption spectra. II. Chloroacetic acids. W. H. Bennett and F. Daniels (J. Amer. Chem. Soc., 1927, 49, 50—57).—The predicted shift of a band in the near infra-red absorption spectrum of acetic acid with increased substitution of chlorine has been observed for the band at 5·9 μ (corresponding with the $\cdot CO_2H$ band), which moves about 0·05 μ towards shorter wave-lengths for each chlorine atom substituted in the methyl group (cf. Daniels, A., 1926, 108). The absorption spectra of methyl acetate and acetic anhydride were also determined. Improvements in technique are described, notably a micrometer absorption cell, the use of which permits the rapid and accurate determination of the spectra of a liquid at different thicknesses. With its aid, Lambert's law is tested for chloroform; the law is valid when the transmission is high, but the calculated transmission becomes too high as the thickness of the liquid is increased beyond 2 or 3 mm. The deviations, which are most pronounced for the band at 3·32 μ, may be due to imperfections in the spectrometer, which lead to scattered radiation. S. K. Tweedy.

Absorption spectrum of solid benzene at −180°. P. Pringsheim (Physikal. Z., 1926, 27, 856—859).—Riemann has shown that the relatively diffuse bands observed in the fluorescence spectrum of benzene are partly resolved at −180°, and the spectrum shows a close resemblance to that of the vapour. The absorption spectrum of benzene has now been investigated at −180°. Films 10 μ in thickness were frozen between quartz plates immersed in liquid air.

Intense bands between 230 and 270 μμ are shown by liquid air, so that this material must not occur in the path of the light. A hydrogen discharge-tube with a quartz window served as a source of light with a continuous spectrum. Solid benzene at 0° gives an absorption curve not differing appreciably from the curve for liquid benzene due to Henri; eight approximately equidistant broad bands are shown in such a curve. The vapour spectrum shows the bands resolved into a complicated fine structure, whilst for solid benzene at −180° a roughly intermediate degree of resolution is attained.

The results for benzene at −180° may be expressed by $\nu=\nu_0+an-bp$ (n and p are integers 0, 1, 2 . . ., $\nu_0=37{,}000$, $a=920$, $b=80$ cm.$^{-1}$). In Henri's scheme of levels, b is connected with the unexcited and a with the excited state. The difference between a and b is regarded as too great to harmonise with this view, and for the above and other reasons a somewhat different scheme is adopted for systematising the observed constant frequency differences (cf. Marsh, A., 1925, ii, 625). R. A. Morton.

Ultra-violet absorption spectra of some substances with two benzene nuclei. A. Castille (Bull. Acad. roy. Belg., 1926, [v], 12, 498—519).—The substances were examined in hexane solution and also when possible in the state of vapour, curves being plotted between the logarithm of the coefficient of molecular absorption and the wave-length and frequency, respectively. With diphenylmethane and *s*-diphenylethane, where the nuclei are connected by a grouping which is saturated, the same bands occur, although somewhat more diffuse, as with benzene, showing that the two nuclei interfere only very slightly. Where the nuclei are connected by an unsaturated grouping which is moreover not a chromophore (diphenyl, stilbene, diphenylbutadiene, diphenylamine, and *as*-diphenylethylene), the spectrum contains one large band common to all the substances and resulting from the fusion of corresponding narrow bands in benzene. These facts are explained by Henri's theory ("Structure des molecules," 1925), according to which the two nuclei have opposite polarities, and when connected by a saturated grouping, only the electronic vibrations are neutralised, each nucleus thus retaining its characteristic vibration; but when connected by an unsaturated grouping, the opposite charges of the nuclei are completely neutralised and a band results. As the length of the connecting chain increases, the bands are displaced increasingly towards the red, since the energy required to raise the molecule from one level to another will be less, and the frequency therefore also less, as the nuclei become farther apart. The coefficient of absorption increases with the number of ethylenic linkings, and since diphenylamine has the greatest coefficient of the substances examined, it is inferred that the :NH group is unsaturated. The case of nuclei connected by a grouping which contains a chromophore is also considered. S. J. Gregg.

Polarisation of fluorescence light. Mean period of activated molecules. F. Perrin (J. Phys. Radium, 1926, [vi], 7, 390—401).—The light emitted from fluorescent solutions is usually partly polarised. Accepting fluorescence as due to the return from an activated state of period τ to the normal state, a quantitative formulation of the relations existing between τ, viscosity of solvent, and polarisation of the light emitted is advanced. This leads for glycerol–water solutions of fluorescein to a value for τ of $0{\cdot}43\times10^{-8}$ sec. R. A. Morton.

Two problems in the extinction of iodine fluorescence. G. Ramsauer (Z. Physik, 1927, 40, 675—685).—The sensitivity of the various resonance series of iodine to the effect of collisions between excited iodine molecules and oxygen molecules has been examined, and data are given for the relative extinction produced by frequencies characteristic of sodium, cadmium, and carbon arcs between the limits 5153 and 6295 Å. R. W. Lunt.

Correlation of the fluorescence and absorption spectra of iodine. F. W. Loomis (Physical Rev., 1927, [ii], 29, 112—134).—The lines near Hg 5460 Å. in Wood's fluorescence spectrum of iodine excited by the quartz mercury arc are identified with definite lines in the absorption spectrum, whereby new values of the constants of the iodine spectrum are obtained. The calculation of absolute rotation quantum numbers furnishes direct evidence for the hypothesis of half-quantum numbers. Three new series of fluorescence doublets were observed. The fluorescence spectrum confirms Lenz's theory to account for the simple fundamental series of doublets excited by the narrow green mercury line. A. A. Eldridge.

Spectrum of luminescence of cæsium in electrodeless discharge. G. Balasse and O. Goche (Bull. Acad. roy. Belg., 1926, [v], 12, 621—630).—Wave-lengths between 2300 and 7000 Å. in the spectrum produced by the action of the electrodeless discharge on cæsium at 170° are recorded. They are in general agreement with Sommer's spark-spectrum figures (A., 1925, ii, 4). R. Cuthill.

Decay of phosphorescence of zinc sulphide. H. A. Taylor (J. Physical Chem., 1927, 31, 115—123).—The effect of temperature on the rate of decay of phosphorescence over the range 25—110° has been investigated by measuring the time taken by a sample of zinc sulphide, saturated with the exciting radiation, at a given temperature, to decay to a fixed photometric standard. The temperature coefficient in the case of five different samples of sulphide is $1{\cdot}20/10°$ in the neighbourhood of 70°, corresponding, on the basis of the radiation theory, with $\lambda = 6{\cdot}65\,\mu$, in contradistinction to the value $1\,\mu$ given by Perrin (A., 1922, ii, 628). The values of the temperature coefficient tend to increase with increasing temperature, in harmony with Lenard's view that different processes of short, medium, and long duration are involved. Further, the smallness of the value suggests that phosphorescence is a photochemical rather than a thermal process. The abnormal decaying effect of radiation on zinc sulphide phosphorescence is not confined to any particular frequency or region of the spectrum, but all frequencies incapable of causing phosphorescence accelerate decay. The line of demarcation is quite sharp. The contradictory nature of previous data is pointed out.
L. S. Theobald.

Validity of Stokes' law for phosphors. F. Schmidt and W. Zimmermann (Ann. Physik, 1927, [iv], 82, 191—200).—According to Stokes' law, the light emitted by a phosphor must be of longer wave-length than the exciting light. Monochromatic light was obtained by the use of filters and a quartz mercury-vapour lamp. For the isolation of the line at 435 $\mu\mu$, the filtering system consisted of dilute cuprammonium solution, blue glass, copper sulphate solution, and dilute æsculin solution, whereas, for the 492 $\mu\mu$ line, dark green gelatin was substituted for blue glass. The following phosphors were used in the investigation of the momentary luminescence (fluorescence): ZnS–Cuα, CaS–Cuα, SrS–Biα. In each case, illumination with radiation down to 365 $\mu\mu$ caused the appearance of the entire emission band, but the use of monochromatic radiation of 492 $\mu\mu$ brought about the excitation of only the portions on the long-wave side of the line. Stokes' law thus holds rigidly for the momentary or true fluorescence effect. When, however, the phosphorescence or luminescence of longer duration is considered for the phosphors CaS–Biα, SrS–Biα, excited by the 435 $\mu\mu$ line, light of wave-lengths shorter than 435 $\mu\mu$ is emitted. Stokes' law is therefore not valid for this process. It is concluded that the energy emitted in the fluorescence effect springs from the absorbed light energy, whereas the emission centres must supply energy at the expense of the heat content, in the phosphorescence effect of longer duration. R. A. Morton.

Activation of hydrogen in the electric discharge. G. A. Elliott (Trans. Faraday Soc., Jan., 1927, advance proof).—The formation of monatomic hydrogen is investigated quantitatively. The activated hydrogen produced by submitting pure hydrogen to an electric discharge in a Siemens ozoniser is measured by its reducing action on sulphur and is found to vary inversely as the rate of flow of the gas through the apparatus. The yield also varies with the pressure, and shows no linear relation to the voltage used, being negligible above 7 cm. and below 3000 volts.

The results are considered in the light of the expressions deduced (Elliott, Joshi, and Lunt, this vol., 212) for the velocity of a chemical reaction in the silent electric discharge. A. S. Corbet.

Activation of molecular hydrogen by electron impact. G. Glockler, W. P. Baxter, and R. H.

Dalton (J. Amer. Chem. Soc., 1927, 49, 58—65).—The activation of hydrogen molecules commences with electrons of energy 11·4 volts, indicating that the first stage in the activation process at low voltages is the formation of a resonated hydrogen molecule (cf. Witmer, A., 1926, 552). There was no evidence that electrons of energy 3—5 volts dissociate hydrogen molecules. S. K. Tweedy.

Ionisation phenomena in active nitrogen. P. A. Constantinides (Nature, 1927, 119, 163).—Differences in the ionisation effects according to the gases mixed with the nitrogen are held to indicate that active nitrogen may be due to a metastable state of the nitrogen molecule with energy between 9·4 and 10·4 volts. A. A. Eldridge.

[Ionisation phenoma in active nitrogen.] (Lord) Rayleigh (Nature, 1927, 119, 163).—A brief reply to Constantinides (preceding abstract). A. A. Eldridge.

Ionisation in hydrogen chloride vapour. H. A. Barton (Nature, 1927, 119, 197—198).—The ions previously observed have been identified as: $(Cl^{35})^+$, $(HCl^{35})^+$, $(Cl^{37})^+$, $(HCl^{37})^+$, $(Cl^{35})^-$, and $(Cl^{37})^-$. The isotopic ratios were equal to that computed from the at. wt. of chlorine. The only ion produced by an impact of an electron of between 4 and 75 volts' energy on a hydrogen chloride molecule is $(HCl)^+$, corresponding with an ionisation potential of 13·8 volts. Reasons are given for discrediting the assumption that the primary process consists of the formation of H^+ and Cl^- ions. A. A. Eldridge.

Meaning of the time-effect in the formation of hydrogen bromide from its elements. A. Skrabal (Ann. Physik, 1927, [iv], 82, 138—142; cf. Bodenstein and others, A., 1925, ii, 218; 1926, 680; Rideal, *ibid.*, 484; Herzfeld, *ibid.*, 1919, ii, 503).—A new mechanism for the reaction is advanced which leads to an equation identical with that based on the experiments of Bodenstein and Lind. R. A. Morton.

Electricity in flames. J. A. J. Bennett (Phil. Mag., 1927, [vii], 3, 127—146).—The electrical conductivity of a Bunsen flame containing the spray of very dilute solutions of rubidium chloride and of cæsium chloride has been measured at different temperatures between 1920° and 1570° Abs. The conductivity of the salt-free flame is several times less than that of the flame containing the spray. The conductivity of the flame increases with the temperature and with the concentration of the solution used for the spray. The ionisation equilibrium constant for rubidium chloride has been calculated from the flame conductivities, and the values are in good agreement with those calculated from Saha's thermodynamical theory of temperature ionisation. There is better agreement between the values, obtained by the two methods, at the higher than at the lower temperatures, indicating that Saha's theory holds good only at high temperatures. From the conductivity measurements, the velocities of electrons in the Bunsen flame have been calculated. The results show that the velocities change from 2700 cm./sec. at 1920° Abs. to 1800 cm./sec. at 1570° Abs. A. E. Mitchell.

Pressure dependence of dielectric constant of gases and vapours at low pressures. K. Wolf (Physikal. Z., 1926, 27, 830; cf. A., 1926, 1081).—An addendum. R. A. Morton.

Dielectric constant and diamagnetism of hydrogen and helium in the new quantum mechanics. J. H. Van Vleck (Proc. Nat. Acad. Sci., 1926, 12, 662—670).—Theoretical. The new Heisenberg–Schrödinger quantum mechanics is applied to the calculation of dielectric constants and diamagnetic susceptibilities of hydrogenic atoms. The values so calculated are usually in much closer agreement with available experimental data than are those calculated on the basis of the older quantum theory. The dielectric constant calculated for monatomic hydrogen is 1·000229, Langer's experimentally determined value (this vol., 93) being 1·000136. In view, however, of the experimental difficulties, it is possible that the error introduced into this determination is greater than the tentative estimate, ±0·000034. Langer's theoretical value (*loc. cit.*), 1·000338, is held to be erroneous. J. S. Carter.

Influence of a magnetic field on the dielectric constant of a diatomic dipole gas. L. Pauling (Physical Rev., 1927, [ii], 29, 145—160).—The dielectric constant of a diatomic dipole gas in a magnetic field is calculated according to both the old quantum theory and the new quantum mechanics. The latter treatment, which predicts no effect in a magnetic field, is in accord with the experimental result of Mott-Smith and Daily (this vol., 92) for hydrogen chloride and nitric oxide. A. A. Eldridge.

Molecular and atomic volumes. XII. Volume of ammonia in some ammoniates of cuprous, silver, and aurous halides. W. Biltz [with H. Herzer] (Z. anorg. Chem., 1926, 159, 96—102).—The value of the volume of a molecule of ammonia in the ammoniates of cuprous, silver, and aurous halides lies between 19 and 25, the mean being 21·5 c.c. This value approximates to the zero-point value for ammonia, *i.e.*, 18—20 c.c., and it is only slightly greater than the value determined for ammonia from other ammoniates. The volume of the ammonia molecule appears to depend to a certain extent on the anion. With increasing numbers of ammonia molecules in the compounds, the value for the volume of a single molecule is smaller; moreover, the densities of the original halides vary with their previous treatment. M. Carlton.

Optical anomalies of calcite under pressure. S. Nishio (Proc. Imp. Acad. Tokyo, 1926, 2, 395—397).—From a knowledge of the optical anomalies shown by a specimen of calcite, it is possible to discuss its geological history. R. W. Lunt.

Thickness of the optical transition layer in liquid surfaces. C. V. Raman and L. A. Ramdas (Phil. Mag., 1927, [vii], 3, 220—223).—The coefficient of ellipticity of light reflected from pure water and from a number of organic liquids has been measured. In all cases, the coefficient is positive, irrespective of the value of the refractive index of the bulk of the liquid, and there is no definite correlation between the refractive index of the liquid and the magnitude of the ellipticity. From these results, it follows that the surface layer is optically less dense than the body of the liquid. Hence it is suggested that there is no orientation of the molecules of the surface of a pure liquid. With the aid of Drude's formula, it is shown that the thickness of the transition layer is of the same order as the linear dimensions of the molecules forming the liquid. Examination of the ellipticity of light reflected from films of oleic and palmitic acids spread on water shows that the film is unimolecular.

A. E. Mitchell.

Ionic refractivity and the scattering of light by gases. T. H. Havelock (Phil. Mag., 1927, [vii], 3, 158—176).—From a consideration of the constituents of a molecule as isotropic resonators in fixed relative positions in the molecule, formulæ for the refractivity of gases have been derived for both straight-line and triangular configurations. The formulæ have been applied to an examination of the refractivities of hydrogen chloride, hydrogen bromide, hydrogen sulphide, steam, carbon dioxide, and carbon disulphide. From experimentally-determined values of the refractivity and of the polarisation of the scattered light with the aid of the distance between nuclei inferred from infra-red measurements, the refractivities of the hydrogen and chlorine constituents of the hydrogen chloride molecule have been deduced. The value of the hydrogen refractivity has been combined with other data for the examination of the other gases. The molecular refractivities of the ions obtained by this method are $H^+=0{\cdot}13$, $Cl^-=6{\cdot}14$, $Br^-=8{\cdot}62$, $O^{--}=2{\cdot}58$, $S^{--}=8{\cdot}19$, and $C^{++}=0{\cdot}045$. These values are discussed in relation to those obtained from other sources. A. E. Mitchell.

Preparation, refractive index, and dielectric constant of red crystalline selenium. S. Kyropoulos (Z. Physik, 1926, 40, 618—620).—Crystals were obtained about 2 mm. long by means of a circulating convection stream of selenium in carbon disulphide; they are ruby red by transmitted light and have a blue metallic lustre by reflected light. The index of refraction for polarised light of wave-length 620 μμ was 2·8 for vibrations parallel to the (100) surface and 2·3 perpendicular thereto. The dielectric constant at 2·7° was 7·39, agreeing with the Maxwell relation and indicating no special absorption frequency in the infra-red. E. B. Ludlam.

Molecular refraction and the parachor. W. Herz (Z. anorg. Chem., 1927, 159, 316—318).—Calculations are made of the molecular refraction and of the parachor for 51 organic liquids, using values previously published, and it is shown that the quotient of the parachor divided by the molecular refraction is a constant, independent of the liquid. Abnormal values were obtained for liquefied gases. A close relation between refractive index and surface energy is indicated. E. S. Hedges.

Determination of refractive indices from reflexion measurements in the infra-red. A. Krebs (Ann. Physik, 1927, [iv], 82, 113—137).—The relation between angle of incidence and reflexion has been studied for the residual rays from calcium carbonate, silica, and fluorite. The Fresnel formulæ fit the reflexion data for the transparent substances selenium, sodium chloride, potassium chloride, potassium bromide, and calcium fluoride. Brewster's law affords a means of calculating refractive indices from the angle of polarisation corresponding with the reflexion data. By combining the Fresnel formulæ, a simpler method can be used. The reflexion of residual rays from various commercial glasses has enabled their refractive indices to be determined experimentally. R. A. Morton.

Theory of mixed substances and the logarithmic mixture rule. K. Lichtenecker (Physikal. Z., 1926, 27, 833—837).—Various mixture rules are discussed and compared with experiment. The logarithmic mixture law is applied to two- and three-dimensional aggregates, and a correction curve is utilised. The electrical conductivity of artificial gold–silver particles, the heat conductivity of tin–zinc alloys, and the dielectric constant of carbon tetrachloride–chloroform mixtures all obey the logarithmic mixture rule after certain simple corrections have been made. The rule has been applied to lead metasilicates as a means of arriving at the refractive index of a molten liquid containing a definite lead oxide–silica ratio. The logarithmic mixture rule, corrected for three-dimensional aggregates, reproduces quantitatively the refractive index of common salt solutions over the range 0—25% by weight of salt.

R. A. Morton.

Stereochemistry of platinous salts. H. Reihlen and K. T. Nestle (Z. anorg. Chem., 1927, 159, 343—348).—A reply to Grünberg (this vol., 34; cf. Reihlen and Nestle, A., 1926, 699). E. S. Hedges.

Model for the molecules of methane and other compounds of the type XY_4. I and II. J. H. de Boer and A. E. van Arkel (Z. Physik, 1927, 41, 27—37, 38—47).—I. A calculation of the energy of ionisation of compounds of the type CX_4 and SiX_4 is made on the assumption that the X atoms behave as negative ions (A., 1926, 888). By means of a cyclic process, the ionisation energy is calculated for the silicon compounds from experimentally-determined constants. The agreement in value between the calculated energy of ionisation and that experimentally determined is good.

II. The dipole moment and energy of ionisation of chloroform and methyl chloride are calculated on the assumption that the hydrogen exists as negative ions in these two compounds. The calculated energies of ionisation are in good agreement with the values obtained from experimentally-determined constants by means of a cyclic process. W. E. Downey.

Polarisation of a medium and its molecular structure. Benzene and *cyclo*hexane. J. Errera (Bull. Acad. roy Belg., 1926, [v], 12, 327—339).—Measurements of the specific inductive capacity of benzene and *cyclo*hexane in the liquid and solid states at and near the m. p. indicate the absence of molecular doublets. The polarisation due to atomic vibrations is 1·48 for benzene and 0·74 for *cyclo*hexane.

H. F. Gillbe.

Molecular diameter of unassociated liquids at their b. p. N. de Kolossovski (Z. Elektrochem., 1927, 33, 11).—An equation derived by Schuster

(A., 1926, 670) connecting the molecular diameter, surface tension, and internal pressure of an unassociated liquid at its b. p. is compared with relations developed by Walden (A., 1909, ii, 119, 547).

H. J. T. Ellingham.

Element of atomic number 61 : florentium [illinium]. III. L. Rolla and L. Fernandes (Gazzetta, 1926, **56**, 862—864 ; Atti R. Accad. Lincei, 1926, [vi], 4, 498—499 ; cf. A., 1926, 1083 ; this vol., 9, 31).—The authors give the text of a paper which was deposited under seal with the Reale Accademia dei Lincei in June 1924 and announces the discovery of the element of atomic number 61. They claim that the name florentium then given to this element should be retained.

T. H. Pope.

Existence of the element of atomic weight 61. R. Brunetti (Atti R. Accad. Lincei, 1926, [vi], 4, 515—518).—This note, deposited under seal with the Accademia on June 21, 1924, gives the results of investigation of the *K*-absorption spectra of rare earths supplied by Rolla (cf. preceding abstract). An absorption band observed in the spectral region between samarium and neodymium has a wave-length agreeing closely with that calculated for the previously unknown element of atomic number 61.

T. H. Pope.

Identification of the element of atomic number 61. R. Brunetti (Atti R. Accad. Lincei, 1926, [vi], 4, 518—521 ; cf. preceding abstracts).—The results previously obtained are confirmed, the samarium fraction obtained by Rolla and Fernandes containing a small proportion of the element of atomic number 61.

T. H. Pope.

Concentration and identification of the element of atomic number 61. J. M. Cork, C. James, and H. C. Fogg (Proc. Nat. Acad. Sci., 1926, **12**, 696—699).—Since an examination of the *X*-ray *K* emission lines of certain specimens of samarium and neodymium suggested the presence of small amounts of the element of atomic number 61 as impurity, attempts have been made to increase its concentration. The small amount of neodymium which accompanied the yttrium earths derived from a large quantity of Brazilian monazite sand was concentrated by fractional crystallisation of the bromates and magnesium double nitrates. The resulting sample, containing about 1% of element 61, was submitted to *X*-ray examination. Seven *L*-series lines were obtained, viz., α_1, α_2, β_1, β_2, β_3, γ_1, γ_2 (Siegbahn's notation), the wave-lengths being 2·279, 2·289, 2·078, 1·952, 2·038, 1·799, and 1·725, respectively.

J. S. Carter.

Crystal structure of nickel oxide, cobalt oxide, and lead sulphide. F. M. Bravo (Anal. Fís. Quím., 1926, **24**, 611—646).—Measurements made by the Debye–Scherrer *X*-ray method show that nickel oxide, cobalt oxide, and lead sulphide have lattices of the sodium chloride type. The mean values obtained for the length of side of the lattice cube are 4·244, 4·32, 5·96 Å. for nickel oxide, cobalt oxide, and lead sulphide, respectively.

G. W. Robinson.

Crystal structure of magnesium dizincide. J. B. Friauf (Physical Rev., 1927, [ii], **29**, 34—40).—The crystal has hexagonal axes, with *a* 5·15, *c* 8·48 Å. ; the unit cell contains four molecules. The atoms have the positions : zinc : $u, \bar{u}, \frac{1}{4}$; $2\bar{u}, \bar{u}, \frac{1}{4}$; $u, 2u, \frac{1}{4}$; $\bar{u}, u, \frac{3}{4}$; $2u, u, \frac{3}{4}$; $\bar{u}, 2\bar{u}, \frac{3}{4}$; 0, 0, 0; 0, 0, $\frac{1}{2}$; magnesium : $\frac{1}{3}, \frac{2}{3}, v$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{2} - v$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{2} + v$; $\frac{2}{3}, \frac{1}{3}, \bar{v}$, where $u = 0·830$ and $v = 0·062$. The least distance between two magnesium atoms is 3·15 Å., between two zinc atoms 2·52 Å., and between a magnesium and a zinc atom 3·02 Å.

A. A. Eldridge.

Space-lattice of "permalloy." R. Forster (Physikal. Z., 1926, **27**, 829—830).—"Permalloy" (78% nickel, 22% iron) shows a face-centred cubic lattice of side 3·56 Å. The lattice constant increases with increasing iron content, since the value 3·54 is obtained for pure nickel and 3·63 for γ-iron (corrected to the ordinary temperature). McKeehan's result of 3·60 Å. for the alloy 30% nickel, 70% iron confirms the additivity of the lattice constant. The lattice is independent of magnetic properties.

R. A. Morton.

Crystalline structure of zircon. W. Binks (Min. Mag., 1926, **21**, 176—187).—Zircon (*d* 4·67) examined by the spectrometer and powder *X*-ray methods shows a structure corresponding with the space-group D^{19}_{4h}. The unit cell containing eight molecules of $ZrSiO_4$ has dimensions $a = 9·30$, $c = 5·93$ Å. The silicon and zirconium atoms form two interpenetrating face-centred lattices, and the oxygen atoms are arranged tetrahedrally around the silicon atoms.

L. J. Spencer.

***X*-Ray examination of aramayoite.** (Miss) K. Yardley (Min. Mag., 1926, **21**, 163—168).—Laue photographs through the perfect basal cleavage of aramayoite show an absence of symmetry. Spectrometer and powder data show that the mineral is triclinic with $a = 5·672$, $b = 5·688$, $c = 5·623$ Å., $\alpha = 86° 55'$, $\beta = 90° 53'$, $\gamma = 93° 18'$. The structure is pseudo-tetragonal with two molecules of $Ag(Sb,Bi)S_2$ in the minimum cell.

L. J. Spencer.

Structure of baddeleyite and of prepared zirconia. (Miss) K. Yardley (Min. Mag., 1926, **21**, 169—175).—Spectrometer measurements made on a crystal of baddeleyite (*d* 5·82) from Ceylon give for the unit monoclinic cell containing four molecules of ZrO_2 the dimensions $a = 5·21$, $b = 5·26$, $c = 5·37$ Å., $\beta = 80° 32'$. A better agreement in the calculated spacings is obtained when the mol. wt. is taken as slightly higher (viz., 128), probably due to the presence of some hafnia in the mineral. Baddeleyite crystals from Brazil gave similar results. Powder photographs of the nodular fibrous zirconia from Serra de Caldas, Brazil (A., 1903, ii, 554), prove the identity of this material with baddeleyite. Similar results were also obtained with artificially prepared zirconia (which has previously been described as tetragonal and as cubic).

L. J. Spencer.

Crystal structure of some oxalates. J. F. Wood (Proc. Univ. Durham Phil. Soc., 1925—1926, **7**, 111—116).—Using the Bragg ionisation spectrometer and the rhodium $K\alpha_2$ line (0·616 Å.) as the *X*-radiation, the dimensions of the unit cell, assuming the latter to contain two molecules in each case, have been determined for oxalic acid, for which $a = 6·10$, $b = 3·61$, $c = 12·05$ Å., $\beta = 106° 12'$; ammonium oxalate, $a = 8·06$, $b = 10·34$, $c = 3·82$ Å.; and methyl oxalate, $a = 3·93$, $b = 11·84$, $c = 6·17$ Å., $\beta = 103° 22'$.

The orientation of the molecules in the cell is discussed.
M. S. Burr.

Polymorphism of fatty acids. J. Thibaud (Compt. rend., 1927, **184**, 96—98).—*X*-Ray measurements of the crystal-spacings of fatty acids show that these are a function of the number of carbon atoms in the molecule. For the various crystalline forms of certain acids (*e.g.*, stearic), different values are obtained according to their number (cf. this vol., 98). It is suggested that the variations are due to the different projections of the carbon chains on the base of the molecule, the spacings of the chains themselves being identical. Apart from slight variations due to the positions of the terminal groups, this is in agreement with the observed and calculated crystal-spacings. For stearic acid, the values obtained are 1·41, 1·22, and 1·0 Å., where 1·41 is the true distance between the consecutive carbon atoms. There is a tendency for the acids to crystallise preferentially in one particular form according to their structures.
J. Grant.

Crystallography of phenyl α-naphthyl ketone. T. J. Woyni (Rocz. Chem., 1926, 6, 653—660).—The crystallographic and optical constants of crystals of phenyl α-naphthyl ketone were determined by the theodolite method. R. Truszkowski.

Electron distribution in the atoms of crystals. Sodium chloride and lithium, sodium, and calcium fluorides. R. J. Havighurst (Physical Rev., 1927, [ii], 29, 1—19).—With certain assumptions, Fourier analysis is applied to the determination of electron density. Curves show the variation of electron density along the cube edges of the unit cells of sodium chloride, lithium fluoride, and sodium fluoride, and along the cube diagonal of calcium fluoride; radial electron distribution curves are plotted for the various ions. It appears to be definitely proved that the lattice points of the crystals are occupied by ions. The sum of the computed radii of the ions is in every case very slightly less than the distance of closest approach as determined by ordinary *X*-ray analysis. Thus the unit cell of a crystal appears to contain a number of spherical electron systems practically in contact with each other and distributed regularly over the lattice points, each system having a dense electron atmosphere near its centre, which becomes extremely rarefied at its outer limit. The atomic radii correspond closely with those of Wasastjerna (A., 1923, ii, 593; Bragg, *ibid.*, 1926, 780). The electron distribution of an atom may be modified by the external forces which act on it in a crystal; the sodium ion possesses different electron distributions in the chloride and fluoride, whilst those of the fluorine ion are the same in the lithium, sodium, and calcium compounds. The radial distribution curve for the chlorine ion is not in agreement with that of Compton, and the curve for fluorine contains an unexplained hump. Further, spherical symmetry of the electron distribution has been assumed.
A. A. Eldridge.

Measurements and interpretation of the intensity of *X*-rays reflected from sodium chloride and aluminium. J. A. Bearden (Physical Rev., 1927, [ii], 29, 20—33).—Measurements of the intensity of *X*-rays reflected from sodium chloride and aluminium have been made, and electron distribution curves plotted for sodium, chlorine, and aluminium. There is no evidence of any failure of the classical electrodynamics as applied to calculations of the intensity of *X*-ray reflexion. A. A. Eldridge.

Reflecting power of the carbon atom for high-frequency rays. M. Ponte (Phil. Mag., 1927, [vii], 3, 195—209).—In an examination of the intensity of *X*-ray reflexion from crystals, diamond powder has been investigated by the ionisation chamber method. The structure factor for the amplitude has been found to be $1/\sqrt{2}$, and the law of variation of the reflecting power with the angle of reflexion has been found to be the same for several wave-lengths. For diamond, $f_{C(111)}$ has been found to be 2·75 to about 10% accuracy. Examination, by the same method, of naphthalene and anthracene gives for the reflecting power of these molecules 16·5 and 20·2, respectively. These results lead to values of f_C of 5·7 and 5·9, respectively. The reflecting power of graphite on the cleavage plane led to the value $f_C = 3{\cdot}4$. A. E. Mitchell.

Crystallisation of metals. C. H. Desch (Proc. Univ. Durham Phil. Soc., 1925—1926, 7, 107—110).—An investigation of the influence of surface tension on the process of crystallisation in metals is being conducted. M. S. Burr.

Effect of working on the physical properties of tungsten. J. W. Avery and C. J. Smithells.—See B., 1927, 113.

Formation of twin metallic crystals. L. W. McKeehan (Nature, 1927, **119**, 120—121).—A criticism of conclusions of Carpenter and Tamura (this vol., 10). A. A. Eldridge.

[Formation of twin metallic crystals.] H. C. H. Carpenter and S. Tamura (Nature, 1927, **119**, 121).—A reply to McKeehan (preceding abstract).
A. A. Eldridge.

State of ionisation of the atoms in the space-lattice of beryllium oxide. W. Zachariasen (Z. Physik, 1926, 40, 637—641).—The observed interference patterns can be interpreted as due either to ions or to uncharged atoms. E. B. Ludlam.

Ionic sizes and their relationship to crystal structure type, solid solution, and double salt formation and the stabilities of hydrates and ammoniates. E. J. Cuy (J. Amer. Chem. Soc., 1927, 49, 201—215).—If ions all behaved as point charges, uni-univalent and bi-bivalent salts would be expected to crystallise in the body-centred cubic lattice (cæsium chloride type), this being the structure in which each ion is surrounded by the maximum number of ions of opposite sign. That other lattices occur is attributed to the influence of the relative sizes of ions. On the assumption that the sphere of influence is tangential to the spheres of influence of the surrounding negative ions, a maximum value for the ratio of the radii of the two ions, r'/r'', is computed for the structure types possessed by compounds of the forms AB and AB_2. For uni-univalent and bi-bivalent salts, the sequence of structure types: cæsium chloride, sodium chloride, zinc sulphide, and zinc oxide parallels the order of r'/r''. For salts of the type AB_2, the calcium fluoride structure is to be preferred, except for large ratios of r'/r''. With some additional assumptions, it is shown that the greater this ratio is the greater is the tendency for the salts to form hydrates and ammoniates and the greater the stability of these substances when formed. A parallelism is shown to hold between r_1/r_2 and the four possible types of binary temperature–composition diagrams for salts with a common ion, r_1 and r_2 being the radii of the uncommon ions. Critical footnotes by M. L. Huggins are appended. S. K. Tweedy.

Non-magnetic films of iron, nickel, and cobalt. J. D. Hanawalt and L. R. Ingersoll (Nature, 1927, **119**, 234—235).—Non-magnetic films of nickel may be produced by cathodic sputtering in hydrogen or argon, and of cobalt and iron in helium. The films become ferro-magnetic when heated in a vacuum at 350°. The non-magnetic film has in general the same crystal structure as after heating, but with a larger lattice spacing. The distension may be due to the occlusion by the metal of large amounts of the residual gas. The constancy of the amount of distension suggests that there may be a chemical or quasi-chemical union of the metal and the gas. It is not believed possible that the metals could sputter as non-magnetic oxides. A. A. Eldridge.

Principal magnetic susceptibilities of crystals. I. I. Rabi (Physical Rev., 1927, [ii], 29, 174—185).—The principal magnetic susceptibilities are tabulated for the following crystals: (*a*) sulphates of the form $MSO_4,R_2SO_4,6H_2O$: copper ammonium, copper potassium, copper rubidium, nickel ammonium, nickel potassium, nickel rubidium, cobalt ammonium, cobalt potassium, cobalt rubidium, ferrous potassium, manganous ammonium, which are paramagnetic, the values depending almost entirely on the paramagnetic ion, (*b*) sodium nitrate, calcite, aragonite, potassium nitrate, and strontium nitrate, which are diamagnetic. A. A. Eldridge.

Molecular theory of solidity and solidification. A. Smekal (Physikal. Z., 1926, 27, 837—844).—In actual crystals, a not inconsiderable fraction of the lattice cells which make up the entire crystal show deviations from the theoretical structure. Apparently, the outer electrons of the atoms making up these anomalous aggregates are not arranged in the ordinary way. On this basis, the phenomena of "inner" photo-electric sensitivity, electrical conduction, phosphorescent materials (Lenard's phosphors), and the coloration of materials like sodium chloride by *X*-ray bombardment, all receive a rational explanation connected with deviations from the normal lattice. Defective cohesion appears to be related to the existence of gliding planes in actual crystals, which owe their properties primarily to defects in the lattice. R. A. Morton.

Polishing of surfaces. N. K. Adam (Nature, 1927, 119, 162—163).—It appears unnecessary to suppose that actual liquefaction occurs, an amorphous layer indistinguishable from a supercooled liquid being formed by any mechanism which rearranges the surface molecules at random. Moreover, the resolidification of a liquefied surface layer might result in crystallisation (cf. Macaulay, A., 1926, 998; Preston, this vol., 100). A. A. Eldridge.

Diamagnetism of mesomorphic substances; orientation of smectic substances by the magnetic field. G. Foëx (Compt. rend., 1927, **184**, 147—149).—The decrease in diamagnetism produced when a substance passes from the isotropic to the oriented nematic state is due to the corresponding change of the electronic orbits responsible for diamagnetism from a haphazard to an ordered orientation parallel to the field. In general, orientation is not produced unless the substance is cooled in the magnetic field, so that the latter acts during the passage from the isotropic to the smetic phase. The diamagnetism then decreases continuously with increase in the field-intensity, and it is shown that orientation is still incomplete in fields having intensities above 12,600 gauss. The coefficient of magnetisation is almost independent of temperature. When passing from the oriented to the isotropic state, nematic substances show no discontinuity on the curve of the variation of diamagnetism. Ethyl azoxybenzoate, however, shows a marked discontinuity when passing from the smetic to the isotropic state. Smetic substances tend to approach a crystalline state more readily than nematic substances. J. Grant.

Relative resistivity of metals at temperatures of liquid helium. W. Tuyn and H. K. Onnes (Arch. Néerland., 1927, III A, **10**, 5—41).—The ratio of the resistivity at temperatures in the range 2—20° Abs. to the normal resistivity has been determined for tin, lead, radioactive lead (radium-Ω), cadmium, zinc, germanium, aluminium, platinum, copper, and alloys of lead with tin. It is concluded that the phenomena of superconductivity are confined to the metals mercury, thallium, lead, indium, and tin. R. W. Lunt.

Electrical conductivity of technical aluminium. G. Masing and C. Haase.—See B., 1927, 112.

Electrostatic charge on glass floats in very dry liquids. H. V. A. Briscoe, P. L. Robinson, and H. C. Smith (Phil. Mag., 1927, [vii], 3, 63—64).—When glass floats were placed in very dry liquid silicon tetrachloride, any slight movement or vibration of the liquid was sufficient to cause them to acquire a charge of positive electricity. The effect was so great as to make the floats adhere firmly to the walls of the containing glass tubes and to render impossible measurements of the flotation temperatures of calibrated glass floats. When the liquid was left undisturbed for a considerable period after being distilled, the floats lost the greater part of their charge, and it became possible to make the measurements with the desired precision. The loss of charge points to a progressive increase in the conductivity of the glass, and it is suggested that this is due to a reaction between the liquid and the glass. Similar results were obtained in very pure boron trichloride. The floats were again positively charged, but the magnitude of the effect was not sufficient to interfere with the precision of measurement. The charges were completely lost after a period of one day, whilst with silicon tetrachloride slight charges remained even after four months. A. E. Mitchell.

Specific heat of gaseous nitrogen tetroxide. E. D. McCollum (J. Amer. Chem. Soc., 1927, 49, 28—38).—The specific heat, C_p, of gaseous nitrogen tetroxide was determined in an improved constant-flow calorimeter between the temperatures 33° and 98°. The apparent heat capacity is large, and attains a maximum at 62°; on subtraction of the heat of dissociation, the true heat capacity is obtained, which increases with rise of temperature. Calculation indicates that C_p is slightly greater for nitrogen tetroxide than for nitrogen dioxide. S. K. Tweedy.

M.-p. curve of helium. G. Tammann (Ann. Physik, 1927, [iv], 82, 240—243).—Keesom (A., 1926, 893) has shown that the vapour pressure and m.-p. curves of helium between 1·13° and 4·21° Abs. do not intersect, and that a triple point in which solid, liquid, and vapour are in equilibrium does not occur. The expression $T-1=\log(p-24{\cdot}0)$ fits the observations over the range $T=1{\cdot}13$—$2{\cdot}50°$. At higher temperatures, the temperature increases more rapidly than is given by $\log(p-24)$. For $T=0$ dT/dp equals 4·3° per atmosphere, and $\bar{R}_p/T=0{\cdot}23\Delta v$ cm./kg. Thus dT/dp is large, but not infinite, and $\bar{R}_p/T$ is small, but not zero, as would be expected from Nernst's theory. R. A. Morton.

Latent heats of fusion of metals and specific heats at high temperatures. S. Umino (Sci. Rep. Tôhoku Imp. Univ., 1926, 15, 597—617).—The specific heats of the metals detailed below were determined at high temperatures by the method of mixture, and the latent heats of fusion obtained by extending the heat content curves in the liquid and solid phases to the m. p. With the ferromagnetic metals iron, cast iron, cobalt, and nickel, the heat content–temperature curves are complex below the m. p., owing to the numerous transformations, and are linear above the m. p. Their mean specific heat increases more rapidly than linearly in the ferromagnetic range, and then linearly to the m. p., at which it increases abruptly, and may then either remain constant or decrease. With the non-magnetic metals, the mean specific heat below the m. p. increases slowly and almost linearly with rise of temperature, increases abruptly at the m. p., and then gradually decreases. The true specific heats of non-magnetic metals below the m. p. increase linearly or more rapidly than linearly, and decrease abruptly at the m. p., except with antimony and zinc, which, like the ferromagnetic metals, show an increase. The true specific heats of all metals do not change above the m. p. With the ferromagnetic metals and alloys, the true specific heats show abnormal changes in the ferromagnetic range. The following new values are found for the latent heats of fusion and m.p. Tin 14·20, bismuth 14·10, cadmium 12·90, lead 5·50, zinc 23·60, antimony 40·75, aluminium 79·64, silver 24·90, gold 15·73, copper 49·95, nickel (1450°) 70·40, cobalt (1489°) 67·00, chromium (1600°) 70·05, iron (0·04% C, m. p. 1520°) 69·20, iron (4·22% C, m. p. 1169°) 47·00. When the latent heats of fusion are plotted against the at. wts., a periodic type of curve is obtained. W. Hume-Rothery.

Latent heat of vaporisation and density. W. Herz (Z. anorg. Chem., 1927, 159, 304—306).—The quotient $L_t/(d_t-d_c)$, where, at the temperature t, L is the latent heat of vaporisation, d_t the density of the liquid, and d_c the critical density, is independent of the temperature for each of the non-associated liquids examined, and also for certain associated liquids. The value of the constant is characteristic for each liquid. Results are shown over a wide temperature range for the liquids octane, stannic chloride, methyl alcohol, and ammonia, using previously-recorded values of the terms. The quotient is not constant for propyl alcohol, ammonia, or acetic acid. In the last case, the variation of the latent heat of vaporisation with temperature is known to be abnormal. E. S. Hedges.

Latent heats of vaporisation. M. de Hemptinne (Bull. Acad. roy. Belg., 1926, [v], 12, 296—308).—An experimental verification of Prud'homme's formula connecting latent heat of vaporisation and b. p. (A., 1925, ii, 188). Good agreement is obtained for water, ammonia, pentane, hexane, heptane, octane, carbon tetrachloride, chlorobenzene, and benzene. For methyl and ethyl acetates and methyl alcohol, the agreement is less satisfactory. The formula is inapplicable to acetic acid, on account of the maximum in its specific heat–temperature curve. H. F. Gillbe.

Heat of formation of surface layer at the bounding surface of solutions. P. Rehbinder (Physikal. Z., 1926, 27, 825—829).—For dilute solutions and an extended surface, the author's expression $Q=RT(1-T/G\,.\,dG/dT)$ (G is surface activity) can be deduced from well-known thermodynamic equations without special assumptions. On this basis and using earlier measurements, the heats of adsorption for solutions of surface active materials (aliphatic acids) have been calculated. The expression $Q=1/\Gamma(\Delta\sigma-T\,.\,d\Delta\sigma/dT)$ is a special case of the author's formula above if $-d\sigma/dc=G=(\sigma_0-\sigma)/c$ (cf. A., 1924, ii, 662; 1926, 674). R. A. Morton.

Heats of combustion of proposed secondary standard substances and of position and optical isomerides. L. J. P. Keffler and F. C. Guthrie (J. Physical Chem., 1927, 31, 58—68).—There is described an adiabatic calorimeter of the submarine type which gives results of an accuracy sufficient for use in the determination of the heats of combustion of standard substances. Increased accuracy results from selecting for all combustions the same initial and final temperatures on the Beckmann scale. The heats of combustion found, in g.-cal.$_{15}$ per g. (air, v=constant), are, for naphthalene 9614·2, for salicylic acid 5243·1 (cf. Verkade and Coops, A., 1926, 785; Berner, *ibid.*, 116), and for *m*- and *p*-hydroxybenzoic acids, 5244·2 and 5237·8, respectively (cf. Stohmann, *ibid.*, 1889, 1096), the maximum deviation from the mean value being approximately 2 g.-cal. Naphthalene, and especially salicylic acid, on account of its lower volatility, are very suitable secondary standards for bomb calorimetry. From the results obtained with the hydroxybenzoic acids, it is concluded that the energy contents of the *o*- and *m*-isomerides are the same, whilst that of the *p*-isomeride shows a slight difference. The two optically active forms of borneol gave practically the same values for their heats of combustion. L. S. Theobald.

Reconciliation of values obtained for thermochemical constants of organic compounds. W. Swientoslawski (Rocz. Chem., 1926, 6, 578—602).—Values obtained for the heats of combustion of various organic compounds by different authors are compared and correction coefficients determined for them. R. Truszkowski.

Friction, heat conductivity, and diffusion in gaseous mixtures. I. M. Trautz (Ann. Physik, 1927, [iv], 82, 227—239).—A new conception of the theoretical treatment of friction, heat conductivity, and diffusion in gaseous mixtures is outlined with special reference to friction in pure gases and in mixtures. The theory of collisions between like and unlike molecules forms the basis of the work. The experimental evidence will shortly be published. R. A. Morton.

Allotropy of tin. A. Travers and Huot (Compt. rend., 1927, 184, 152—155).—Tin exists in three allotropic forms, rhombohedric, quadratic, and grey tin, with densities of 6·55, 7·28, and 5·8, respectively. The transformation from one type to another has been followed by density, dilatometric, and calorimetric measurements, anomalous results having been previously obtained. It is now shown that the results are dependent on the previous thermal treatment of the metal, irrespective of its purity. Thus samples heated at 350° for some minutes showed no discontinuities on the calorimetric curve, whilst heating at 500° for 2 hrs. produced a sharp break at 170—171°, this being accentuated by an increase in the time or temperature. Solid samples showed no break even after 52 hrs. at 190°. The transformations denoted by the breaks are accompanied by characteristic decrepitations. J. Grant.

Association of liquids and a relation between the capillary constant and the heat of vaporisation. P. Walden (Z. anorg. Chem., 1926, 158, 244—248).—The relation, $E=0{\cdot}000095MT$, for the molecular elevation of the b. p., in which T is the b. p. of a solvent of mol. wt. M, deduced by de Kolosovski (A., 1926, 1008), is not new, having been previously advanced by Beckmann (*ibid.*, 1896, ii, 236). The author claims priority for the conclusion reached by de Kolosovski, that the ratio of the heat of vaporisation of a liquid to its capillary constant is independent of temperature for a non-associated liquid (*ibid.*, 1909, ii, 119). A. S. Corbet.

Density, compressibility, and at. wt. of nitrogen. G. P. Baxter and H. W. Starkweather (Proc. Nat. Acad. Sci., 1926, 12, 703—707).—The average values for the densities of nitrogen at 0° and 253·33, 506·67, and 760 mm. at sea-level, latitude 45°, are 0·41667, 0·83348, and 1·25036, respectively. If the value of PV at 1 atm. be assumed to be 1, the values at $\frac{2}{3}$ and $\frac{1}{3}$ atm. are 1·00011 and 1·00028, respectively, the average value of the coefficient of deviation from Boyle's law between 0 and 1 atm. being —0·00045, a value in agreement with existing data. These results lead to the value 14·007 for the at. wt. of nitrogen. J. S. Carter.

Density of oxygen and its compressibility below one atmosphere. II. G. P. Baxter and H. W. Starkweather (Proc. Nat. Acad. Sci., 1926, 12, 699—703; cf. A., 1925, ii, 188).—If the most recent value for the gravitational constant be used, the densities of oxygen at 0° and at 190, 380, 570, and 760 mm. at sea-level, latitude 45°, are 0·35699, 0·71415, 1·07149, and 1·42897, respectively. If the value of PV be assumed to be 1 at a pressure of 1 atm., the values of PV at 0·75, 0·50, and 0·25 atm. are 1·00022, 1·00047, and 1·00071, respectively, whence the coefficient of deviation from Boyle's law per atm. is —0·00092, a value very near to the mean value, —0·00094, calculated by Pickering (A., 1926, 569). J. S. Carter.

Ten years' work on gases. E. Moles (Gazzetta, 1926, 56, 915—947).—A review, containing also an account of unpublished work on the density of atmospheric air. Tables and graphs show the variation of the weight of a normal litre of air with the atmospheric pressure at Madrid (mean weight 1·29315) and Barcelona (mean 1·29285). The results are in agreement with the Loomis–Morley–Guye law, that all minima of atmospheric (reduced) density correspond with maxima of pressure; most density maxima correspond also with pressure maxima. As the maximum variation in the normal density of air at any one place may be as great as 0·1%, the use of air as a standard of gas density should be abandoned. E. W. Wignall.

Method of measuring vapour pressure by air bubbling. H. I. Downes and E. P. Perman (Trans. Faraday Soc., Jan., 1927, advance proof).—The apparatus previously devised by Perman (Proc. Roy. Soc., 1903, 72, 72) for measuring vapour pressure by air bubbling has been considerably improved to give accurate results over a large temperature range. The vapour pressures and densities of aqueous sucrose solutions have been determined between 40° and 80°, and the values of the osmotic pressures of such solutions, calculated by three methods from the vapour-pressure values, are concordant and in agreement with those obtained by other workers. A. S. Corbet.

Vapour pressure and resistance thermometers in the region of liquid nitrogen and liquid hydrogen. F. Henning (Z. Physik, 1927, 40, 775—785).—By means of a constant-volume helium gas thermometer, the vapour pressure of liquid and solid nitrogen was determined between 60° and 80° Abs., and of hydrogen between its normal b. p., 20·4° Abs., and its triple point, 14·04° Abs. The change of resistance of pure platinum was determined over the same range. The triple point of nitrogen is 63·12° Abs., at which temperature the vapour pressure is 92·89 mm. The vapour pressure of hydrogen at 14·04° Abs. is 54·86 mm. E. B. Ludlam.

Critical constants of various gases. S. F. Pickering (U.S. Bur. Standards Sci. Paper 541, 1926, 21, 597—629).—From a review of the available data for the more common gases and the inert gases the most trustworthy values have been tabulated. The constant RT_cd_c/MP_c seems to vary from 3·0 for krypton to 4·12 for ammonia. The critical data for krypton appear to be inaccurate. In ammonia, the high values are due to the abnormality of the substance. The equations of van der Waals and of Dieterici require values of 2·67 and 3·70, respectively, for $RT_c d_c/MP_c$, as against $3{\cdot}52_3$, the mean of the values available. R. A. MORTON.

Pressure–temperature formula for vapours. A. BATSCHINSKI (Nature, 1927, **119**, 198).—A satisfactory formula is $t+c=k[p^{1/4}-10^{\alpha-(\beta/\log p_k-\log p)}]$, where p_k is the critical pressure and c, k, α, β are constants, different for different substances. At sufficiently high pressures (*e.g.*, 1—3 atm. to the critical pressure), the formula becomes $t+c=kp^{1/4}$.

A. A. ELDRIDGE.

Sublimation pressures of substituted quinones and quinols. A. S. COOLIDGE and (MISS) M. S. COOLIDGE (J. Amer. Chem. Soc., 1927, **49**, 100—104).—The sublimation pressures, p, of twelve substituted quinones and quinols are recorded for various temperatures. In each case log p is a linear function of $1/T$. S. K. TWEEDY.

Influence of centrifugal force on rate of evaporation. E. MACK, jun. (J. Amer. Chem. Soc., 1927, **49**, 135—142).—The rate of sublimation of iodine as observed in a small high-speed centrifuge is directly proportional to the centrifugal force up to values of the latter equal to 250 times gravity and probably higher, always provided that an adsorbent at the end of the diffusion space absorbs the iodine vapour as fast as it arrives. The somewhat amorphous solid iodine surface probably loses molecular aggregates and loosely-held molecules under the influence of the force. When the iodine vapour diffuses against centrifugal force, the rate of evaporation is the same as that found when normal diffusion occurs in the centrifuge at rest. S. K. TWEEDY.

Transformation phenomena of low-melting alloys (Rose's metal). R. FLEISCHMANN (Z. Physik, 1927, **41**, 8—17).—Rose's metal (1Sn, 1Pb, 2Bi) is shown, by dilatometric and resistance measurements, to exist in three different modifications, named σ, α, and β. The σ-form is obtained in the just-solidified metal. The α-form is stable below, and the β-form above, 76°. Below the m. p., only the following transformations are possible : $\sigma\rightarrow\alpha$, $\alpha\rightarrow\beta$, $\beta\rightarrow\alpha$. Thermo-electric experiments on the alloy confirm these results. W. E. DOWNEY.

The characteristic equation of gases. K. SHIBA (Proc. Imp. Acad. Tokyo, 1926, **2**, 398—400).—A discussion of the equation of state advanced by the author (Nippon Sûgaku-Buturigakkwai Kizi, 1926, [iii], **8**, 31), in which it is concluded that the equation of Clausius cannot be considered as a corrected form of that of van der Waals. The limitations of Goebel's equation are discussed (A., 1904, ii, 311, 706); and the law of intermolecular force is deduced to be of the inverse 8th or 9th power for carbon dioxide, in approximate agreement with Debye's theory (*ibid.*, 1919, ii, 211). R. W. LUNT.

Relation between surface tension and temperature. J. E. VERSCHAFFELT (Bull. Acad. roy. Belg., 1926, [v], **12**, 566—572).—The effect of the temperature T, on the surface tension, γ, can be expressed by the empirical formula $\gamma=A(T_c-T)^B$, where T_c is the critical temperature, and $B=1{\cdot}2$, approximately, for "normal" liquids. A similar expression can be deduced from van der Waals' theory of capillarity, but B then has the value 1·5. This is probably because the theory admits of the equation of state being continuous in the neighbourhood of the critical point, which seems to conflict with the experimental evidence (cf. A., 1923, ii, 533). On the assumption of discontinuity, a value is obtained for B which agrees satisfactorily with that found by experiment. R. CUTHILL.

Simple lecture experiment on the viscosity of gases. K. PRZIBRAM (Physikal. Z., 1926, **27**, 830).—A small hollow brass cube is fitted with glass windows on opposite sides. A movable stiff wire traverses the cube in a horizontal direction. A cloud of ammonium chloride falls slowly in the cube, and when this is placed in the beam from a projection lantern, the viscosity of air can be demonstrated by deflexion of the falling cloud as the wire is moved to and fro. R. A. MORTON.

Laws of viscosity of fluids. J. DUBIEF (J. Phys. Radium, 1926, [vi], **7**, 402—413).—No law is yet known which expresses viscosity in terms of density or pressure for the entire fluid state. Maxwell's law ($\eta_0=mu/3\pi\rho^2\sqrt{2}$) is applicable only to perfect gases, since for actual fluids it fails as Boyle's law fails. On the basis of the kinetic theory, $\eta=\eta_0 v/(v-b)$ (η being viscosity of a fluid of volume v, η_0 that of a perfect gas at the same temperature, b the co-volume of van der Waals). The unusual form of this expression leads to a consideration of the following expression for the equation of state : $pv=(1-\gamma\phi(T)/v)\,.\,\eta RT/\eta_0-\pi$, π being a linear function of the density. The latter function appears to be discontinuous, but the argument may be vitiated by experimental errors, and existing compressibilities may be subject to systematic errors. R. A. MORTON.

Viscosity [of copper, brass, and bronze] at high temperatures. J. COURNOT and R. PAGÈS.—See B., 1927, 112.

Passage of hydrogen through metals. G. BORELIUS and S. LINDBLOM (Ann. Physik, 1927, [iv], **82**, 201—226).—The passage of hydrogen through the walls of tubes of iron, nickel, monel metal, and a palladium–platinum alloy (80% palladium, 20% platinum) has been investigated at pressures below 1 atm. and at temperatures up to 700°. For iron, the investigation was extended to high pressures over the temperature range 25—700°, and also to the diffusion of hydrogen into the tube during electrolysis. The tube was immersed in an electrolyte and used as an electrode, and the quantity of gas entering was investigated for different current densities and temperatures between the ordinary temperature and 100°. The diffusion showed a normal relation with the dimensions of the tube. At constant pressure, the temperature effect is a function of $e^{-b/T}$, where b is a constant and T is temperature Abs. The diffusion of hydrogen through iron when electrolysis is carried out at a constant current density shows the same temperature relationship as the constant pressure–high temperature diffusion. In each case b is the same.

At constant temperature, the measurements indicate an approximate proportionality to $\sqrt{p}$, where p

is the gaseous pressure. More exact proportionality is given by $\sqrt{p}-\sqrt{p_t}$ for $p>p_t$, where p_t is a threshold value for the pressure. For iron at different temperatures, p_t decreases with increasing temperature. Bodenstein has recorded that at constant temperature the effect varies as $\sqrt{I}$, where I is current density. Over the range 0·005—0·05 amp./cm.^{2}, the proportionality follows the relation $\sqrt{I}-\sqrt{I_t}$, where $I>I_t$ and I_t is a threshold value for current density. The electrolysis and the gaseous diffusion are thus strictly analogous, and current densities can be equated with pressures. Thus 1 amp./cm.^{2} is equivalent to 1700 atm. for iron and 2% sodium hydroxide solution. At moderate temperatures, hydrogen molecules are adsorbed from a gas, and either at the surface or in the metal suffer dissociation, but recombination must occur before the gas can be set free in either the electrolytic or the gaseous process. R. A. MORTON.

Density of binary liquid mixtures at 25°. R. M. WOODMAN (Chem. News, 1927, **134**, 36).—Values of d_4^{25} are recorded for binary mixtures of water with acetic acid, pyridine, and phenol, of benzene with phenol and acetic acid, and of acetic acid with toluene. R. CUTHILL.

Theory and properties of binary mixtures. F. SCHUSTER (Z. anorg. Chem., 1927, **159**, 307—315).—A theoretical paper, in which it is shown that Dolezalek's theory (A., 1909, ii, 22; 1910, ii, 184) cannot be regarded as a general law. From the properties of negative vapour-pressure curves, it is deduced that the saturation of residual valencies, to which molecular-compound formation is due, does not follow stoicheiometrical rules, as in the solid state, but is controlled by a strengthened attraction between the molecules. E. S. HEDGES.

Principles of the analysis of rectification of liquid mixtures. C. GRABOWSKI (Rocz. Chem., 1926, 6, 815—823).—The application of various theoretical considerations to the fractionation of liquids is illustrated and certain graphical methods used in distilleries are explained. R. TRUSZKOWSKI.

Rate of crystallisation of binary and ternary mixtures from which the pure components separate. G. TAMMANN and A. A. BOTSCHWAR (Z. anorg. Chem., 1926, **157**, 27—40).—The crystallisation of supercooled fused mixtures of acetanilide and 2 : 4-dinitrophenol and of azobenzene and benzil, respectively, has been studied by observing the rate of growth of the crystals. For each system there is a range of mixtures for which the eutectic crystallisation occurs more rapidly than the primary crystallisation. The velocity of the former is a minimum for the mixture of the composition of the eutectic. With increase in the rate of crystallisation and the degree of supercooling, the size of the crystals formed diminishes. Observations have also been made on the ternary system acetanilide–2 : 4-dinitrophenol–benzil. R. CUTHILL.

Thermal conductivity and conductivity-relation of alloys in relation to constitution. A. SCHULZE (Z. anorg. Chem., 1927, **159**, 325—341).—The constitution of alloys is investigated from the curves obtained by plotting values of thermal conductivity, λ, electrical conductivity, K, and conductivity-ratio, λ/K, against the composition. A pair of completely miscible metals (silver and gold) give curves for λ and K having a pronounced minimum, showing that the conductivity of either pure metal is lowered considerably by slight amounts of the other; the λ/K curve exhibits a corresponding maximum, which is more pronounced at 100° than at 0°. With heterogeneous alloys (tin and zinc), points on the λ and K curves lie on a nearly straight line connecting the extreme values; the conductivity-ratio is here a constant. Alloys of partly miscible metals (lead and bismuth) represent combinations of the two preceding examples, and the curves are compounded of the two forms. With pairs of metals which form chemical compounds, sharp peaks occur in all three curves, indicating their composition. In this case, the type of curve varies according to whether the compound is immiscible with the pure metals (antimony and cadmium) or is completely miscible with the pure metals (antimony and bismuth), or forms more than one compound (copper and palladium). E. S. HEDGES.

Colour of copper–nickel alloys. J. A. M. VAN LIEMPT (Rec. trav. chim., 1927, 46, 8—10).—Copper–nickel alloys of varying composition were annealed at 900°, and their colours determined by comparison with a revolving circular disc of copper the surface of which could be partly or completely covered with sectors of nickel, the colour being measured by the relative areas of the disc covered by each metal. The colour is not an additive effect. Alloys containing more than 25 vol.-% of nickel are indistinguishable from pure nickel, whilst between 0 and 25 vol.-% of nickel the graph connecting the colour and volume composition is a curve and not a straight line. This indicates that the electron shells of the copper and nickel atoms are deformed by their close proximity in the solid solution. W. HUME-ROTHERY.

Transformations in homogeneous, anisotropic phases without crystallisation. G. TAMMANN and O. HEUSLER (Z. anorg. Chem., 1926, **158**, 349—358).—It is suggested that the β-transformation in copper–zinc alloys containing 51—55% Cu at 453—470° (cf. Haughton and Griffiths, A., 1925, ii, 973) represents a new type of change which may be due to molecular dissociation. An explanation is given based on the lattice structure of the Cu–Zn compound, and the degree of dissociation is then defined as the ratio of the number of unbound atoms to the total number present. The difference between the β-brass transformation and that of the copper–gold alloy containing 0·25 mol. Au (cf. Johansson and Linde, *ibid.*, 1926, 112) lies in the tendency of the latter to supercool and may depend on a slow suspension of the dissociation equilibrium in the Cu_3Au alloy. The loss of ferromagnetism is analogous to the β-brass transformation. A. S. CORBET.

Limits of resistance of tungsten–molybdenum mixed crystals. II. J. A. M. VAN LIEMPT (Rec. trav. chim., 1927, 46, 11—17; cf. A., 1926, 896).—The action of various mixtures of water and one or more acids on tungsten–molybdenum alloys of varying composition has been investigated at different temperatures. In some cases, corrosion starts rapidly at a particular composition, whilst in others the corrosion increases continuously with increase in the percentage of molybdenum. Where a sharp corrosion limit is shown, it is not a constant, but depends on the nature of the reagent, the temperature, and usually also on the time of reaction. The positions of the resistance limits do not agree with the $N/8$ molecular content demanded by Tammann's theory, and the author's previous criticisms of this theory (*loc. cit.*) are confirmed. W. Hume-Rothery.

Thermo-electric properties of certain metallic solid solutions. A. L. Norbury (Phil. Mag., 1926, [vii], 2, 1188—1198).—The *E.M.F.* set up at temperatures between −191° and 500° by a series of copper α-solid solutions, containing aluminium, manganese, nickel, zinc, silver, and tin, when coupled against pure copper, have been determined. Except with manganese alloys, which give complicated results, the results are normal and simple in nature. When the effects on the thermo-electric properties of copper, of equal atomic proportions of the different solute elements except manganese are compared, the order of magnitude of the atomic effects is that in which the elements appear in the periodic table. A similar result is obtained from an analysis of the results of other observers for different types of solid solutions. It is shown that the temperature–*E.M.F.* relationship of the platinum–platinum rhodium (rhodium 10%) thermocouple is most accurately represented by a formula of the type $E.M.F.=-a+bT+c\,.\,10^{-dT}$, where T is the absolute temperature of the hot junction and a, b, c, and d are constants dependent on the thermocouple and the cold junction temperature. A. E. Mitchell.

Thermo-electric force of alloys. E. van Aubel (Bull. Acad. roy. Belg., 1926, [v], 12, 559—566).—The thermoelectric *E.M.F.* referred to copper of alloys of bismuth and thallium, antimony and tin, and antimony and silver have been measured. The *E.M.F.*–composition curves show points of inflexion or minima corresponding with alloys of the composition Ag_3Sb, SbSn, and Bi_5Tl_3, respectively.
R. Cuthill.

What are mixed crystals ? E. Halpern (Rocz. Chem., 1926, 6, 661—678).—Data for the solubility of mixed crystals of zinc and copper ammonium sulphates at 6·8° and of nickel and copper ammonium sulphates at 0° and 8·5° are recorded. The results are in agreement with Retgers' (A., 1889, 931) and Thiel's laws (*ibid.*, 1903, ii, 531). Nernst's distribution law is, however, only approximately satisfied, applying more closely when the solubilities of the constituent salts of a mixed crystal are close to one another. R. Truszkowski.

Additive qualities of mixed crystals. D. Ostersetzer (Rocz. Chem., 1926, 6, 679—688).—The solubilities of mixed crystals of ferrous and zinc ammonium sulphates at 7° and of copper and nickel ammonium sulphates at 0° and 8° have been determined. Temperature differences do not appear to affect the relative solubilities of the constituent salts in the latter case. The results confirm the conclusions of Halpern (cf. preceding abstract).
R. Truszkowski.

Nature of mixed crystals. A. Ploin (Rocz. Chem., 1926, 6, 690—699).—The solubilities of mixed crystals of copper and cobalt potassium sulphates at 0° and 7·8° and of copper and zinc potassium sulphates at 6·8° are recorded. The results confirm the conclusions of Halpern (cf. *supra*).
R. Truszkowski.

Relation between composition and solubility of mixed crystals. B. Haber-Chuwis (Rocz. Chem., 1926, 6, 700—704).—Data representing the solubility of mixed crystals of copper and ferrous ammonium sulphates at 0° and at 8·2° and of ferrous and zinc potassium sulphates at 6·8° are recorded. Thiel's law (cf. Halpern, *supra*) is followed in both cases. Nernst's distribution law is, however, true only for the former pair of salts, where the solubilities of the constituent salts are low and close to one another, but not for the second pair, where the solubility difference is greater. R. Truszkowski.

Solubility of mixed crystals. B. Bertisch (Rocz. Chem., 1926, 6, 705—710).—The solubilities of mixed crystals of copper and cobalt ammonium sulphates at 0° and at 8° and of copper and manganese ammonium sulphates at 7° confirm the conclusions of Halpern (cf. preceding abstracts).
R. Truszkowski.

Solubility of pure and atmospheric nitrogen in distilled- and sea-water. J. H. Coste (J. Physical Chem., 1927, 31, 81—87; cf. A., 1923, ii, 852).—A theoretical paper in which the data of previous investigators are discussed. After due allowance has been made for the effect of argon on the solubility of atmospheric nitrogen, considerable uncertainty still exists as to the absorption coefficient of this mixed gas and of pure nitrogen in both distilled- and sea-water. The probable causes of such uncertainty are considered, chief among which is the difficulty of completely removing the gases of the air from water (cf. Leduc, A., 1906, ii, 155). Congelation appears to be the best means of effecting such removal. L. S. Theobald.

Solubilities of rare-earth salts. II. C. James, H. C. Fogg, B. W. McIntire, R. H. Evans, and J. E. Donovan (J. Amer. Chem. Soc., 1927, 49, 132—135).—The solubilities in water of the bromates $M(BrO_3)_3,9H_2O$, where M represents lanthanum, praseodymium, neodymium, samarium, gadolinium, or terbium, are recorded for 5° intervals between 0° and 45°. The solubility curves for the salts of the cerium group are of a similar type.
S. K. Tweedy.

Capillarity and displacement. K. Schultze (Kolloid-Z., 1927, 41, 6—11; cf. A., 1926, 1094).—Experiments are described on the behaviour of pairs of non-miscible liquids in capillary spaces. When light petroleum is contained in a capillary tube, and water, coloured with ammoniacal cupric oxide, is drawn up into the tube, the water begins to spread from the meniscus separating the two liquid phases, and along the sides of the glass tube, displacing therefrom the petroleum. Finally, the petroleum–glass interface becomes entirely a water–glass interface, irrespective of which liquid is placed on top.

E. S. Hedges.

Solubility of strong, simple electrolytes in water. G. Åkerlöf (J. Physical Chem., 1926, 30, 1585—1596; cf. McAulay, A., 1926, 1089).—It is suggested that the solubility of strong electrolytes in water is dependent on the ability of the ions of the electrolyte to change the dielectric capacity (*D.C.*) of the solvent. Each ion influences the solubility, which is a function of the algebraic sum of the individual changes of the ions on the *D.C.* of the solvent, the ion with the greatest effect on the state of the solvent being the most soluble. When the total influence on the *D.C.* is zero, the solubility is zero, and as the change produced in the *D.C.* of the medium increases, the solubility always increases. In general, a fair agreement has been found between the calculated changes in *D.C.* and the observed solubilities of electrolytes (cf. Harned and Åkerlöf, A., 1926, 796; Åkerlöf, *ibid.*, 688).

L. S. Theobald.

Solubility of solids at low temperatures. W. Jacek (Rocz. Chem., 1926, 6, 501—509).—The solubility of iodine in pentane, *iso*pentane, and carbon tetrachloride is very small at temperatures of about −100° (0·018% in pentane at −71°, 0·017% in *iso*pentane at −79°, and 0·148% in carbon tetrachloride at −24°). At these low temperatures, the iodine solutions are colourless, probably owing to the formation of an unstable compound between iodine and the solvent. The solubility of sulphur in carbon tetrachloride and in toluene was also determined. In all cases, the solubility *s* agrees with $d \log s = \theta dt$, where θ is a constant for the given solvent and solute.

R. Truszkowski.

Adsorption by carbon in viscous media. G. Weissenberger and S. Fränkel (Kolloid-Z., 1927, 41, 14—27).—The amount of iodine adsorbed by various charcoals from glycerol solutions was determined by titration after equilibrium was attained. Measurements of the viscosity of the solutions were also made. Experiments were also carried out on the adsorption of iodine from aqueous solution by carbon, kaolin, and reddle. The results show that the formula of Lockemann and Paucke (A., 1911, ii, 720) holds in highly viscous solutions, and that the relation between total adsorption and the viscosity of the medium is given by the formula $m_r = \Gamma . \eta^{l/r}$, where Γ and *l*/*r* are constants. The formula $m_r = K . \gamma^p$, where γ is the initial concentration and *K* and *p* are constants, was found to hold in the cases examined, but is of only empirical significance. It is shown that colouring matters can be determined in boiling solution containing strong sulphuric acid by means of permanganate titration. The maximum error observed was ±1·2%.

E. S. Hedges.

Active charcoal. Charcoal activated by mineral substances. M. Swiderek (Rocz. Chem., 1926, 6, 603—632).—Charcoal activated by carbonisation in presence of mineral substances such as zinc chloride or asbestos owes its activity to the extension of its surface by the fine division of the charred mass on the mineral basis. Its adsorptive power is determined by the dimensions of the pores, and this, again, depends on the rapidity of carbonisation. Such charcoal-covered granules adsorb gases and decolorise liquids at about the same rate as ordinary charcoal. The activity of such activated charcoal varies with the proportion of the charcoal in the preparation.

R. Truszkowski.

Adsorption of gases by metallised silica gels. L. H. Reyerson and L. E. Swearingen (J. Physical Chem., 1927, 31, 88—101; cf. this vol., 16).—The adsorption of various gases by silica gels metallised with silver, copper, platinum, and palladium by the method of Latshaw and Reyerson (A., 1925, ii, 412) has been measured at 0°, 64·5°, 100°, 138°, and 218°. Hydrogen is appreciably adsorbed by the copper, platinum, and palladium gels, carbon monoxide by all the gels except that of copper, whilst ethylene is absorbed more strongly than by silica gel alone. Oxygen is specifically absorbed by all the gels, especially by the copperised gel. Methane shows no specific effect, neither does carbon monoxide, except possibly in the case of copper. Rise of temperature rapidly reduces adsorption. Successive metallisations of the gel by platinum have no great effect except in the case of carbon monoxide, where a steady increase in the amount adsorbed occurs up to four metallisations. With silica gel alone, the amounts of the above-mentioned gases adsorbed at 0° and 760 mm. increase with the b. p. of the gas, except in the case of carbon monoxide. For all gels, metallised or not, the Freundlich equation holds whenever considerable adsorption takes place. The adsorption isotherms, together with comparative data for the different gases, and for helium and nitrogen on silica gel at 0°, are given.

L. S. Theobald.

Adsorption of benzene vapour on the plane surfaces of glass, fused quartz, and platinum. Isosteric heat of adsorption of benzene on platinum. S. Lenher (J.C.S., 1927, 272—281).—The adsorption of benzene on different surfaces at pressures above 90% of the equilibrium pressure has been measured by a method previously described (McHaffie and Lenher, A., 1925, ii, 854; Lenher, *ibid.*, 1926, 898). The adsorption is expressed in terms of the number of molecular layers. The equilibrium film on glass which will just exert the saturated vapour pressure of benzene remains of practically constant thickness, approximately 20 mols. over the temperature range considered, viz., about 294—303° Abs. The free energy decrease on undergoing adsorption is very low, indicating that there is very little affinity between benzene vapour and a glass surface. Since the amount of adsorption decreases as pressure and temperature are increased, the temperature coefficient of desorption must be greater than the pressure coefficient of adsorption. The adsorption values on silica are very similar. On platinum, the adsorption is from five to seven times as great as that on glass or silica. From 295° to 300° Abs., the amount of benzene vapour adsorbed on a platinum surface at saturation pressure increases with increasing temperature and pressure, but from 300° to 305° Abs. it decreases rapidly. The isosteric heats of adsorption on platinum at constant pressure of benzene vapour are found to be of practically the same magnitude as the latent heat of condensation to liquid at the same temperature. Data are also given of the thickness of films of both benzene and water exerting the saturated equilibrium pressure at different temperatures. The adsorption of vapours on solid surfaces over a wide range of pressure is briefly discussed. M. S. Burr.

Absorption of water by rubber. H. H. Lowry and G. T. Kohman (J. Physical Chem., 1927, **31**, 23—57; cf. van Rossem, Koll.-Chem. Beih., 1918, **10**, 43; Boggs and Blake, B., 1926, 374).—The mechanism of the absorption of water by simple rubber–sulphur compounds has been investigated by studying the various factors which influence the amount and the rate of absorption. The vapour pressure–absorption curves at 25° show that for vapour pressures below 16 mm. the solubility of water is directly proportional to the pressure, and thus indicates the formation of a true solution. The time–absorption curves support this view by showing that soluble impurities in rubber do not affect the amount of water absorbed at low pressures, although at pressures above 16 mm. they have a noticeable effect. Above this pressure, the solubility of water in rubber is greater than Henry's law predicts. Removal of soluble impurities reduces the amount of water absorbed. Measurements at 0°, 15°, 25°, and 40° showed that the rate of absorption increases with increasing temperature, but the amount absorbed is not greatly influenced. A hydrostatic pressure of 10,000 lb./sq. in. reduced the rate, but had no effect on the amount absorbed at equilibrium (cf. Schulze, Gummi-Ztg., 1898, **12**, 118). A slow ageing process occurring in rubber compounds immersed in solution from which air is not excluded increases the amount absorbed. This ageing takes place to the greatest extent on the surface of rubber compounds containing approximately 7% of combined sulphur.

It is inferred that the most important factor determining the amount of water absorbed is the vapour pressure of the water with which a given sample of rubber is in equilibrium, and that absorption consists of (i) a true solution of water in rubber and (ii) the formation of solutions internal to the rubber of water-soluble constituents which can be removed by washing. Finally, the amount of water absorbed decreases greatly with increased rigidity of the rubber compound. L. S. Theobald.

Derivation of adsorption isotherms. II. B. Tamamushi (Bull. Chem. Soc. Japan, 1926, **1**, 257—260; cf. A., 1926, 1201).—Theoretical. A further adsorption isotherm is deduced, involving Gibbs' adsorption formula and Volmer's surface correction, and resembles Freundlich's general parabolic equation. The expression is applied to data for the adsorption of acetic acid from solution by animal charcoal.

A. S. Corbet.

Do substances in solution retain any of the properties characteristic of them in the solid state? C. Montemartini and L. Losana (Notiz. chim.-ind., 1926, **1**, 205—207).—The density–temperature curves for dissolved substances have been compared with those for the substances in the solid state. The curve for sulphur (9%) in nitrobenzene changes direction at about 90° and shows an arrest at 115°; those for 3 and 20% acetamide show arrests at 42° and 65°, respectively. Naphthalene (3·5 and 30%) in xylene shows arrests at 58° and 80°; at concentrations of 2, 4, 10, and 20% in toluene it shows arrests at 48°, 58°, 63°, and 67°. The curves for solutions of *p*-toluidine in xylene (5 and 10%), toluene (10%), and benzene (10%) show arrests at 30°, 41°, 36°, and 33°, respectively. Aqueous (25%) nickel sulphate hexahydrate has an arrest at 42—50°; ammonium nitrate (5, 15, and 25% and solution saturated at 15°) changes direction without arrest at 28°, 30°, 31°, and 32°, respectively. Aqueous (10%) hydrazine sulphate changes direction at 35° and shows an arrest at 55°; 20% aqueous lithium ammonium sulphate shows an arrest at 45°, and 15% aqueous sodium magnesium sulphate tetrahydrate an arrest at 22—23°. In general, but more particularly in the case of concentrated solutions, characteristic breaks are found which are not far removed from the temperatures at which changes occur in the solid state.

Chemical Abstracts.

Rhythmical precipitation of calcium hydroxide. W. M. Fischer and A. Schmidt (Rocz. Chem., 1926, **6**, 404—414).—Periodic variation in light intensity may cause rhythmical precipitation of calcium hydroxide. True rhythmical precipitation, due to chemical factors alone, may be observed when calcium chloride solution diffuses into a sodium hydroxide solution, under a cover-glass. The calcium hydroxide which is at first precipitated soon disappears, being replaced by an unstable hydrate, $2Ca(OH)_2,H_2O$, which then rapidly changes back to the stable normal hydroxide. The optical and crystallographic constants of these two hydroxides are determined and compared. R. Truszkowski.

Liesegang rings. D. Namasivayam (J. Proc. Asiatic Soc. Bengal, 1924, **20**, 367—369).—Experiments on the formation of rings in capillary tubes are described in which ammonia solution diffused into a copper–agar-agar sol gave alternate bands, pale green and dark blue in colour. In every case, the central band in the tube was pale green. An explanation of ring formation on the basis of the movements of electrically-charged colloidal particles is advanced. Chemical Abstracts.

Liesegang phenomenon and stratification. M. Copisarow (J.C.S., 1927, 222—234; cf. *ibid.*, 1923, **123**, 785).—It has been shown that, in the formation of Liesegang rings, the two salt or salt–acid systems may be substituted by (1) one basic salt, *e.g.*, sodium carbonate, sodium hydroxide, barium hydroxide, etc., and (2) a gas or its aqueous solution, hydrochloric acid, formaldehyde, ammonia, etc. Liesegang rings may also be formed in an aqueous medium, *e.g.*, when a solution of sodium carbonate is carefully run over a solution of calcium chloride. Another phenomenon may also be observed in this case, viz., the formation of trees or streamers. Both this phenomenon and ring formation are greatly influenced by temperature, and the former is inhibited by the presence of gelatin or agar-agar. Light has a directive action on tree formation and also on the formation of rings. It is considered that Liesegang rings are due to a primary and a secondary cause.

The primary cause is the periodic deformation or coagulation of the fibrillar structure of the colloid under the influence of the electrolyte. The secondary cause, which really contributes to the viscosity and thickness of the rings rather than to their formation, is the salting out or deposition of the electrolyte on the coagulated membrane. The action of formaldehyde or hydrochloric acid, for example, on gelatin shows that the secondary cause may be eliminated without interfering with the periodic effect. When the initial substances taking part in the Liesegang formation are neutral in character, the formation of acidic or basic substances by hydrolysis often precedes ring formation. These facts, together with the phenomena observed in aqueous solutions, show that no single theory hitherto put forward affords a sufficient explanation. The influence of the presence of hydroxy-compounds such as glycerol, and also of gelatin, on the formation of colloidal calcium carbonate has been studied. These and previous results (*loc. cit.*) show that it is only hydration to pentahydrate which is absolutely necessary for the stratification of calcium carbonate, but that the presence of colloids and salts, and experimental conditions such as temperature and pressure, which influence hydration, have an important effect on the nature of the product. M. S. Burr.

Theory of periodic precipitation. N. R. Dhar and A. C. Chatterji (Z. anorg. Chem., 1926, **159**, 129—144).—Conductivity and diffusion experiments show that silver chromate in gelatin is present as a colloid and not as a supersaturated solution. The same applies to lead chromate, iodide, chloride, etc. in agar and to other substances present in different gels. The theories of Bradford, Wilhelm Ostwald, Wo. Ostwald, and Fischer on the formation of periodic precipitation are discussed and shown to be inadequate.

If silver chromate were present in gelatin as a supersaturated solution, inoculation by some crystals of the solid must suffice to destroy the supersaturation. Experiment shows that a large amount of silver chromate is necessary to cause coagulation.

The most important points of the theory of periodic precipitation are that periodic precipitations are formed by the coagulation of a peptised sol and that the coagulated masses in their formation and after their precipitation absorb and completely or partly coagulate the sol of the same material in the neighbouring layer. M. Carlton.

Anomalous osmosis through collodion membranes. P. J. Jurišić (Physikal. Z., 1926, **27**, 774—778).—When a collodion membrane of the same size and shape as a large test-tube is fitted with a capillary, filled with a salt solution, and immersed in distilled water, it is claimed (Loeb, A., 1919, ii, 399; 1920, ii, 94, 358, 476) that the capillary rise is anomalous. Observations with sodium sulphate have shown that for many of the membranes used, the capillary rise increases with the concentration in a continuous manner. The anomalies are in no case so well marked as in the work of Loeb (*loc. cit.*) and of Preuner. The results are, however, anomalous in the sense that the osmotic values are much higher than those which would correspond with isotonic dextrose solutions. Anomalous osmosis is thus not a general property of collodion membranes in the sense indicated by Loeb and by Preuner. The anomalous results depend on other factors, such as perhaps the size of the pores in the membrane. Preuner's claim that a parallelism exists between diffusion *P.D.* values on the two sides of the membrane and the capillary rise in the anomalous osmotic concentration range is not confirmed. R. A. Morton.

Spheroidal state of liquids on heated metallic surfaces. I. Móscicki and J. Broder (Rocz. Chem., 1926, **6**, 321—354).—Apparatus is described for the concentration of nitric acid in iron vessels, corrosion being avoided by heating the iron to such a temperature that no wetting of the surface takes place. Experiments were made to determine the limiting temperatures at which the wetting of wires immersed in various liquids comes to an end. The conception of "adsorption pressure" is introduced, this being the pressure exerted on the metal surface by the molecules of the layer of liquid wetting it; the actual pressure exceeds this by the pressure of the atmosphere. Hence the b. p. of this layer is higher than that of the rest of the liquid, and is identical with the limiting temperature at which wetting ceases. It is shown that this temperature is a constant for a given liquid and metal, invariably higher than the b. p. of the former, and independent of its temperature. The limiting wetting temperature for aqueous solutions of non-electrolytes at a platinum surface is higher than for pure water (130°), pointing to a greater concentration of solute in the surface layer. It increases according to the series Pt, Fe, Ag, Ni, Cu, Pb. R. Truszkowski.

True and colloidal viscosity. J. Sameshima (Bull. Chem. Soc. Japan, 1926, **1**, 255—257).—True and colloidal viscosity may be distinguished by electrical conductivity measurements. The conductivity of solutions of the same relative viscosity and containing $0 \cdot 1N$-potassium chloride was markedly depressed by the presence of alcohol, glycerol, or sugars (true viscosity), but was almost normal in presence of gum-arabic, soluble starch, or gelatin (colloidal viscosity). A. S. Corbet.

Viscosity measurements of certain sols in presence of electrolytes. D. N. Chakravarti and N. R. Dhar (J. Physical Chem., 1926, **30**, 1646—1659).—Viscosity measurements at 23·1° and 25° have been made on sols of chromium hydroxide, gum dammar, gamboge, ferric arsenate, stannic hydroxide, Congo-red, Nile-blue, and thioflavin, in presence and absence of suitable electrolytes. In every case, there is first a decrease in viscosity on addition of small amounts of the electrolyte, followed by an increase in viscosity with increasing amounts of the latter. This decrease is attributed to the increase in the charge and the consequent dehydration of the particles of the sol (cf. A., 1926, 123). Sols of vanadium pentoxide and ceric hydroxide become more viscous as dialysis proceeds, and this is explained on the view that the less the charge on the sol the greater is its viscosity. The surface tension of sols in relation to viscosity is discussed. L. S. Theobald.

Graphical method for the construction of the viscosity–shear gradient curve. E. HATSCHEK (Kolloid-Z., 1927, **41**, 11—14).—A purely graphical method of constructing the viscosity–shear gradient curve is developed from an equation derived in a previous paper (A., 1926, 1003). E. S. HEDGES.

Viscosimetry by variation in velocity of flow, and a new viscosimeter. WO. OSTWALD and R. AUERBACH (Kolloid-Z., 1927, **41**, 56—62).—Existing forms of viscosimeter are described and critically discussed. A new type of viscosimeter (the "overflow" viscosimeter) is described. In this form, the liquid is contained in a vertical, graduated tube, falls through hydrostatic pressure through a capillary tube, and overflows by means of a U-tube into a receptacle. The methods of measurement and calculation of results are demonstrated. E. S. HEDGES.

Visible and latent differentiated zones in macroscopic homogeneous suspensions. A. STEIGMANN (Kolloid-Z., 1927, **41**, 18; cf. A., 1921, ii, 46, 147).—A description is given of the differentiated zones formed by colloidally-precipitated silver salts. These have in some cases a cellular structure and resemble anatomical preparations. The differentiation is more apparent when the system is exposed to bright daylight than in diffused light. E. S. HEDGES.

Formation of layers in clay suspensions. E. UNGERER (Kolloid-Z., 1927, **41**, 51—54).—The frequent formation of parallel layers observed in suspensions of clay which are left undisturbed (A., 1921, ii, 96) is not a coagulation phenomenon. Observations were made of the particle-density of the layers and of their movement in an electric field. The layers are due solely to the size and weight of particles falling in accordance with Stokes' law. The layer formation takes place also in electrolyte-free clays. E. S. HEDGES.

Anisotropic copper, silver, and gold. S. BERKMAN, J. BÖHM, and H. ZOCHER (Z. physikal. Chem., 1926, **124**, 83—95).—The dichroism and double refraction of finely-divided copper, silver, and gold impregnated in ramie threads and of streaming colloidal solutions of silver and gold have been investigated with results in accordance with Zocher's rule (Naturwiss., 1925, **13**, 1015). *X*-Ray examination of the silver and gold threads shows that the metallic crystals are irregularly disposed; it is inferred that rod-anisotropy is exhibited by such preparations. L. F. GILBERT.

Reactions of colloidal gold with electrodialysed serum-albumin. R. WERNICKE and F. MODERN (Anal. Asoc. Quím. Argentina, 1926, **14**, 270—287).—See A., 1926, 1005.

Colloid chemistry of "viscose" solutions. I. Velocity function of viscosity. T. MUKOYAMA (Kolloid-Z., 1927, **41**, 62—71).—Measurements of the viscosity of glycerol made with the Ostwald–Auerbach viscosimeter (cf. *supra*) showed the Hagen–Poiseuille formula to hold. Measurements were also made of the viscosity of "viscose" solutions of varying age. These all showed "structure-viscosity," and the older solutions exhibited "structure-turbulence" (A., 1926, 240). The absolute value of the critical velocity corresponding with this structure-turbulence decreases with increasing age of solution. E. S. HEDGES.

Preparation of different-coloured gold sols by means of biological fluids. S. UTZINO (Kolloid-Z., 1927, **41**, 28—35).—The biological fluids examined were saliva, serum, cerebrospinal fluid, and urine, all obtained from man. In the general case, the liquid was diluted with a large volume of distilled water and boiled, and a measured quantity of a solution of gold chloride added to the boiling liquid. The boiling was continued for several hours, the progress of formation of the colloidal solution being observed meanwhile. The results obtained were as follows: dialysed saliva gave gold sols of a bright red colour, whilst the dialysate produced blue or green sols; serum gave a bright red and cerebrospinal fluid a dark red sol, although the latter produced a blue sol in presence of potassium carbonate; light red gold sols were obtained from dialysed urine, whilst the dialysate gave violet sols; with undialysed urine, violet sols were formed in presence of a small amount of potassium carbonate, but red sols with larger amounts. All the sols were characterised by considerable stability. E. S. HEDGES.

Colouring of starch grains. R. HALLER (Kolloid-Z., 1927, **41**, 81—87).—The colouring of starch grains with indigo, Prussian-blue, methyl-violet, methylene-blue, fuchsin, purple of Cassius, and iodine was studied. After colouring, the grains were allowed to swell in a suitable liquid, causing the outer skin to burst and the contents of the cell to exude. Examination of this process under the microscope showed that in all cases only the outer cuticle was concerned with the colouring, the contents of the cell remaining colourless. The effect of different swelling agents was studied, and a concentrated solution of calcium nitrate proved to be the most suitable. Further evidence was obtained that the blue substance formed between starch and iodine is an adsorption compound. This system shows a close analogy to the colouring of cotton. E. S. HEDGES.

Condition of silver chromate in gelatin from electric conductivity and diffusion experiments. A. C. CHATTERJI and N. R. DHAR (Trans. Faraday Soc., 1927, **23**, 23—30).—See A., 1926, 1203.

Birefringence of cellulosic gels. O. FAUST (Kolloid-Z., 1927, **41**, 54—55).—When "viscose" is allowed to flow from a fine opening into a hot concentrated ammonium chloride solution, a thread-like structure, consisting of the xanthate, is formed. This does not exhibit birefringence, nor does the hydrated cellulose regenerated when the product is treated with a mineral acid, but the substance is doubly refractive when stretched. The birefringence of artificial silk is due to this state of tension, and not to crystalline form. *X*-Ray examination of cellulose esters fails to reveal a crystalline structure. E. S. HEDGES.

Effect of chemically active rays on gelatin. H. BRINTZINGER and K. MAURER (Kolloid-Z., 1927, **41**, 46—50).—Gelatin subjected to the rays from a quartz lamp was altered so that its tendency to swell in water was lessened, the effect being proportional to the duration of illumination. Further, the solubility of the swollen gelatin in water was reduced, prolonged boiling being necessary to effect dissolution. Elementary analysis failed to detect a difference, but the irradiated specimen was found to reduce ammoniacal silver nitrate solution. The same effect was observed when the gelatin was irradiated in an oxygen-free atmosphere, but was considerably reduced by rigorous purification of the gelatin. The effect of light is dependent on the presence of an iron catalyst normally found in the ash of gelatin.

E. S. Hedges.

Flocculation of mastic suspensions. A. Boutaric (J. Chim. phys., 1926, 23, 850—870).—The flocculation of mastic suspensions in dilute alcohol has been determined under a large number of conditions by measuring the opacity of such solutions with a Féry spectrophotometer for the light of wave-length 5900 Å. Aqueous solutions of sulphuric acid, potassium chloride, and barium chloride increase the velocity of flocculation for grains of constant size; with increasing grain size the velocity diminishes. The influence of temperature is specific to the coagulating electrolyte. No difference could be observed in the velocity when the coagulation was carried out in the dark, in red, and in blue light. The influence of the addition of stable organic colloids and of protective electrolytes has also been examined.

R. W. Lunt.

Mechanical and electrical coagulation. Wo. Ostwald (Kolloid-Z., 1927, 41, 71—80).—The effect observed by Freundlich and Kroch (this vol., 18) that certain colloid systems are coagulated by mechanical stirring is discussed, and their conclusions are criticised. It is considered more likely that the coagulation is due to electric charges set up by differences of potential between the stirrer and the colloid system. It is shown that the observations of Freundlich and Kroch can be explained quantitatively on this basis.

E. S. Hedges.

Equilibrium in colloid systems. II. Coagulation. O. K. Rice (J. Physical Chem., 1926, 30, 1660—1668).—A theoretical paper in which the conclusions of a previous paper (A., 1926, 352) are revised and extended. On the assumption that surface tension and other properties of colloid particles do not vary with particle size when this is large, the disperse state is shown to be stable when the surface tension of the particles is negative, and unstable when the surface tension is positive. Coagulation occurs at certain definite concentrations and potentials of the particles corresponding with $\gamma=0$.

L. S. Theobald.

Influence of alcohols on the coagulation of dispersoid solutions. A. Janek and B. Jirgensons (Kolloid-Z., 1927, 41, 40—46).—A study was made of the effect of methyl, ethyl, propyl, and *iso*butyl alcohols on the coagulation of dialysed sols of ferric hydroxide, silver, and arsenious sulphide by electrolytes. When coagulation was carried out by means of sodium chloride, small amounts of the alcohols sensitised the sols (*i.e.*, rendered coagulation easier), the effect increasing with increasing mol. wt. of the alcohol. Higher concentrations of alcohols stabilised the sols. This effect, although not very noticeable with ferric hydroxide, was easily recognisable with silver sol and quite pronounced with arsenious sulphide. In the case of arsenious sulphide, a maximum stabilising concentration was reached, further increase of alcohol causing sensitisation again. In this case, also, methyl alcohol differed from the others in sensitising throughout. The best stabilising effect was found in the coagulation of arsenious sulphide by barium chloride, with small quantities of alcohol. In this case also, methyl alcohol exerted a sensitising effect, and at higher concentrations ethyl alcohol did likewise.

E. S. Hedges.

Lyotropic properties of the fluorine ion. H. Freundlich and M. Aschenbrenner (Kolloid-Z., 1927, 41, 35—40).—The fluorine ion is regarded as the extreme end of the Hofmeister series. The experimental data on which this conclusion rests are the following effects, due to the presence of fluorine ions: (1) the lowering of the solubility of highly soluble substances, (2) the large increase of surface tension at a water–air interface, (3) the change in the electropotential at a water–air interface, (4) the favourable influence on the sol–gel transformation of a gelatin solution. Fluorine ions have a strong coagulative effect on the weakly hydrophilic colloid, ferric hydroxide, but a weaker effect than the chlorine ion on the hydrophobic cupric oxide sol.

E. S. Hedges.

Influence of hydrophilic colloids on the colour change of indicators. A. Gutbier and H. Brintzinger (Kolloid-Z., 1927, 41, 1—6).—The effect of hydrophilic colloids on the end-point, as shown by various indicators, was determined by direct titration of 0·1N-hydrochloric acid with 0·1N-sodium hydroxide and *vice versa*. In the cases where a difference was noticed, the amount of deviation increased progressively with increasing amounts of colloid, and the result depended on whether the neutral point was approached from the acid or alkaline side. The colloids studied were gelatin, gum arabic, and dextrin, and the results obtained with the indicators were as follows: azolitmin and neutral-red underwent the colour change at the normal value of p_H; phenolphthalein and rosolic acid behaved normally in the titration of acid, but the end-point was premature in the titration of alkali; alizarin behaved normally in the titration of acid, but the end-point was delayed in the titration of alkali; Congo-red and methyl-orange gave a premature end-point in the titration of acid and a delayed end-point in the titration of alkali. The use of indicators in such cases is thus very limited. Parallel experiments, following the course of the titration electrometrically, showed that the presence of the colloid depresses the concentration of hydrogen ions in acid and of hydroxyl ions in alkaline solutions. The electrometric titration curve of hydrochloric acid and sodium hydroxide in presence of 3% of gelatin or gum arabic resembles that of a weak acid and a weak base. In addition to the buffering effect of the colloid, it is considered that the degree of dispersion of the indicator partly accounts for the effect. Excepting solutions of methyl-orange and alkaline solutions of phenolphthalein, rosolic acid, and Congo-red, the indicators were found to be colloidally dispersed. E. S. Hedges.

Relations of phenol to proteins and other colloids. Disinfectant action. E. A. Cooper and E. Sanders (J. Physical Chem., 1927, 31, 1—22; cf. Cooper and Woodhouse, B., 1923, 1094A).—The nature of the change produced in various proteins by phenol and the mechanism of disinfection have been studied. Precipitation commences when the concentration of phenol reaches 1% for serum-albumin, 0·5% for euglobulin, and 0·001% for pseudoglobulin, and is complete at 1·8, 1·5, and 2·0%, respectively. Experiments with dialysers of "viscose" give a partition coefficient of 11 between phenol and serum-albumin, and the absorption of phenol in this case is a reversible process. Comparison with egg-albumin shows that the precipitating action of phenol is not primarily determined by the absolute amount present. With pseudoglobulin, the values 6·6 and 12 were obtained for the partition coefficient, but absorption here is not strictly reversible. Myosinogen and paramyosinogen are completely precipitated at concentrations of 1·2% and 0·8% of phenol, respectively, and this suggests a similarity with the action of heat, myosinogen being coagulated at a higher temperature.

The distribution ratio between phenol and edestin, as in the case of casein (Cooper, A., 1912, ii, 1199), increases with increasing concentration of phenol. The distribution of phenol between gliadin and water, gliadin and 70% alcohol, and between gliadin and absolute alcohol was also investigated.

In order to test the hypothesis that the precipitation of protein by phenol is due to chemical action, the distribution ratios of gelatin derivatives were measured. The substitution of the methylene group, the quinone nucleus, and bromine in the amino-groups increases the solubility of phenol, although treatment of the gelatin is without effect on the partition coefficient. In general, phenol is distributed between water and proteins in the emulsoid state according to the partition law, but at a certain concentration the protein is precipitated, and this is accompanied by an increased absorption of the former. With certain precipitated proteins, viz., casein, edestin, gliadin, gelatin and its derivatives, the coefficient continues to increase with the concentration of the phenol, in agreement with the view that phenol is associated when dissolved in precipitated proteins. The behaviour of gelatin is anomalous. With resorcinol as the precipitant, the partition coefficient does not increase with increasing concentration.

The bactericidal action of the phenols is not determined merely by their solubility in proteins, but is apparently due to a subsequent action on the colloidal structure of the bacterial cell.

L. S. Theobald.

Imbibition of colloids. P. Bary (Rev. gén. Colloid., 1926, 4, 322—327).—A theoretical paper in which the failure of the Noyes and Whitney expression for the velocity of imbibition (J. Amer. Chem. Soc., 1897, 19, 930) is discussed on the hypothesis that a colloid is a homogeneous solvent into which the liquid diffuses. It is shown that the discrepancies cannot be traced to a non-uniform distribution of liquid through the solid colloid; and they are explained by suggesting that imbibition is accompanied by the depolymerisation of the solid, and that the liquid must in some way combine with the solid.

R. W. Lunt.

Physico-chemical structure of the collagenic substance. I. Spiral arrangement and hygroscopic torsion of collagenic bundles of tendons. G. C. Heringa and (Miss) H. A. Lohr (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1081—1086).—Dark-field observation of longitudinal and transverse sections of various tendons shows that they consist of collagenic bundles intertwined in a spiral form, and a similar condition was found in microscopic preparations of skin and loose connective-tissue. Further evidence was obtained from experiments on the swelling and desiccation of tendons and of isolated bundles of collagen fibres. Torsion occurs in both swelling and desiccation, but in opposite senses. The conclusions were strengthened by the results of an *X*-ray spectrographic examination.

E. S. Hedges.

Physico-chemical structure of the collagenic substance. II. An optical phenomenon. G. C. Heringa and M. Minnaert (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1087—1091).—A description is given of a peculiar diffraction figure obtained when longitudinal sections of a cow's tendon (enclosed in a lævulose–gelatin mixture) are held in front of a source of light. The phenomenon is shown not to be due to a periodic ridging of the surface, or to a periodic variation in the ordinary refractive index, but is believed to indicate a periodic change in double refraction throughout the fibre. Microscopical examination also indicated an undulatory structure, and direct measurement of the period of a group of clearly-defined wavelets gave a wave-length of 40 μ. The bundles of fibre behave like uniaxial crystals the axes of which are disposed in a spiral form. E. S. Hedges.

Physico-chemical structure of the collagenic substance. III. *X*-Ray investigation. G. C. Heringa and N. H. Kolkmeijer (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1092—1094).—A rough analysis was made of *X*-ray spectrographs obtained from the tendon of a mouse-tail. The striations which appeared are believed to be due to the occurrence of a linear succession of equal elements in the long axis of the fibres. E. S. Hedges.

Fibrillous coagulation *in vitro* of collagen dissolved in a dilute acid. J. Nageotte (Compt. rend., 1927, 184, 115—117).—Collagen from the tendons of the tail of a rat swells up and partly dissolves in acetic acid solution (1 in 25,000), but is reprecipitated as a clot after some days. The fibrils of the coagulum are cylinders with pointed ends, usually long, and of thicknesses varying from 1 μ downwards. Under the ultramicroscope, needle-shaped crystals like those of tyrosine can be seen. The fibrils, but not the crystals, give the tinctorial reactions characteristic of collagen. Their great sensitiveness to dilute acids and bases is suppressed by the action of fixing agents. The structure is definitely colloidal and independent of the medium.

J. Grant.

Equilibrium constant $[K_g]$ of the esterification reaction in the gaseous phase. W. Swientoslawski and S. Poznanski (Compt. rend., 1927, 184, 92—94; cf. A., 1924, ii, 601).—The value K_g has been redetermined with an improved apparatus for a series of mixtures of alcohol, acetic acid, water, and ester in a state of equilibrium. A mean value of 58 was obtained, the mean experimental error being ±10%.

J. Grant.

Methane equilibrium. R. C. Cantelo (J. Physical Chem., 1927, 31, 124—130; cf. this vol., 20).—Calculations of the equilibrium constants for the ten possible reactions involved in the thermal decomposition of methane, ethane, or ethylene indicate that above 400° the final system consists of methane, carbon, and hydrogen, whatever the initial hydrocarbon might be. This conclusion agrees with the experimental results of previous investigators on the decomposition of ethylene or ethane by heat, alone and in presence of catalysts (cf. Bone and Coward, J.C.S., 1908, 93, 1197).

L. S. Theobald.

Theory of perfect solutions. W. Daniewski (Rocz. Chem., 1926, 6, 556—568).—Theoretical.

R. Truszkowski.

Conductivity and mol. wt. of halogen acids in dry and moist nitrobenzene. M. Hlasko and E. Michalski (Rocz. Chem., 1926, 6, 534—555).—The conductivities of hydrogen chloride and bromide in dry nitrobenzene and nitromethane are, in spite of the high dielectric constants of the latter solvents, very small. Thus for dry nitrobenzene, α is $4{\cdot}0\times10^{-4}$ for $0{\cdot}6N$-hydrogen chloride, and $6{\cdot}7\times10^{-4}$ for $0{\cdot}6N$-hydrogen bromide, whilst in nitromethane α is $9{\cdot}4\times10^{-4}$ for $8{\cdot}7N$-hydrogen chloride. The presence of 0·1% of moisture increases the conductivity tenfold. Hydrogen bromide is in all cases more dissociated than the chloride. Cryoscopic measurements show that water, hydrogen bromide, and hydrogen chloride, dissolved in nitrobenzene or in formic acid, are present as simple molecules, but that the addition of hydrogen bromide or chloride to wet nitrobenzene produces little depression of f. p., owing to the formation of hydrates of the type HCl,H_2O, provided that it is added in quantities not greater than the water content. It follows that conclusions relative to the association of dissolved substances in the above solvents are not valid unless precautions are taken to eliminate water, and for this reason the results of Zanninovich-Tessarin (A., 1896, ii, 352) and of Beckmann and Lockemann (*ibid.*, 1907, ii, 845), which indicated polymerisation of hydrogen halides in the above solvents, are not acceptable.

R. Truszkowski.

Soret effect. C. C. Tanner (Trans. Faraday Soc., Jan., 1927, advance proof).—The concentration difference set up in a solution by a temperature gradient has been studied by an optical method involving measurements of the change of refractive index. Solutions of acids, bases, and metal halides, nitrates, and sulphates of varying normality have been thus examined for temperature differences of 14° and 20°. The fractional change per degree of the normality of the solution passes through a maximum for hydrochloric and sulphuric acids, whilst the low values for lithium and magnesium salts and the large values for alkali hydroxides are in substantial agreement with the results obtained by Chipman (A., 1926, 1206).

A. S. Corbet.

Dilution law for strong electrolytes. B. Szyszkowski (Rocz. Chem., 1926, 6, 510—534).—The equivalent conductivities of strong electrolytes (univalent anion and cation) satisfy the following law from 0·0001 to $0{\cdot}1M$-solutions: $1-\lambda/\lambda_0=0{\cdot}5\beta C^{1/2}-\gamma c+1{\cdot}5\delta C^{3/2}$, where β, γ, and δ are constants. This expression agrees fairly well with Kohlrausch's experimental values and affords a confirmation of Debye and Hückel's theory for solutions of completely dissociated electrolytes.

R. Truszkowski.

Dissociation constant of carbonic acid. A. Klemenc and M. Herzog (Monatsh., 1927, 47, 405—413).—The conductivity of sodium hydrogen carbonate in aqueous solution at 0° and 12·5° and of carbonic acid at 12·5° has been determined, the method of Walker and Cormack (J.C.S., 1900, 77, 5) being employed. Extrapolation of the equivalent conductivity values for sodium hydrogen carbonate by means of the Noyes equation $1/\lambda=1/\lambda_\infty+K(C\lambda)^{n-1}$, where $n=1{\cdot}5$, gives the values 49·8 and 73·1 for λ_∞ at 0° and 12·5°, respectively. The degree of hydrolysis of sodium hydrogen carbonate solution is discussed, and the authors confirm the conclusion of Auerbach and Pick (A., 1911, ii, 1078) that the hydrolysis is independent of the concentration. Calculations of the mobility of the HCO_3 ion and of the limiting conductivity of carbonic acid from the new data give values in good agreement with those of Kendall (*ibid.*, 1916, ii, 512). The value of the apparent first ionisation constant of carbonic acid $[H'][HCO'_3]/[CO_2+H_2CO_3]$ obtained from the conductivity measurements is $2{\cdot}65\ (\pm0{\cdot}04)\times10^{-7}$ at 12·5°. The values of the true dissociation constant and the apparent second ionisation constant of carbonic acid obtained by previous authors (cf. Thiel, *ibid.*, 1917, ii, 134, and references there quoted; and McCoy, *ibid.*, 1903, ii, 413) are examined in the light of the new data, and suggest that carbonic acid H_2CO_3 is completely ionised.

J. W. Baker.

Dissociation constant of nitroamide. J. N. Brönsted and C. V. King (J. Amer. Chem. Soc., 1927, 49, 193—200; cf. A., 1925, ii, 982).—Nitroamide decomposes in pure water at 15° 10% faster than in acid solution. The conductivities of aqueous nitroamide solutions were determined between unplatinised electrodes; the (acid) dissociation constant is $2{\cdot}55\times10^{-7}$ at 15°. The conductivities of the sodium salt were also determined.

S. K. Tweedy.

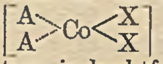
Determination of the dissociation constants of phenol and of the hydroxyl group of tyrosine by means of absorption measurements in the ultra-violet. W. Stenström and N. Goldsmith (J. Physical Chem., 1926, 30, 1683—1687; cf. Stenström and Reinhard, A., 1926, 10).—The dissociation constant is calculated from the expression

$D=[\mathrm{H}](\varepsilon-a)/(b-\varepsilon)$, where a is the extinction coefficient for molecules not ionised at the hydroxyl group, b that for molecules which are so ionised, and ε that for a mixture of ions and molecules. A suitable value for ε lying between a and b is determined graphically for a certain p_{H} value, at a chosen wave-length. Between 18° and 24°, two aqueous solutions of phenol (N/1570) gave $D=1{\cdot}38\times10^{-10}$ and $1{\cdot}21\times10^{-10}$, respectively, when $\lambda=2825$ Å.; N/1550 tyrosine solutions gave $D=1{\cdot}24\times10^{-10}$ and $1{\cdot}83\times10^{-10}$ at $\lambda=2840$ Å. L. S. THEOBALD.

Cupriammonia ion and its stability. P. JOB (Compt. rend., 1927, **184**, 204—206).—The coefficients of absorption of various mixtures of solutions of cupric and ammonium salts have been measured with a Féry spectrophotometer. The molecular concentrations of the copper and ammonia, respectively, varied from 0·2 to 0·01 and 1·0 to 0·1, the salts being dissolved in a concentrated solution of ammonium nitrate to prevent the formation of cupric hydroxide by retarding the electrolytic dissociation of the ammonia. Curves connecting the absorption as a function of the composition showed marked maxima, corresponding in the case of equimolecular mixtures with the formula $Cu(NH_3)_4$. For the non-equimolecular solutions, the dissociation constant was calculated, and was found to agree with the results obtained from the absorption data. A value of 5×10^{-10} was found at 16°. The tetra-ammonia ion, therefore, is probably the only cupriammonia ion stable at the ordinary temperature. The affinity of ammonia for the cupric ion is 12,400 g.-cal. J. GRANT.

Rotatory power of organic compounds as a function of the p_{H}; malic acid. E. VELLINGER (Compt. rend., 1927, **184**, 94—96).—The curves obtained for the dispersion and rotatory power of malic acid as functions of its p_{H} value resemble those given by tartaric acid. The rotation curve is expressed by the same formula, the two ends, however, being depressed to a greater extent, whilst the position of the point of inflexion indicates that the greatest variations in the rotatory power are determined by the first stage dissociation. When plotted according to the method of Darmois, the dispersion lines do not all converge to the same points, as in the case of tartaric acid (A., 1926, 1201). This may be accounted for by an experimental error of 3—5%.

J. GRANT.

Solvation and complex formation as causes of colour change in cobaltous halides. A. HANTZSCH (Z. anorg. Chem., 1927, **159**, 273—303).—Previous work on the subject is reviewed, and it is shown that the colour change cannot be due to the formation of ions of the type CoX_4''. Consideration of the colour of solid compounds of the type CoX_2A_2 (blue or violet), CoX_2A_4 (red), and CoX_2A_6 (rose), where X is a halogen atom and A is a molecule capable of addition (*e.g.*, H_2O, NH_3, etc.), indicates that solvation is a primary cause. The constitutions of the first and third types are, respectively,  $\left[{}^{A}_{A}{>}Co{<}^{X}_{X}\right]$ and $[CoA_6]X_2$, whilst that of the second type is doubtful. Since *cis–trans* isomerism is possible with the first type, this explains the existence of a blue and a violet form. The change of the red forms to blue when heated or on concentration of the solution is in agreement with the solvation theory. The absorption spectra of a large number of representatives of this type were examined in various solvents. In general, a large optical difference was found between the salts CoX_2A_2 and CoX_2A_6, but, in each of these groups, the nature of the halogen atom and of the combined group A made little difference. The absorption was strengthened slightly in the order $Cl<Br<SCN$. Experiments on the dehydration of cobalt chloride hexahydrate did not indicate the existence of the hydrates $CoCl_2,4H_2O$ and $CoCl_2,1{\cdot}5H_2O$ described in the literature. The cobalt thiocyanate tetrahydrate described by Grossmann and Hünseler (A., 1906, i, 7) appears to be a trihydrate, but the existence of the hemihydrate described by Rosenheim and Cohn (*ibid.*, 1901, i, 455) was confirmed. Methods of preparation of the following new *compounds* are described: the dimethyl-alcoholates of cobalt bromide and of cobalt thiocyanate, $Co(CH_3{\cdot}OH)_2X_2$; the hexamethyl-alcoholates of cobalt bromide and of cobalt chloride, $Co(CH_3{\cdot}OH)_6X_2$; the corresponding thiocyanate could not be isolated; the tetrabenzyl-alcoholates of cobalt chloride and of cobalt bromide, $Co(C_6H_5{\cdot}CH_2{\cdot}OH)_4X_2$; diacetonitrile cobalt bromide, $Co(CH_3{\cdot}CN)_2Br_2$; dipyridine cobalt sulphate, $CoSO_4,2C_5H_5N$; dipyridine cobalt oxalate, $CoC_2O_4,2C_5H_5N$. E. S. HEDGES.

Molecular structure in solution. I. Densities and viscosities of aqueous solutions of cobalt chloride and hydrochloric acid. O. R. HOWELL (J.C.S., 1927, 158—170).—The change from red to blue when hydrochloric acid is added to a solution of cobaltous chloride is probably due to a change from six to four in the number of groups or atoms with which an atom of cobalt is associated, as already shown by X-ray examination for red and blue cobalt pigments (Hill and Howell, A., 1924, ii, 817). In the aqueous solution, the cobalt is probably present as hydrated ions $Co(H_2O)_6^{\cdot\cdot}$, which, as the concentration of hydrochloric acid is increased, are progressively converted into $CoCl_4''$ ions. The densities and viscosities of a series of aqueous solutions containing a constant amount of cobalt chloride, but increasing amounts of hydrochloric acid, have been determined and compared with a similar series of values for hydrochloric acid alone. Differences in viscosity and density for corresponding solutions have been plotted against concentration of acid. At the same concentration of acid, there is, in the density difference curve, a point of inflexion, and in the viscosity difference curve a well-defined maximum. These points are considered to mark the concentration at which equal numbers of the two different kinds of ions are present. This point does not mark the maximum colour change, because the blue colour is much more intense then the red. M. S. BURR.

Complex formation amongst the nitrates. I. Ternary system copper nitrate–cobalt nitrate–water. K. W. WILCOX and C. R. BAILEY (J.C.S., 1927, 150—153).—The system copper nitrate–cobalt nitrate–water has been examined at 14°, 20°, and 30°. The so-called trihydrate of copper nitrate has the composition $Cu(NO_3)_2,2\frac{1}{2}H_2O$, and its transition point to the hexahydrate is 25·4°. A double salt of the probable composition $6Cu(NO_3)_2,Co(NO_3)_2,(42\pm1)H_2O$ has been isolated. It is smoke-blue in colour, crystallising from a purple solution, is very deliquescent, melts at about 17°, and is decomposed by water.

M. S. Burr.

Revision of some activities in water–alcohol mixtures. G. Scatchard (J. Amer. Chem. Soc., 1927, **49**, 217—218).—The activity coefficients of hydrogen chloride in aqueous alcohol are revised, an error in the calculations of the previous paper being corrected (A., 1925, ii, 971). The theoretical calculations are improved by utilising the vapour-pressure measurements of Dobson (J.C.S., 1925, **127**, 2866). The revised results do not preclude the combination of 1 mol. of hydrogen chloride with 2 mols. of water, although this is considered to be unlikely. The ionic size of lithium chloride calculated from the results of Drucker and Schingnitz (A., 1926, 911) agrees much better with the effect of lithium chloride on the activity of non-electrolytes than the results of Pearce and Hart (*ibid.*, 1923, ii, 7).

S. K. Tweedy.

Activity coefficients, ionic concentrations, and kinetic salt effects of formic acid in neutral salt solutions. H. S. Harned (J. Amer. Chem. Soc., 1927, **49**, 1—9).—The ionisation constant, K, of a weak acid is affected by the addition of neutral salt, and this interferes with the calculation of velocity constants from the rate of hydrolysis of esters in neutral salt solutions (cf. Manning, J.C.S., 1921, **119**, 2079). The activity coefficient products of formic acid in various halide and sulphate solutions are calculated from Manning's results, on the assumption that K varies on the addition of neutral salts, but is constant during a reaction in a medium of practically constant ionic strength. The concentration hypothesis yields more reasonable values for the products than the activity theory. The activity coefficient products are higher the lower the activity coefficient of the neutral salt. This effect is considered to be due to a distortion of the readily-deformed, unsymmetrical anions of these substances by the electrical field produced by the neutral salt.

S. K. Tweedy.

Activity coefficients of the ions in certain phosphate solutions. Theory of buffer action. E. J. Cohn (J. Amer. Chem. Soc., 1927, **49**, 173—193).—The p_H values for concentrated solutions containing both potassium dihydrogen phosphate and dipotassium hydrogen phosphate are recorded. The graph of the concentration of the latter salt against p_H shows that the more concentrated the solution the more acid is the reaction and the greater is the deviation of the curve from that required by the mass law. This divergence is greater in concentrated acid than in concentrated alkaline solutions. The activities of the ions in the solutions are calculated and equations representing p_H are deduced with the aid of the Debye–Hückel theory, the results being discussed in the light of the theory of buffer action. Tables and graphs are given facilitating the preparation of buffer solutions of the same ionic strength and varying p_H and *vice versa*. S. K. Tweedy.

Relation between pseudobinary lines and solid solutions in metallic ternary systems. R. A. Morgen (J. Amer. Chem. Soc., 1927, **49**, 39—43).—Mixtures corresponding with the pseudobinary line of the ternary metallic system A–B–C (*i.e.*, the line joining A with the point representing BC, the compound existing in the solid phase) do not behave like ordinary binary systems. Since BC dissociates in the liquid phase, a consideration of the f.-p. diagram for the system A–BC shows that the above mixtures are represented by a two-dimensional point distribution on the surface of a ternary diagram, solid solution occurring at the expense of the compound BC if the latter is "weak." Experiment supports these conclusions. S. K. Tweedy.

Mass unit of chemical potential. W. D. Bancroft (J. Physical Chem., 1927, **31**, 69—80).—Selected passages from the work of Gibbs ("The Collected Papers of J. W. Gibbs") are quoted and explained. Chemical potentials may be referred to any mass units, but general relations are more clearly shown if the appropriate units are employed. For reactions which involve the pressure of gases, or the osmotic pressures of solutions, the mol. wt. of the reacting substance or ion is the appropriate unit, as is the electrochemical equivalent for electrochemical reactions. The appropriate mass units in the case of electrical endosmose or of frictional electricity have yet to be worked out. With organic compounds, there are as many chemical potentials as there are linkings to be broken or activated. Equations for velocity of reaction have still to be deduced from relations between potentials. L. S. Theobald.

Vapour pressures of mixtures of (*a*) methyl acetate and water, (*b*) methyl acetate, sucrose, and water. A. McKeown and F. P. Stowell (J.C.S., 1927, 97—103).—Total vapour pressures at 25° and 35° of methyl acetate–water mixtures, up to concentrations of ester of about 2*N*, and also of solutions containing a constant concentration of ester of 0·2542*N* along with sucrose of concentration varying up to 600 g. per litre of solution, have been determined by a static method (cf. Morton, A., 1919, ii, 448). The partial vapour pressures of ester and water have been determined by a dynamical method. The ratio of the partial pressures of ester at 35° and 25° decreases as the concentration of ester increases. The same result is obtained if, with a constant concentration of ester, its molar fraction is artificially increased by addition of sucrose. This behaviour suggests the possibility of compound formation between water and methyl acetate in aqueous solution of the ester. M. S. Burr.

Vapour pressure of water over sulphuric acid–water mixtures at 25°. I. R. McHaffie (J.C.S., 1927, 112—116).—The vapour pressure of water over sulphuric acid–water mixtures, of concentration varying from 65·9 to 83·5% of acid, has been determined by a method previously described (A., 1926, 700) for the measurement of small amounts of water vapour in permanent gases. The results are in agreement with those obtained by a number of other investigators, and thus confirm the accuracy of the method of measurement. M. S. Burr.

Vapour pressures of potassium nitrate solutions. J. C. W. Frazer, B. F. Lovelace, and R. K. Taylor (J. Physical Chem., 1926, 30, 1669—1677).—The vapour pressures of 0·1—2·9*N*-solutions of potassium nitrate have been measured at 19·94°, and show this salt to be a more nearly ideal solute than other electrolytes which have been examined. A comparison of these results with f.-p. and b.-p. data shows that von Babo's law is not obeyed, except in the case of very dilute solutions when the heat of dilution is small. Certain changes in technique (cf. Frazer, Lovelace, and Sease, A., 1921, ii, 239) are described. L. S. Theobald.

System sodium nitrate–sodium chloride–water. F. Hölzl and H. Crotogino (Z. anorg. Chem., 1926, 159, 78—86).—The isotherms of the system sodium nitrate–sodium chloride–water were determined at 0°, 15°, 25°, 50°, 83°, and 103° for solutions saturated with only one component at a time. They approximate to straight lines as the temperature rises. The investigation covers the ice region and the limit of the b. p. of the system and indicates a moderate tendency to hydration in the case of sodium nitrate. M. Carlton.

Vapour pressure and heat of dilution of aqueous solutions. II. and III. W. R. Harrison and E. P. Perman (Trans. Faraday Soc., 1927, 23, 1—22).—Vapour-pressure and density measurements of calcium and potassium chloride solutions, at concentrations up to saturation, and at temperatures from 40° to 80°, have been made by a statical method which is a modification of that used by Perman and Saunders (A., 1923, ii, 737). The heats of dilution of these solutions have also been determined, over the same temperature range, by an electrical method, which is independent of the sign of the heat change. Calcium chloride has thus been found to have a large negative heat of dilution increasing with temperature, and the values obtained experimentally are in fairly good agreement with those calculated from the vapour pressure. Potassium chloride has a small positive heat of dilution below 70°, but in the neighbourhood of this temperature it becomes negative. In this case also, there is agreement between calculated and experimental values. By taking into account the heat of dilution, a more reasonable value for the mol. wt. of calcium chloride in solution is obtained. M. S. Burr.

Concentration of water vapour in compressed hydrogen, nitrogen, and a mixture of these gases in the presence of condensed water. E. P. Bartlett (J. Amer. Chem. Soc., 1927, 49, 65—78).—The water-vapour content of compressed hydrogen and compressed nitrogen in contact with liquid water at 50° and at pressures up to 1000 atm., and of mixtures of these gases (3 : 1 by volume) at 25°, 37·5°, and 50°, was investigated. It depends on the nature of the gas, the differences for the two gases not being explained by differences in free space. Poynting's law is not obeyed (Phil. Mag., 1881, [iv], 12, 32). In the case of the mixture, the effect of compression is greater at 50° than at 25°. The proportional effect at 37·5° is not the mean of the effects at 25° (at which it is greatest) and 50°. The Leduc rule of additive volumes at constant temperature and pressure holds for the mixture at 50° and probably also at the other temperatures. No quantitative expression of the results has been obtained; qualitatively, the compressed gas appears to act as a solvent for the water vapour. S. K. Tweedy.

Temperatures of magnetic transformations in the system iron–iron sesquioxide. J. Huggett and G. Chaudron (Compt. rend., 1927, 184, 199—201; cf. this vol., 11).—Mixtures of iron and iron sesquioxide obtained by partial reduction of the latter were analysed by complete reduction in hydrogen, and the temperatures at which anomalies occurred in the temperature–magnetisation curves plotted as a function of the ratio of the oxygen removed by reduction to the total oxygen present in the mixture. The points representing the true points of magnetic transformation were also plotted, the anomalies being due to decomposition of the protoxide into iron and magnetic oxide, and to the reverse reaction. In the system iron sesquioxide–magnetic oxide, reversible transformations were observed at 570° and 650°, corresponding with Fe_3O_4 and a saturated solid solution of Fe_3O_4 in Fe_2O_3, respectively. The systems Fe_3O_4–FeO and FeO–Fe showed transformation points at 570° (due to Fe_3O_4) and 765°, respectively. The graphs also show the point of decomposition of FeO, the resulting transformation point of Fe_3O_4, and the recombination of iron and the magnetic oxide. J. Grant.

Properties [thermal decomposition] of diaspore and bauxite. Y. Yamaguchi and T. Takebe (Bull. Chem. Soc. Japan, 1926, 1, 240—244).—Air was passed over the heated sample, and from the weight of water formed, its dissociation pressure *p* was calculated. In agreement with the Clausius–Clapeyron equation, log *p* was found to vary linearly with $1/T$, but with bauxite two curves were obtained, one covering the range 200—340° and the other the range 350—450°. The calculated heats of decomposition are: diaspore, $Al_2O_3,H_2O = Al_2O_3 + H_2O - 42{,}300$ g.-cal.; bauxite, $Al_2O_3,2H_2O = Al_2O_3,H_2O + H_2O - 10{,}100$ g.-cal.; $Al_2O_3,H_2O = Al_2O_3 + H_2O - 8100$ g.-cal. S. J. Gregg.

Nernst's heat theorem and the impossibility of absolute zero. A. Schidlof (J. Chim. phys., 1926, 23, 814—820).—From statistical considerations, it appears highly probable that the absolute zero of temperature and infinitesimal absolute temperatures have no physical significance. If this is so, it can be shown that Nernst's heat theorem is a direct consequence, and that at 0° Abs. the coefficient of expansion and specific heat at constant volume of all substances would be zero. R. Cuthill.

Heats of adsorption of several gases and vapours on charcoal. F. G. Keyes and M. J. Marshall (J. Amer. Chem. Soc., 1927, 49, 156—173).—The heats of adsorption, *q*, of oxygen, chlorine, carbon dioxide, ammonia, ether, chloropicrin, and water at 0° on ash-free charcoal are very large initially and fall rapidly to an apparently constant value as the concentration increases. In the case of water, there is a tendency for *q* to rise with increasing concentration. The empirical relation $q=ac^b$ appears to hold fairly well, except for oxygen. The final energies of adsorption are proportional to the potential energies of the molecules from a state of contact to infinity, a magnitude which is calculated from the constants A and β in the Keyes equation of state; in the case of molecules of the non-permanent electrical moment type, the energy of adsorption is proportional to the electrical polarisation of the molecule as calculated from dielectric constant data. It is suggested that the adsorbed material is in a condition in which only the first layer is under the direct influence of the adsorbent. Each succeeding layer constitutes a fresh adsorbing surface, but the peculiarities of the first layer are progressively lost, until a layer is eventually reached in which the molecular state is practically a molecular "contact" arrangement. S. K. TWEEDY.

Partial molal heat capacity of the constituents and the specific heat of aqueous solutions of sodium and hydrogen chlorides. M. RANDALL and W. D. RAMAGE (J. Amer. Chem. Soc., 1927, 49, 93—100).—The partial molal heat capacities, c, of the two constituents and the specific heats of the above dilute solutions at 25° have been determined directly in a twin calorimeter (cf. Randall and Bisson, A., 1920, ii, 289). The following values were obtained (m is the molality; c_1 refers to the solvent and c_2 to the solute): sodium chloride, $c_1=17·98—0·1082m^{1·5}$, and $c_2=-21+18m^{0·5}$; hydrogen chloride, $c_1=17·98—0·0842m^{1·5}$, and $c_2=-41+14m^{0·5}$. S. K. TWEEDY.

Conductivity and velocity measurements in *iso*butyl alcohol. H. GOLDSCHMIDT [with V. K. LUND, A. THUESEN, E. MATHIESEN, and L. THOMAS] (Z. physikal. Chem., 1926, 124, 23—40).—The electrical conductivities of solutions of hydrogen chloride, bromide, and iodide, of piperidine hydrochloride and picric acid in *iso*butyl alcohol, and of hydrogen chloride and picric acid in aqueous *iso*butyl alcohol have been determined. The conductivities of the hydrogen halides are less in the *iso*- than in the *n*-alcohol. On addition of water to the hydrochloric acid solutions, the conductivity is depressed, passing through a minimum and subsequently rising with increasing concentration of water. With picric acid, there is no initial fall on the addition of water. The rates of esterification of twelve different organic acids in *iso*butyl alcohol, with hydrogen chloride as catalyst, were measured. Water formed in these reactions reduces the rate in accordance with a formula previously advanced (A., 1925, ii, 976); this, however, does not hold for larger (added) quantities of water. An approximate direct proportionality obtains between the velocity coefficient and the concentration of hydrochloric acid. The ratio of the coefficients for phenylacetic acid in *iso*butyl alcohol with two different concentrations of picric acid as catalyst is roughly equal to the ratio of the conductivities of the picric acid. When picric acid is the catalyst, addition of aniline picrate lowers the rate of esterification, but the addition of aniline hydrochloride when hydrogen chloride is the catalyst has little influence. Hydrogen bromide and hydrogen iodide are more efficient catalysts than is the chloride, as in the case of *n*-butyl alcohol (cf. *ibid.*, 1926, 686). The results are generally similar to those observed with other alcohols.

L. F. GILBERT.

Flow potentials. H. LACHS and J. KRONMAN (Rocz. Chem., 1926, 6, 641—652).—Glass and quartz tubes acquire a negative charge if water is run through them. This charge is reduced by the addition of various electrolytes; at certain concentrations of aluminium or thorium ions, it may even be reversed in sign. The maximum potential attainable under similar conditions with the same apparatus cannot be reproduced with an accuracy greater than 14%. This is due to the flow potential not being constant; at the beginning of the experiment it rises to a maximum value, after which it falls. This variation is probably the result of physicochemical changes at the boundary of the liquid, which lead to variations in the thickness of the layer of liquid in contact with the tube. Thus all results obtained for the flow potentials of such systems must be considered to be merely qualitative.

R. TRUSZKOWSKI.

Behaviour of the quinhydrone electrode in solutions of neutral copper sulphate. J. B. O'SULLIVAN (Trans. Faraday Soc., 1927, 23, 52—56).—An attempt has been made to determine the cause of the gradual change in potential of the quinhydrone electrode in a solution of neutral copper sulphate (cf. A., 1925, ii, 822). Experiment has shown that the effect is not due to autoxidation of quinol nor to the formation of complexes between copper ions and the organic matter. A precipitate containing copper is, however, gradually formed from a mixture of copper sulphate and quinol or quinhydrone in solution, the amount of copper increasing with the reducing power of the mixture. It seems probable, therefore, that the potential change and gradual production of a precipitate are due to the formation and slow hydrolysis of cuprous sulphate. M. S. BURR.

Diffusion oxygen electrode. S. VON NÁRAY-SZABÓ (Z. Elektrochem., 1927, 33, 15—20).—Diffusion oxygen electrodes (cf. diffusion hydrogen electrodes, Schmid, A., 1924, ii, 324) of various types have been prepared and their behaviour has been examined at the ordinary temperature. By passing oxygen under a few mm. excess pressure into a porous carbon tube closed at the other end and dipping into an aqueous electrolyte solution, an oxygen electrode was obtained, the potential (ε_h) of which eventually reached the following approximately constant values: +0·83 volt in $2N$-sulphuric acid, +0·38 in 27% ammonium chloride solution, +0·20 in 15% sodium hydroxide solution. The electrodes were easily polarised even by small current densities, but recovered completely afterwards. Oxygen electrodes in which Pasteur–Chamberland filter candles coated externally with a very thin film of sputtered platinum were used as diffusion tubes gave more positive equilibrium potentials than the above, but were much more readily polarised. The best results were obtained by using a carbon tube coated with a sputtered platinum film (1·7 μ thick); its potentials in the above-mentioned solutions were, respectively, +0·96, 0·43, 0·22 volt. With a current density of 0·4 amp./dm.^{2} these values became +0·22, +0·01, −0·09; and with 2 amp./dm.^{2} −0·11, −0·36, −0·38 volt. Up to 4—5 amp. could be obtained from the cells of the type: oxygen (platinised carbon)|electrolyte|zinc. Diffusion oxygen electrodes prepared from carbon rods made by the firm Le Carbone could also be used at high current densities, but did not behave as well as the above platinised carbon tubes. The mechanism of the behaviour of oxygen electrodes is discussed. When carbon is the intermediary, a surface compound of the type C_xO, where x is probably about 3, is regarded as the electromotively active substance. At platinised carbon, however, this oxide is assumed to react rapidly with platinum, yielding the hypothetical platinum "Primäroxyd," which is regarded as the electromotively active substance at oxygen–platinum electrodes. It is concluded that stable diffusion oxygen electrodes can be prepared, giving high power yield per unit area, which are undamaged by short-circuiting.

H. J. T. Ellingham.

Electrode equilibrium in the Weston standard cell. W. C. Vosburgh (J. Amer. Chem. Soc., 1927, 49, 78—92).—The high initial *E.M.F.* of Weston cells, the subsequent lack of constancy, hysteresis (cf. Vosburgh and Eppley, A., 1924, ii, 149), and the abnormal values obtained in rotation experiments (Hulett, Physical Rev., 1907, 25, 16), are attributed to the presence of the mercuric ion in the cathode system at a concentration in excess of that required for equilibrium. Cells prepared with mercurous sulphate free from mercuric salt can be duplicated with respect to their *E.M.F.* after a month or so. High initial values resulted when basic mercuric sulphate was added. The presence of 0·02*M*-sulphuric acid increases the solubility of the basic sulphate and prevents the high initial values. The cathode of an acid cell is in stable equilibrium; such cells are more trustworthy than neutral cells, in which the *E.M.F.* tends to decrease indefinitely. The continual decrease observed in some (neutral) cells (Smith, Trans. Roy. Soc., 1908, 207, 407) is possibly due to mercurous sulphate, prepared in acid solution, tending to change slowly into a more stable state (*e.g.*, solid solution) in presence of neutral saturated cadmium sulphate solution. The maintenance of a low hydrogen-ion concentration is essential for the change, which, however, is stopped by 0·01*M*-acid. Hysteresis is caused by a change in the equilibrium between mercury, mercurous, and mercuric ions with temperature, which leaves an excess of mercuric ion in the cell after a decrease in temperature. The presence of sulphuric acid makes the two electrode systems univariant (pressure and temperature constant), but they become practically invariant if the acid concentration is kept low enough; 0·01 mol./litre is recommended (cf. A., 1925, ii, 1164).

S. K. Tweedy.

Mechanism of oxidation–reduction potential. M. Dixon (Proc. Roy. Soc., 1927, B, 101, 57—70; cf. Wieland, A., 1913, i, 1304).—If it is assumed that the hydrogen atoms on the surface of platinum-black immersed in a solution of, say, quinol, are in equilibrium, not only with hydrogen molecules and hydrogen ions, but also with the quinol and quinone in the solution, the ordinary equation for oxidation–reduction potential follows at once. This theory, which postulates the direct transfer of hydrogen atoms as such from the solution to the electrode, necessarily leads to the same result as the thermodynamically equivalent theory of Clark (U.S. Pub. Health Rep., 1923, No. 826; 1925, No. 1017), according to which the doubly-charged anions produced by the ionisation of the quinol first give up to the electrode their pairs of electrons, thus rendering it more negative, so that it then withdraws hydrogen ions from the solution. It is not yet possible to say which theory is correct. There will always be a slight diffusion of hydrogen from the electrode into the solution, but usually this effect will be small. With the sulphydryl compounds examined by Dixon and Quastel (J.C.S., 1923, 123, 2943), however, the reduction process is irreversible, so that considerable diffusion must occur, or the hydrogen pressure at the electrode would increase indefinitely. These authors' results can, in fact, be accounted for quantitatively on the assumption that the irreversible transfer of hydrogen to the electrode is compensated for by diffusion. In such cases as this, the observed reduction potential will not, in general, be a measure of the real reducing power of the solution, and will be the more negative the slower the diffusion from the electrode, *i.e.*, the higher the overvoltage of the electrode. This is borne out by experiment.

R. Cuthill.

Normal oxidation–reduction potential of mercury. S. R. Carter and R. Robinson (J.C.S., 1927, 267—272).—The oxidation–reduction potentials of solutions containing varying proportions of mercuric and mercurous perchlorates have been measured at 18°. Correction has been made for hydrolysis of the salts, and also for the degree of ionisation on the assumption that it is the same as that of barium perchlorate of the same concentration. The normal potential deduced for $2Hg^{\cdot\cdot} \longrightarrow Hg_2^{\cdot\cdot}$ is then found to be 1·1902 volts, with an average error of ±0·0008 volt, referred to the calomel electrode as 0·560 volt, or 0·913 volt referred to hydrogen. The effect of varying concentration of perchloric acid on the potential has been determined, and is satisfactorily explained as due to decrease in the degree of ionisation of the perchlorates, and not to complex ion formation.

M. S. Burr.

Reaction between bromine and chloride ion in hydrochloric acid. Bromine monochloride. G. S. Forbes and R. M. Fuoss (J. Amer. Chem. Soc., 1927, 49, 142—156; cf. A., 1926, 128).—The graph representing the oxidation potential of a hydrochloric acid solution of chlorine containing a bromide as a function of the bromide concentration reveals two steeply-descending linear portions, the "bromine monochloride point" and the "bromine point." These two points are investigated (at 25°) with the aid of cells of the type $Pt(H_2)|HCl|HCl|HCl+Cl_2+BrCl+Br_2+Br'|PtIr$. The molal potential of bromine monochloride in 6*N*-hydrochloric acid is 1·1548±0·0005 volts referred to a hydrogen electrode in the same acid; in 4*N*-acid, the value is 1·221±

0·001 volts. The dissociation constant of bromine monochloride is $3{\cdot}2\pm0{\cdot}2\times10^{-4}$ in either $6N$- or $4N$-acid, the main reaction being assumed to be $Br_2+Cl_2 \rightleftharpoons 2BrCl$. The constant $K=[Br']^2[Cl_2]/[Br_2][Cl']^2$ is $3{\cdot}0\times10^{-12}$ in $6N$-acid and $5{\cdot}6\times10^{-12}$ in $4N$-acid; the ratio of these values of K may be calculated from the activity coefficients of hydrobromic and hydrochloric acids. The amount of bromine which reacts in hydrochloric acid to give bromide ion and bromine monochloride appears to increase as the bromine concentration diminishes. A general mathematical analysis of electrometric titration curves is given. S. K. Tweedy.

Decomposition potentials and metal overvoltages in liquid ammonia and in water. A. A. Groening [with H. P. Cady] (J. Physical Chem., 1926, 30, 1597—1615).—" Dynamic " decomposition voltages and metal overvoltages have been determined by the direct method for many salts in liquid ammonia and in water. Rapid rotation of the electrodes was employed. The straight portions of the current–voltage curves were extrapolated to the voltage axis to give the " dynamic " decomposition voltages. Similarly, the current–cathode overvoltage curves gave the metal overvoltage at zero current density. Measurements were made for solutions of silver, nickel, cadmium, mercuric, lead, zinc, copper, and ferric nitrates in ammonia and in water, of cadmium and zinc iodides and silver nitrite in ammonia and in water, of silver and mercuric iodides and mercuric chloride in ammonia, as well as of ammonium nitrate, chloride, bromide, and iodide in the same solvent. The dynamic decomposition voltages of nitrates and chlorides are lower in ammonia than in water, but the metal overvoltages are generally higher. Traces of water in liquid ammonia and traces of ammonia in water have marked effects on the decomposition voltages and the overvoltages of copper nitrate. Ammonium salts have the same dynamic decomposition voltage of 2·1 volts in dry liquid ammonia. The bromide and the nitrate show several breaks in the current-voltage curve. Temperature has little effect on the dynamic decomposition voltage in liquid ammonia. L. S. Theobald.

Electromotive behaviour of aluminium. A. Dadieu (Monatsh., 1927, 47, 497—510).—The potentials of aluminium and its amalgam in a molten mixture of aluminium and potassium bromides and in a solution of aluminium bromide in ethyl bromide have been derived from the *E.M.F.* of cells fitted with a standard electrode and from the decomposition potentials, using both platinum and mercury cathodes. The values obtained in the molten solution are −0·372 volt ±0·0040 for aluminium, and −0·370 volt ±0·0027 for the amalgam, the corresponding values obtained in solutions in ethyl bromide being −0·372 ±0·0037 and −0·368 ±0·0056 volt, respectively. Thus in each case the values obtained for aluminium and for its amalgam are the same. The metal in these solutions thus shows normal electromotive behaviour, and there is no evidence of the activation by mercury found by Smits (cf. Smits and Gerding, A., 1925, ii, 794). The author considers that the abnormal reactions observed in aqueous solutions are due to interaction of the metal and the solvent, and considers that the oxide film theory of the passivity of aluminium (cf. Günther-Schulze, A., 1921, ii, 535) best explains the facts. J. W. Baker.

Effect of neutral salts on the potentials of glycine solutions as compared with the hydrogen electrode. S. Kawai (J. Biochem. Japan, 1926, 6, 101—115).—Various cations have the effect of diminishing the p_H and thus increasing the acid dissociation constant of glycine and decreasing the basic dissociation constant. This effect of the neutral salts on an ampholyte substance is therefore essentially the same as was found for very dilute acids or alkalis. Chemical Abstracts.

Electrostatic capacity of aluminium and tantalum anode films. N. A. de Bruyne and R. W. W. Sanderson (Trans. Faraday Soc., 1927, 23, 42—51).—By a bridge method, the capacity of an aluminium or tantalum rectifier has been determined for different audio-frequencies. Assuming that an electrolytic condenser is the equivalent of a network of simple and calculable form, it may be shown that the values of the constituent parts are not independent of frequency. No simple network can be found, however, which is an exact equivalent of the condenser, so that no exact physical significance can be attached to any values of capacity which may be obtained. The reciprocals of the capacity at successive intervals of time after the application of different formation voltages, for the frequencies 1945 and 1170 cycles per second, have been plotted against time. The curves are only approximately logarithmic. The results, however, are in agreement with the law that film thickness is proportional to formation voltage. M. S. Burr.

Anodic overvoltage measurements with the cathode-ray oscillograph. E. Newbery (Proc. Roy. Soc., 1927, A, 114, 103—110; cf. A., 1925, ii, 405).—By means of a rotating commutator and a cathode-ray oscillograph, measurements have been made of the overvoltage of the following metallic anodes in N-sulphuric acid solution: platinum, gold, lead (unattackable electrodes); nickel, iron, chromium (electrodes showing passivity); antimony, bismuth, tantalum (electrodes showing valve action). The apparatus was identical with that previously described (*loc. cit.*). The phenomena of overvoltage and transfer resistance shown by unattackable electrodes and by passive electrodes in the passive state are similar in every way to those observed during cathodic treatment. It is very probable that a lead anode in dilute sulphuric acid must be classed as a passive metal, and that, as with nickel and iron, the cause of passivity is the formation of an insoluble, electrically conducting coating of an overvoltage compound which may, or may not, form a solid solution in the electrode surface. The fact that lead gives a visible coating of appreciable thickness, as compared with the invisible coating on iron and nickel, is due to the porosity of the lead dioxide, which permits deeper action on the electrode surface. Chromium is to be regarded as a metal which is easily passivated with respect to the formation of tervalent ions, but which cannot be passivated with respect to the formation of sexavalent ions. Valve action is due to the formation of an insoluble, electrically insulating coating of oxide or other compound, which forms the dielectric of a condenser made up of the electrode as one plate and the electrolyte as the other. From the data available from the curves, the capacity of such a condenser is roughly calculated as being of the order of a microfarad per sq. cm.; the thickness of the film of oxide, in the case of antimony, is calculated as being of the order of 4×10^{-5} mm., and in the case of tantalum, of the order of 10^{-6} mm. It is suggested tentatively that the action of an electrolytic rectifier may be due partly to condenser action, and partly to the oxide film acting as a semi-permeable membrane, permeable only to hydrogen ions.

L. L. Bircumshaw.

Electrolysis of water. J. E. Verschaffelt (Natuurwetensch. Tijdschr., 1926, 8, 121—130).—A theoretical discussion of the mechanism of electrolysis of water, and of solutions of salts, strong acids, and strong bases. The ions produced by dissociation of the solutes play only a passive part, raising the conductivity of the liquid, but not being liberated at the electrodes; hydrogen is liberated at the cathode directly from the water, and oxygen at the anode by dissociation of the hydroxyl ions of the water. The term electrolysis should be reserved for cases of actual chemical decomposition; the residual current, for example, is due only to simple transport of electricity by the ions of the electrodes or by hydrogen ions occluded by them. S. I. Levy.

Magnetic chemical effect. A. N. Schukarev (J. Russ. Phys. Chem. Soc., 1926, 57, 426—427).—The author, in abandoning work on this subject (cf. A., 1914, ii, 618; 1916, ii, 172), describes his final experiments. When a chloride is electrolysed in a strong magnetic field, dissolved in 10% potassium chloride solution containing a little potassium iodide and starch solution, a coloured ring is formed, which is at first symmetrically disposed about a central electrode. In some cases (*e.g.*, barium chloride, potassium chloride solution), the ring moves in the direction of the positive field; in others (calcium chloride, potassium chloride solution), it moves in the opposite direction. Photographs have been taken and are offered to anyone investigating this problem.

E. Rothstein.

Velocity of chemical reactions. J. J. Boguski (Rocz. Chem., 1926, 6, 291—320).—A reprint of an earlier paper (Ber., 1876, 9, 1646).

R. Truszkowski.

Supposed law of flame speeds. W. Payman and R. V. Wheeler (Nature, 1927, 119, 238).—Importance is not attached to the mixtures mentioned by White (this vol., 115) from the point of view of flame speeds, since they exhibit the peculiar phenomena of the "cool flame." A. A. Eldridge.

Movement of flames in closed vessels. Correlation with development of pressure. O. C. de C. Ellis and R. V. Wheeler (J.C.S., 1927, 153—158).—The direct synchronisation of the rate of development of pressure and the rate of spread of flame in an explosive mixture is effected by simultaneous photographic registration on a rapidly-revolving drum. The explosive mixtures were carbon monoxide and air saturated with water vapour at 19°. In spherical vessels, the moment of maximum pressure coincides with the arrival of the flame front at the boundary of the vessel. With a cubical vessel, the pressure develops after the flame front has touched the wall of the cube, but the point of maximum pressure is antecedent to the moment of complete inflammation.

W. Thomas.

"Uniform movement" of flame in mixtures of hydrogen and air. E. H. M. Georgeson and F. J. Hartwell (J.C.S., 1927, 265—267).—The propagation of flame from the open end of a tube towards the closed end in mixtures of hydrogen and air over a considerable portion of the range of inflammability has been analysed by a photographic method, using a quartz explosion tube and a quartz lens. Photographs representing propagation over a distance of 80 cm. from ignition show after a gradual retardation a movement which, although marked by small undulations, is sensibly uniform; this is recorded as the speed of "uniform movement." W. Thomas.

Combustion of carbon monoxide. C. F. R. Harrison and J. P. Baxter (Phil. Mag., 1927, [vii], 3, 31—50).—A method for the investigation of flame velocities at constant volume in a sphere is described and is extended to obtain an insight into the chemical reactions involved and into the variations of temperature at any point in an explosion chamber. The method has been applied to the investigation of the explosion of carbon monoxide and oxygen at an initial pressure of 105 cm. Carbon monoxide may be oxidised with air either in the dry state or in the presence of water vapour. In the second case, the ignition is easier and the flame velocity much higher. In all ordinary cases, both normal oxidation and oxidation through the water-gas reaction occur simultaneously. When the nitrogen diluent is replaced by oxygen or carbon monoxide, the velocity of combustion and of flame propagation is accelerated. Carbon monoxide has a much greater accelerating effect than has oxygen. The presence of small traces only of hydrogen in the mixture produces effects in no way proportional to the amount of hydrogen present. The hydrogen appears to be the chief intermediary for the propagation of the flame.

A. E. Mitchell.

Propagation of flame in mixtures of methane and air. V. Movement of the medium in which the flame travels. W. R. Chapman and R. V. Wheeler (J.C.S., 1927, 38—46).—It is assumed that in the propagation of flame in a tube there is a movement of the unburnt mixture ahead of the flame (cf. B., 1926, 970). When a tube open at both ends was restricted at the end at which the mixture was ignited, the speed of the flame was increased. If, in addition, restrictions were introduced in the path of the flame, the resistance offered thereby to the movement of the medium caused a retardation of the flame; greatly enhanced speeds of flame were obtained after passing the restriction. The effect of restricting the far end of the tube decreases considerably the speed of the flame. Closing the ignition end of the tube had no influence, but closing the far end of the tube resulted in a very slow speed of the flame, which was not greatly affected by restrictions, except locally. Increased speed of the flame in wide tubes is assumed to be due to an increased facility for the movement of the mixture. A simple relationship has been found connecting the diameter of the tube and the speed of uniform movement of the flame along it. W. Thomas.

Inflammability of hydrogen. III. Influence of ethyl selenide and of hydrogen selenide on the limits of inflammability of hydrogen–air mixtures. Y. Tanaka and Y. Nagai (Proc. Imp. Acad. Tokyo, 1926, 2, 494—497).—The limits of inflammability of hydrogen–air mixtures containing (*a*) 0·0—3·0 mol.-% of ethyl selenide and (*b*) 0·0—6·0 mol.-% of hydrogen selenide have been examined by a simple spark-ignition method. In each series, the upper limit of inflammability is lowered and the lower limit raised, and the results are thought to indicate that the temperature of activation of the two diluents is 1750°. R. W. Lunt.

Velocity of chemical reaction in the silent electric discharge. G. A. Elliott, S. S. Joshi, and R. W. Lunt (Trans. Faraday Soc., Jan., 1927, advance proof).—An hypothesis is advanced that the velocity of a chemical reaction produced by electric discharge through a gas is connected with the number of collisions between ions and gas molecules in which the energy of the ions is not less than a definite value, termed the critical activation energy. With certain assumptions, expressions are derived relating the velocity of the reaction and the critical activation potential to the gas pressure, the mean free paths of the ions producing activation, and the electrical factors determining the discharge. A. S. Corbet.

Rate of unimolecular reactions. (Sir) J. J. Thomson (Phil. Mag., 1927, [vii], 3, 241—257).—Hirst and Rideal (A., 1926, 32) have established the result that the rate of the unimolecular reaction $2N_2O_5=2N_2O_4+O_2$ is independent of the pressure when that is above about 0·27 mm. The rate increases as the pressure is diminished below this value. Their analysis of the reaction velocity, taking into consideration both collisions and radiation, gives results of the same form as, but of different magnitudes from, their observed values. An alternative method by which the decomposition may be effected is discussed. It is suggested that even in the absence of collisions and radiation the energy content of a molecule does not remain constant. It is shown that if the forces inside a molecule are intermittent instead of being perfectly continuous, then even if in the initial stages the energy contents of a large number of molecules are the same, they will change so that the energy is distributed among them according to Maxwell's law of distribution. The principle of the conservation of energy does not hold for a single molecule, but holds on the average for a large number, and since the distribution of energy is represented by Maxwell's law, the theory is similar to the classical except for the numerical values, as the rate of reaction is not fixed by the number of molecules which at any time possess enough energy to be active, but is measured by the number which receive this energy in unit time. If N be the number of molecules having, in a steady state, a particular amount of energy, the number passing out of that state in time δt is $N\delta t/T$, where T is a time constant and N/T will measure the rate of reaction. If the energy is conveyed to the molecules by collision, T is the average interval between collisions, and if the energy is conveyed by radiation, T becomes the average interval between collisions of a molecule with light quanta. If, however, the surging of the energy is due to the intermittence of the force, T will depend on the average interval between two impacts and may compare with the interval between collisions either between molecules or between molecules and light quanta. The smaller value of T would thus make the rate due to this cause much more rapid than that due to radiation, or to collisions at low pressures. Numerical results are in fair agreement with the observations of Hirst and Rideal. A. E. Mitchell.

Quasi-unimolecular reactions. Decomposition of ethyl ether in the gaseous state. C. N. Hinshelwood (Proc. Roy. Soc., 1927, A, 114, 84—97).—The author's previous work on chemical kinetics in gaseous systems is briefly reviewed. If the idea of the energy of activation of a molecule is extended to energy of all kinds in every possible distribution in a large number of degrees of freedom, the only condition being that the total energy should exceed E (the "energy of activation"), then the last term in the equation for a homogeneous bimolecular reaction, viz., number of molecules reacting=number entering into collision $\times e^{-E/RT}$, should be replaced by $e^{-E/RT}(E/RT)^{\frac{1}{2}n-1}/\frac{1}{2}n-1$. The discrepancies between the observed and calculated rates of decomposition in certain cases (*e.g.*, the decomposition of acetone) now tend to disappear. The decomposition of ethyl ether ($Et_2O=CO+2CH_4+0{\cdot}5C_2H_4$) was investigated by measuring the increase of pressure developed, and it is shown that this is a true unimolecular reaction above a pressure of 200 mm., below which the velocity coefficient falls. The reaction is predominantly homogeneous, and the addition of sufficient hydrogen completely prevents the decrease of the coefficient below 200 mm. From the temperature coefficient, the heat of activation is found to be 53,000 g.-cal., and values of k calculated from the formula $\log_e k=26{\cdot}47-(53{,}000/RT)$ agree with those determined experimentally. Calculations on the above basis for the condition of a pressure of 0·2 atm., where k begins to fall, shows that the participation of about eight degrees of freedom conforms with activation by Lindemann's mechanism. A table is given showing the relation between the complexity of a molecule and the type of mechanism by which it decomposes. Simple molecules usually decompose bimolecularly, more complex ones in a quasi-unimolecular way, as would be expected on theoretical grounds. L. L. Bircumshaw.

Rate of racemisation of pinene. A first-order homogeneous gas reaction. D. F. Smith (J. Amer. Chem. Soc., 1927, 49, 43—50).—The racemisation of *d*-pinene between 184° and 237° is a unimolecular reaction. The rate is practically the same in both the gas and liquid phases and in solution; in the latter case, it is independent of the concentration and the solvent. Dushman's "activation" equation (A., 1921, ii, 315) is obeyed to the same order of agreement as in the case of nitrogen pentoxide (Tolman, *ibid.*, 248), from which it is concluded either that the life of activated molecules of the dissimilar substances nitrogen pentoxide and pinene is nearly the same, or that the rate of reaction is determined by the rate of activation. S. K. Tweedy.

Velocity of decomposition of potassium persulphate in aqueous solution. A. Kailan and L. Olbrich (Monatsh., 1927, 47, 449—484).—The velocity of decomposition of potassium persulphate, either alone or with the addition of sulphuric acid as a catalyst at 25°, and both alone and with the addition of potassium sulphate, sulphuric, nitric, and phosphoric acids at 99·4°, has been studied in detail by the method of Green and Masson (J.C.S., 1910, 97, 2083). Measurements at both temperatures confirm the conclusion previously reached by Levi and Migliorini (A., 1907, ii, 81) and by Green and Masson (*loc. cit.*) that both in absence and presence of catalysts the decomposition approximates closely to a unimolecular reaction, and the value of the coefficient obtained agrees within the experimental error with that extrapolated from the measurements of the latter authors. For numerical data, the original must be consulted, but the main conclusions reached are as follows: with the same original concentration of potassium persulphate the value of the unimolecular coefficient increases with increasing concentration of added sulphuric acid much more slowly than direct proportionality would require, but for equal sulphuric acid concentrations it decreases with increasing concentration of the persulphate. The velocity of decomposition is considerably increased by the addition of strong acids and is the greater the stronger the acid, but this is not merely a hydrogen-ion effect, since nitric acid has a greater accelerating influence than equivalent quantities of sulphuric or phosphoric acid. Hence acid anions must also affect the reaction velocity, the nitrate ion having an accelerating influence. The non-increase in the unimolecular coefficient during the course of the reaction, in spite of the fact that it is increased by lowering the initial concentration of persulphate, can be explained only on the assumption that the potassium ion exerts a retarding influence on the decomposition. The fact that the decomposition is not autocatalytic, in spite of the production of potassium hydrogen sulphate during the course of the reaction, was explained by Green and Masson on the assumption that no hydrogen ions are produced, ionisation being limited to the formation of potassium and hydrogen sulphate ions, but this hypothesis is shown to be untenable, and the observations are readily explained by the hypothesis that the sulphate ion exerts an intrinsic retarding influence approximately equal to the accelerating influence of the hydrogen ion. The retarding influence of alkali sulphates and the autocatalysis occurring in cases where the sulphate ion is removed either as an insoluble or a practically non-ionised sulphate, observed by Green and Masson, are thus readily explained. Empirical intrapolation formulæ in which the unimolecular coefficient at 25° and 99·4°, respectively, is expressed as a function of the potassium-ion concentration and the difference between the hydrogen- and sulphate-ion concentrations are deduced both for the assumption of partial and complete dissociation, agreement between the calculated and observed values being fairly good. A similar formula is applied with equal success to the observations of Green and Masson. The addition of toluene increases the velocity of decomposition of an aqueous solution of potassium persulphate, but this is not due to reaction between the toluene and the liberated oxygen, since a diminution in the partial pressure of the latter does not increase the velocity of decomposition. J. W. Baker.

Interaction of potassium *m*-tolyloxide with aliphatic esters in aqueous-alcoholic solutions. E. L. Smith (J.C.S., 1927, 170—178).—An equilibrium is established between potassium tolyloxide, water, cresol, and potassium hydroxide; the ester is hydrolysed by the last-named substance. Constants are calculated which are the product of an equilibrium constant and a velocity coefficient. The equilibrium constant in aqueous solution has been measured by a dynamic and by an electrometric method. The constants decrease appreciably as the water concentration increases. Certain esters react abnormally, giving rise to the corresponding *m*-tolyl ethers (cf. Gyngell, A., 1926, 1134). The value of the temperature coefficient has been determined. *Ethyl* m-*tolyloxyacetate* is an oil, b. p. 264° (slight decomp.). W. Thomas.

Rate of hydrolysis of solutions of proteins in acids as measured by the formation of amino-nitrogen. D. M. Greenberg and N. F. Burk (J. Amer. Chem. Soc., 1927, 49, 275—285).—The hydrolysis of gelatin and silk fibroin by sulphuric and hydrochloric acids (0·75—3·0*N*) has been studied at 96—98°, 130°, and 142°. The rate of hydrolysis, as measured by the increase in amino-nitrogen, conforms to the equation for a bimolecular reaction. The rate of hydrolysis of wheat gliadin (cf. Vickery, A., 1922, ii, 754) also conforms to this order of reaction, whilst that of casein (cf. Dunn, *ibid.*, 1925, i, 1477) conforms to the equation for a unimolecular reaction. The catalytic effect of acids on the hydrolysis of proteins is shown to be proportional to the thermodynamic activity of the hydrogen ion, and an equation connecting the rate of hydrolysis of gelatin with temperature is derived. F. G. Willson.

Kinetics of dissolution of aluminium in acids and alkalis. K. Jabłczyński and E. Hermanowicz (Rocz. Chem., 1926, 6, 466—482).—The velocity of dissolution of aluminium in 0·1*N*-hydrochloric acid or sodium hydroxide is independent of the rate of stirring, and increases by 126% and 137%, respectively, per 10° rise in temperature, showing that this is a purely chemical reaction. The velocity is proportional to the concentration of the acid, whence it follows that this is a unimolecular reaction. The metal may be rendered passive by immersion in oxidising solutions, the effect being greatest with hydrogen peroxide, less with potassium permanganate, and least with bromine water. It may then be activated by contact with a platinum wire, but more vigorously by the addition of mercuric chloride, which so accelerates the rate of dissolution that the process becomes one of diffusion; in this case, the temperature coefficient is small and the velocity depends on the rate of stirring. The velocity of dissolution in $0{\cdot}1N$-sodium hydroxide is 18·5 times as great as that in acid.

R. Truszkowski.

Thickness of the passive surface layer, and the velocity of dissolution of aluminium. M. Centnerszwer (Rocz. Chem., 1926, 6, 383—395).—Metallic aluminium may be covered with a passive layer, in which active nuclei form continuously. The thickness of this layer is greater than unimolecular, attaining from 30 to 84 μ, according to the nature of the treatment applied for passivation. On activation, there is first an induction period, during which the passive layer dissolves with continuously increasing velocity, after which further solution proceeds at uniform velocity. The velocity of solution is virtually independent of stirring, and its temperature coefficient is from 1·7 to 2·4 per 10°. This velocity depends, not on the dissociation constant of the given acid, but on its individual character, *i.e.*, on the affinity of aluminium for its anions. The addition of chlorides to hydrochloric acid increases the velocity of dissolution by increasing the concentration of undissociated acid, whilst sulphates and nitrates, which augment dissociation, have the opposite effect. These facts indicate that the dissolution of aluminium in acids is determined by a reaction between the metal surface and undissociated anions [?]; it is not an ionic reaction.

R. Truszkowski.

Rate of formation of insoluble anhydrite. P. P. Budnikov (Z. anorg. Chem., 1926, 159, 87—95).—In the determination of the rate of formation of the insoluble modification of calcium sulphate with regard to time and temperature of heating, an electrical conductivity method was adopted. The amount of insoluble anhydrite formed depends on the temperature, the time, and the state of division of the gypsum. Excessive time of heating and a high temperature favour the formation of insoluble anhydrite, which lowers the quality of the plaster of Paris.

M. Carlton.

Influence of moisture on the reaction between nitric oxide and oxygen. E. Briner (J. Chim. phys., 1926, 23, 848—850).—A short discussion of recent work in which it is concluded that, although water may act as a catalyst, it is not essential to the reaction.

R. W. Lunt.

Acid and salt effects in catalysed reactions. IV. Derivation of a general equation for the catalytic activity of acids. General catalytic catenary. H. M. Dawson (J.C.S., 1927, 213—222).—The equation derived is $r=\frac{1}{2}(10^{\Delta p_H}+10^{-\Delta p_H})$, in which r is the velocity due to the positive and negative ions expressed in terms of the velocity for the corresponding *M.V.* mixture, and Δp_H is the difference between the p_H values of the solution in question and of the *M.V.* mixture. The expression, which corresponds with a catenary curve, may be termed the general or reduced catalytic catenary. It appears to be capable of wide application and is independent of the nature of the catalysing acid and of its concentration, of the temperature, of the nature of the solvent, and of the nature of the catalysed reaction. It has been tested by reference to observations on the velocity of the acetone–iodine reaction and to Karlsson's data for the rate of hydrolysis of methyl and ethyl acetates by the addition of acetic acid and sodium acetate (A., 1922, ii, 40).

W. Thomas.

Period of induction in chemical reactions. Interaction of mercuric chloride and sodium hydrogen carbonate. P. Neogi and S. Neogi (J.C.S., 1927, 30—37).—The period of induction is inversely proportional to the concentrations of each reactant. It diminishes with rise of temperature. Light has no effect on the period. Glycerol, *n*-propyl alcohol, chlorides, oxalates, and citrates increase the period, whilst methyl, ethyl, and *iso*propyl alcohols, and tartrates diminish it. The period of induction is not influenced by dextrose, sucrose, mannitol, and dulcitol. A decrease in the period of induction is believed to be due to an increase in the ionisation of the mercuric chloride under certain conditions. Sodium chloride inhibits the reaction owing to the formation of double salts with mercuric chloride.

W. Thomas.

Velocity of autocatalytic decomposition of bromosuccinic acid in aqueous solutions. J. Zawidzki and W. Wyczalkowska (Rocz. Chem., 1926, 6, 415—465).—Various equations for the autocatalytic decomposition of bromosuccinic acid are derived. The addition of hydrobromic acid to the reaction mixture changes the reaction velocity equation from $dx/dt=k_0(a-x)/x$ to $k_0(a-x)/(b+x)$, where b is the concentration of hydrogen bromide and k_0 remains constant (0·0000768). The addition of equivalent quantities of sodium sulphate, which combines with the hydrogen ions produced in the reaction, changes the velocity equation to $k(a-x)/\sqrt{\rho x}$, where k is twice as great as k_0, and ρ is the degree of dissociation of the hydrogen sulphate ion. The same equation holds for the velocity of decomposition of aqueous acid bromosuccinates, substituting for ρ the degree of dissociation of bromosuccinic acid. The normal sodium and potassium salts are hydrolysed according to the equation $dx/dt=k(a-x)^{3/2}/\sqrt{x}$. The retarding influence of nitric acid is half as great as that of equivalent quantities of hydrochloric or hydrobromic acids, the velocity in this case being $k_0(a-x)/\{(b/2)+x\}$, where b is the concentration of nitric acid. The addition of potassium bromide changes the velocity of reaction to $k_0(a-x)/\{(b/2n)+x\}$, where $n>1$. Since, therefore, the velocity of reaction is retarded by both hydrogen and bromine ions, the original equation should be expressed as $k_0(a-x)/2x$, whence it follows that the real value of k is 0·000154.

R. Truszkowski.

Catalytic minimum point. M. Bergstein and M. Kilpatrick, jun. (J. Physical Chem., 1926, 30, 1616—1622).—The catalytic minimum point for the reaction between iodine and acetone lies at p_H 4·8, and the value is unaffected by change of temperature over the range examined, viz., 25—45°, and by the presence of neutral salts. The results do not support the unhydrated ion theory of catalysis (Rice, A., 1924, ii, 98).

L. S. Theobald.

Formation of ammonia from its elements by the silent discharge in Siemens tubes. E. Warburg and W. Rump (Z. Physik, 1926, 40, 557—573).—In contrast with ozone formation, the production of ammonia is mainly a surface effect, the yield per coulomb is much smaller, and reduction of pressure has less influence in reducing the yield. The differences are accounted for by the much greater energy needed to dissociate nitrogen, collisions of ions in the volume of the gas being less effective than catalytic action on the walls; in presence of a suitable catalyst, the formation of ammonia can take place at the ordinary temperature, whilst that of ozone cannot. The formation of hydrogen iodide from its elements resembles that of ozone, being catalysed by the collision of ions. E. B. Ludlam.

Decomposition of ethyl alcohol at the surface of thoria. I. G. I. Hoover and E. K. Rideal (J. Amer. Chem. Soc., 1927, 49, 104—115).—The decomposition of ethyl alcohol into ethylene and into acetaldehyde in presence of thoria at about 300° was investigated. The activation energy is 30,000 g.-cal. for the ethylene reaction and 24,000 g.-cal. for the aldehyde reaction. The presence of water vapour or acetaldehyde diminishes the reaction velocity of the ethylene reaction to a greater extent than that of the aldehyde reaction, which indicates that the two reactions proceed on different active areas of different adsorptive capacities. Whereas these poisons are reversible, excess of chloroform vapour forms an irreversible poison; minute amounts diminish both reactions, and larger quantities cause displacement of the adsorbed ethylene on the catalyst surface, although a promoter effect on the ethylene reaction and a simultaneous poisoning of the aldehyde reaction are also apparent. At pressures of 6 and of 1 mm., the ratio of the extents of the ethylene and aldehyde reactions is 2 : 1, in comparison with 1·25 : 1 at atmospheric pressure. This is proved to be due to the removal of poisons from the catalyst surface; the relative amount of ethylene is greater at low pressures, in harmony with the fact that those patches of the catalyst surface active towards the ethylene reaction are the more easily poisoned. The temperature coefficients are less at low pressures, indicating that the reactions at atmospheric pressure are being mutually poisoned by the reaction products. Thoria catalysts are more active when supported; they then promote the ethylene reaction almost completely, in agreement with the view that the two reactions are promoted by different active areas. S. K. Tweedy.

Decomposition of ethyl alcohol at the surface of thoria. II. Adsorption on the thoria catalyst. G. I. Hoover and E. K. Rideal (J. Amer. Chem. Soc., 1927, 49, 116—123; cf. preceding abstract).—The adsorption isotherms for hydrogen, nitrogen, and ethylene at 0° and at 100°, and ethyl alcohol vapour at 52·3° and at 100°, on thoria were investigated for pressures up to 760 mm. Nitrogen and hydrogen are adsorbed to an extent proportional to the pressure; the surface does not even approach saturation (cf. Lowry and Morgan, A., 1925, ii, 1053). A saturation maximum for ethylene at 0° occurs at about 600 mm.; an irregularity in the low-pressure portion of the 0° and 100° isotherms is attributed to a specially active area. A similar irregularity occurs in the alcohol isotherms. Adsorption and capillary condensation or surface liquefaction occur with alcohol both at 52·3° and at 100°. About 1·3% of the specific catalyst surface is active. The latent heat of capillary condensation of alcohol is about 9900 g.-cal./mol. and that of surface adsorption 14,000 g.-cal./mol. S. K. Tweedy.

Attempts to activate copper for catalytic hydrogenation by oxidation and reduction. R. N. Pease and C. W. Griffin (J. Amer. Chem. Soc., 1927, 49, 25—28).—A copper catalyst of low porosity and high activity was prepared by low-temperature oxidation and reduction of well-sintered copper. The resulting catalyst was only temporarily active in the hydrogenation of ethylene. This deactivation was uninfluenced by the temperature of oxidation or reduction of the copper and by the temperature of evacuation of the catalyst bulb. Neither was it due to the fixation of surface crystals on the catalyst. Apparently an atomic reaction occurs on the metal surface as a result of catalytic action, whereby the atoms become momentarily labile and may subsequently become oriented to a crystal. S. K. Tweedy.

Catalytic oxidation of ammonia and hydrogen cyanide. III. J. Zawadzki and I. Lichtenstein (Rocz. Chem., 1926, 6, 824—837).—The oxidation of ammonia to nitric oxide, using a platinum catalyst, commences at 250°; that of hydrogen cyanide at about 400°. In this reaction, if the rate of flow of the reaction mixture is small, a considerable quantity of free nitrogen is found among the products; at velocities of more than 60 litres per hr. for ammonia and 23 litres per hr. for hydrogen cyanide, part of these gases passes unchanged at a temperature of 600°. The concentration of substrate in the reaction mixtures does not appear greatly to influence the reaction, the course of oxidation depending more on duration of contact and temperature. The yield of nitric oxide at a given temperature at first increases to a maximum and then decreases with increasing rate of flow, the optimal value for the latter increasing with temperature. By selecting appropriate values for the above two factors, yields of up to 100% of nitric oxide may be obtained. R. Truszkowski.

Mechanism of the catalytic decomposition of esters by nickel. J. N. Pearce and C. N. Ott (J. Physical Chem., 1927, 31, 102—114; cf. A., 1924, ii, 843; Sabatier and Mailhe, *ibid.*, 1912, i, 156).—The products of the catalytic decomposition of methyl, ethyl, and propyl acetates, and of methyl propionate by finely-divided nickel, prepared by ignition of the nitrate at 400—450° and subsequent reduction by hydrogen at the lowest possible temperature, have been studied for various temperatures between 300° and 735°. The approximate temperatures at which the esters begin to decompose are: methyl acetate, 310°; ethyl acetate, 280°; propyl acetate, 330°, and methyl propionate, 360°. The proportions of carbon dioxide and methane in the decomposition products increase with rise in temperature, whilst those of hydrogen and carbon monoxide decrease. Hydrocarbons higher than ethane are formed only in traces, and no free acid or other liquid decomposition products appear at any temperature. The addition of hydrogen, one of the products, to the vapour before passage over the catalyst produces no change in the nature of the decomposition products, but the activity of the catalyst is affected by some of the products resulting from the decomposition. The mechanism of decomposition is discussed.

L. S. Theobald.

Catalytic power of [animal] charcoal. V. Podrouzek.—See B., 1927, 95.

Ammonia catalysts. A. T. Larson and A. P. Brooks.—See B., 1927, 72.

Pure iron and promoted iron catalysts for ammonia synthesis. J. A. Almquist and E. D. Crittenden.—See B., 1927, 72.

Electrolysis in the fused state of oxygenated compounds. Preparation of metals and borates. Andrieux (Compt. rend., 1927, **184**, 91—92).—The electrolysis with high cathode current densities in an apparatus previously described (A., 1926, 248) of a molten mixture of a metallic oxide, boric anhydride, or borax, and a fluoride (to produce a stable and homogeneous mass), usually yields the metal of the oxide in the molten or the crystalline state, according as the metal is easily fusible (*e.g.*, lead, zinc, cadmium), or refractory (*e.g.*, tungsten, molybdenum). Most metals the heats of oxidation of which are less than that of sodium have been prepared. Borates of the alkaline earths are produced using low current densities at 1000—1200°, the fluoride in the mass being that of the metal concerned, or that of a metal more difficult to oxidise. J. Grant.

Structure of electro-deposited metals. F. Foerster and J. Fischer.—See B., 1927, 78.

Actinic absorption of chlorine gas with respect to the hydrogen-chlorine reaction. W. Taylor (Trans. Faraday Soc., 1927, **23**, 31—37).—Using an actinometric arrangement similar to that of Bunsen and Roscoe, the rate of combination of hydrogen and chlorine, under the influence of a "white" beam from a "pointolite" lamp, which has passed through a light filter of gaseous chlorine of variable pressure, has been studied. The effect of the varying sensitivity due to the presence, in different proportions, of an anti-catalyst, probably oxygen, is eliminated by the use of a second source of white illumination "B," used as a standard of reference. Exposure was first made with "B," which, by means of a switch, was then exchanged for the illumination under examination, the latter being finally replaced by "B" again. The rate for "B" before and after was, in general, constant. Volume change, due to absorption of hydrogen chloride by water, when plotted against time, for any single pressure of chlorine in the filter, gives a straight line after the Draper expansion has taken place. The curve obtained by plotting reaction velocity against pressure of chlorine is not exponential, although somewhat similar in form. It indicates that, although the greater part of the activating power of the light is cut down by a relatively small thickness of chlorine, there is a "residual effect" which is only slightly reduced by a further increase in concentration of absorbing gas. The shape of the curve is not in accordance with the view that only a narrow range of frequencies is effective in promoting activation. The extinction coefficient of about 45 does not agree with that of 17·17 found by Bunsen and Roscoe. This may be due to the difference in the source of light employed. M. S. Burr.

Residual effect in the actinic absorption of chlorine. W. Taylor and A. Elliott (Trans. Faraday Soc., 1927, **23**, 38—41).—With the view of investigating the "residual effect" observed in the actinic absorption of chlorine (cf. preceding abstract), experiments have been carried out with increased concentration of chlorine in the filter obtained by the use of solutions of chlorine in carbon tetrachloride, and also by increasing the thickness of the absorbing layer to be traversed by the light. The curves thus obtained agree in showing the residual effect. It has also been found that certain types of radiation present in ordinary white light, although only feebly absorbed by chlorine, yet appear capable of bringing about an appreciable amount of activation. M. S. Burr.

Photochemical decomposition of potassium persulphate. I. J. L. R. Morgan and R. H. Crist (J. Amer. Chem. Soc., 1927, **49**, 16—25).—Many organic and inorganic per-compounds were found to be photo-sensitive and the case of potassium persulphate was examined in detail. The reaction is $K_2S_2O_8+H_2O=2KHSO_4+0\cdot5O_2$, no intermediate equilibria being apparent; it is suitable for actinometric use, and the technique is described in detail. The reaction is of the first order when the solution is dilute or when the light intensity is high; it is of zero order when the solution is concentrated and the light intensity is low. The order for intermediate solutions is an accelerated unimolecular one. The reaction is irreversible, since the rate is uninfluenced by variation in the oxygen concentration, although it is increased in the presence of hydrogen or nitrogen. The effect of ageing of the lamp was also studied. Ultra-violet light decomposes solid potassium persulphate also. S. K. Tweedy.

Synthetic formaldehyde from carbon monoxide and hydrogen. Mechanism of the sensitised photochemical reaction. A. L. Marshall (J. Physical Chem., 1926, **30**, 1634—1640; cf. A., 1926, 919).—The dependence of the rate of formation of formaldehyde on the concentrations of hydrogen and carbon monoxide has been studied in the photochemical reaction sensitised by mercury. An equation of the form $d[CH_2O]/dt=Kp_{H_2}{}^{\frac{1}{2}}\cdot p_{CO}(1/p_{\text{total}})^{\frac{1}{2}}$ has been deduced theoretically, but the results actually obtained indicate that the equation $d[CH_2O]/dt=Kp_{H_2}{}^{\frac{1}{2}}\cdot p_{CO}$ determines the velocity. Atomic hydrogen is thus one of the constituents taking part in the reaction, of which formaldehyde is the chief product.

L. S. Theobald.

Production of ions in chemical reactions and the mechanism of induced, photochemical, and catalytic reactions. N. R. Dhar (Z. anorg. Chem., 1926, **159**, 103—120; cf. A., 1924, ii, 746; 1925, ii, 214).—There are many indications which favour the view that ionisation takes place in chemical reactions, more especially in exothermic reactions. Atoms and molecules become activated by the adsorption of ions or electrons or by collision with other stimulated atoms or molecules under suitable conditions. The explanation of induced oxidation, decomposition, etc. depends on the formation of electrons and ions in the primary exothermic reaction and the consequent activation of inactive molecules by adsorption of ions which lead to the secondary reaction. The abnormally large yield obtained in some photochemical reactions is probably due to formation of ions in the chemical transformation. In presence of water vapour or a substance with a high dielectric constant, the mobility of the ions is reduced, and the tendency to formation of complexes consisting of ion, water vapour, and reactant is greatly increased. Consequently in presence of such substances the reacting substance has more opportunity of adsorbing ions and an increased reactivity results.

Adsorption of gases by solid substances is considered as an exothermic chemical reaction in which ions and electrons are produced which lead to the activation of the reacting substances in the presence of the catalyst. M. CARLTON.

Photochemistry of complex compounds. II. R. SCHWARZ and K. TEDE (Ber., 1927, **60**, [*B*], 63—69; cf. A., 1925, ii, 576).—Measurements of the photochemical decomposition of cobalt-tetrammine salts in aqueous solution according to the scheme, $[Co(NH_3)_4X_2]Y+3H_2O=Co(OH)_3+2NH_4X+NH_4Y+NH_3$, by determination of the electrical conductivity show that the stability of the complex nucleus diminishes with increasing electroaffinity of the co-ordinatively united anion, $CO_3'' > C_2O_4'' > NO_2' > Br' > Cl' > SO_4''$. The inverse position of the C_2O_4'' and NO_2' ions is doubtless due to stereochemical factors and probable ring formation in the case of the oxalato-residue. In the cobaltpentammine series, the sequence is $CO_3'' > Cl' > C_2O_4'' > SO_3'' > NO_2' > NO_3' = SO_4''$; the exceptional position of the chlorine ion is attributable to its non-complex character. The observed exceptions indicate that the electroaffinity of the nuclear united acid radical is not the only factor governing the stability of the complex. The presence of water molecules in the complex increases its tendency towards hydrolysis. The complex compounds of chromium are generally less stable than those of cobalt and more susceptible to photochemical change. Examination of the photochemical decomposition of the stereoisomeric salts, $[Co(NH_3)_4(SO_3)_2]NH_4$, shows that the dark brown is less stable than the reddish-brown variety, and hence has the *cis*-configuration. Attempts to apply a similar method to the compounds $[Co(NO_2)_3(OH)_3]X_3$ were unsuccessful, since they are too readily hydrolysed in absence of light. H. WREN.

Photochemistry of complex compounds. III. The hexacyano-complexes of tervalent iron, cobalt, chromium, and manganese. R. SCHWARZ and K. TEDE (Ber., 1927, **60**, [*B*], 69—72).—Potassium ferricyanide is little sensitive to light, decomposition taking place only to the extent of a small percentage after intense illumination. The change consists in hydrolysis to aquo-complex salts and ultimately ferric hydroxide, and in the oxidation of hydrocyanic acid to cyanogen with production of potassium ferrocyanide. With potassium cobalticyanide, the change is $K_3[Co(CN)_6]+H_2O=K_3[Co(CN)_5OH]+HCN$ and $K_3[Co(CN)_6]+H_2O=KCN+K_2[Co(CN_5)H_2O]$. The corresponding chromium compound behaves similarly to the cobalticyanide, whereas the manganese compound is rapidly decomposed in the absence of light into manganic hydroxide, hydrocyanic acid, and potassium cyanide. H. WREN.

Decomposition of ammonia by optically excited mercury atoms. R. G. DICKINSON and A. C. G. MITCHELL (Proc. Nat. Acad. Sci., 1926, **12**, 692—696; cf. Taylor and Bates, following abstract).—The photochemical decomposition of ammonia at low pressures is sensitised by mercury vapour activated by absorption of the line 2537 Å. The sensitised decomposition is accompanied by a diffuse band fluorescence in the green and ultra-violet. The mol. fraction of hydrogen in the non-condensible reaction products is about 0·70. This is to be regarded as a minimum value, since some hydrogen is possibly adsorbed on the walls of the reaction vessel. No evidence of products other than nitrogen and hydrogen was obtained. In the case of the direct photochemical decomposition by light of shorter wavelength, the mol. fraction of hydrogen is about 0·87. Since a mol. fraction 0·75 corresponds with the decomposition, $2NH_3=3H_2+N_2$, it is suggested that probably some condensible product containing more nitrogen than does ammonia, *e.g.*, hydrazine, may have been formed. J. S. CARTER.

Photosensitised decompositions by excited mercury atoms. H. S. TAYLOR and J. R. BATES (Proc. Nat. Acad. Sci., 1926, **12**, 714—717).—Experiments on the photosensitised decomposition of water, ammonia, ethylene, methyl and ethyl alcohols, hexane, benzene, acetone, formic acid, and ethylamine by light of wave-length 2536·7 Å. in presence of mercury vapour demonstrate the extraordinary efficiency of the excited mercury atom in the disruption of the linkings C·H, N·H, and O·H. The decompositions obtained are often many hundredfold those obtained by exposure in quartz apparatus to the whole ultra-violet spectrum of the cooled mercury arc. Since the energy of the excited mercury atom is 112 kg.-cal. per g.-atom it follows that the energies of the linkings C·H, N·H, and O·H are all less than 112 kg.-cal., a conclusion in agreement with available thermal data. Oxygen in addition to hydrogen was identified in the products of decomposition of water (cf. Senftleben and Rehren, A., 1926, 768). Acetaldehyde and its decomposition products, carbon monoxide and methane, in addition to hydrogen, were obtained from ethyl alcohol. With benzene, diphenyl was detected, but the gaseous residue contained hydrocarbons in addition to hydrogen. Hexane yielded nearly pure hydrogen. From ethylene, hydrogen, acetylene, and some saturated hydrocarbons were identified. With ammonia, the percentage of hydrogen in the reaction products was greatly in excess of that required by the simple stoicheiometric decomposition to the elements. It is hence concluded that the decomposition of ammonia occurs in stages, in the first of which hydrogen is eliminated from ammonia molecules, *e.g.*, $2NH_3 \longrightarrow N_2H_4+H_2$. The residual gas from ethylamine is, however, practically free from nitrogen. J. S. CARTER.

Chemical actions of radiations. P. VILLARD (Compt. rend., 1927, **184**, 131—134).—A general theory of the phenomenon of the destruction by ordinary light of a latent image produced by *X*-rays is proposed. The *X*-rays produce a disturbance in the equilibrium of the lower optical levels of the atoms of silver and bromine. This constitutes a latent image. Ordinary light will now set up electronic vibration, which restores the equilibrium and the sensitiveness of the plate to *X*-rays, but destroys the latent image. The suitability of a particular radiation depends on its quantum. The phenomenon first observed in certain cases by Becquerel of the continuation by red rays of the photographic action started by violet rays is equivalent to photographic development, and depends on the presence of a soluble silver salt and of a reducing agent. Thus, tartaric acid will not develop an exposed plate containing a soluble silver salt other than with the help of outside energy in the form of radiation, the quantum of which is such that it supplies the energy without itself affecting the plate. The phenomenon is independent of the intensity of the radiation. J. GRANT.

Chemical actions of radiations. A. G. DE MONCETZ (Compt. rend., 1927, **184**, 284—285; cf. preceding abstract).—The author summarises earlier observations (Compt. rend., 1908, **146**, 1032; 1909, **148**, 406). A plate exposed to *X*-rays has its image weakened if it is subsequently exposed to radiations of 800—920 Å., and intensified if radiations of 920—1350 Å. are used. If ordinary light replaces *X*-rays, the image is always destroyed. If the plate is solarised, the infra-red region of the spectrum subsequently used produces a blackening, the violet-blue region destroys the grey colour of the plate, and the ultra-violet (250—394 Å.) appears white or black on the plate according as the initial exposure is short or long. J. GRANT.

Deoxidation of potassium, sodium, and lithium permanganates in alkaline solution. A. A. MAXIMOV (J. Russ. Phys. Chem. Soc., 1926, **57**, 347—371).—In alkaline solution, sodium and potassium permanganates are decomposed thus: (1) $2M'MnO_4+2M'OH=2M_2'MnO_4+H_2O+0{\cdot}5O_2$; (2) $M'_2MnO_4+H_2O=MnO_2+2M'OH+0{\cdot}5O_2$. When a permanganate is formed by the fusion of an alkali hydroxide with manganese dioxide, the presence of an alkali peroxide assists the reaction. It is supposed that even when no peroxide is added, some is formed during the reaction. In these circumstances, whereas cæsium, potassium, rubidium, and sodium should form the manganate and permanganate on fusion of their hydroxides with manganese dioxide, lithium, which does not form a peroxide, should not undergo the reaction. This has been found to be the case. Lithium permanganate could be formed only by the addition of lithium sulphate to barium permanganate. Under the conditions in which potassium permanganate gave the manganate in potassium hydroxide solution, lithium permanganate in lithium hydroxide solution does not change, except exceedingly slowly, a change which is attributed to the presence of sodium in the glass of the containing vessel.

Hydrogen peroxide so accelerates the reaction that no manganate is formed, and only manganese dioxide. The reaction has been carried out quantitatively by titrating standard solutions of the permanganates with hydrogen peroxide until (i) a green colour is formed and (ii) a grey precipitate appears. This has been accomplished for lithium as well as for potassium. The results obtained are in accord with the equations: (i) $2M'MnO_4+H_2O_2+2M'OH=2M'_2MnO_4+2H_2O+O_2$; (ii) $2M'_2MnO_4+H_2O_2=2M_2'O+2H_2O+2MnO_2+2O_2$. Sodium permanganate in the presence of sodium peroxide undergoes the change: $2Na_2MnO_4+2Na_2O_2+4H_2O=2MnO_2+8NaOH+2O_2$. In the presence of potassium ferricyanide, the reaction is reversed (Dieffenbach, A., 1908, ii, 697). The reaction was effected as follows. Dry sodium hydroxide is added to a little water, and the mixture heated to boiling, when dry manganese dioxide is added. On adding sodium peroxide to the mixture, a gas is evolved with the formation of sodium manganate.

The following scheme is given for the oxidations and reduction of manganese salts: $MnO_2+4KOH+{\cdot}O{\cdot}O{\cdot}=MnO_2(OK)_2+KO{\cdot}OK+2H_2O$; $2KMnO_4+K_2O_2=2MnO_2(OK)_2+O_2$; $MnO_2(OM')_2+HO{\cdot}OH=O_2+Mn(OH)_2(OM')_2=H_2MnO_3+M_2'O+O_2$.

E. ROTHSTEIN.

Combination of potassium with carbon. K. FREDENHAGEN and G. CADENBACH (Z. anorg. Chem., 1926, **158**, 249—263).—Potassium, rubidium, and cæsium react vigorously with different forms of carbon with evolution of heat. Whilst carbides are not formed by the reaction, the resulting product contains 0·24, 0·12, or 0·06 mol. of alkali metal per mol. of carbon, according to the temperature, and has a definite colour, depending on the alkali metal content. Although it is suggested that an adsorption process may be responsible for the phenomena, it is remarkable that different forms of carbon, having different powers of adsorption, should exhibit very little difference in behaviour. With sodium, definite results were not obtained. A. S. CORBET.

Formation of gold from mercury. A. MIETHE and H. STAMMREICH (Z. anorg. Chem., 1926, **158**, 185—243).—Passage of electric discharges through mercury vapour frequently resulted in the appearance of gold. Experiments in liquid dielectrics, such as paraffin, water, etc., gave positive results, but only traces of gold resulted from electric discharges in gaseous dielectrics such as carbon dioxide and hydrogen. Traces of gold only were found by spark discharges through solid paraffin and through quartz and by conduction experiments through iron. The passage of a current through a long mercury column gave negative results. In general, the analytical procedure was that adopted previously (Stammreich, A., 1925, ii, 1208).

Although the majority of a large number of experiments were negative, some series were almost exclusively positive and the results indicate a close dependence of the appearance of gold on the nature of the electric discharge. The most favourable conditions, however, are not yet definitely known.

A. S. Corbet.

Magnesium–silver alloys. P. Laffitte (Bull. Soc. chim., 1927, [iv], 41, 32—34).—Ethyl iodide and anhydrous ether extract all the magnesium from magnesium alloys containing not more than 74·5% of silver, irrespective of whether it is combined or not. S. K. Tweedy.

Behaviour of sparingly soluble metallic oxides in solutions of their salts. Magnesium oxide. I. W. Feitknecht.—See B., 1927, 73.

Volatile barium sulphate. F. L. Hahn.—See B., 1927, 106.

Salts of hydrofluoboric acid. II. H. Funk and F. Binder (Z. anorg. Chem., 1926, 159, 121—124; cf. A., 1926, 1015).—The following *salts* of hydrofluoric acid have been prepared and analysed: $Mn(BF_4)_2,6H_2O$; $Cu(BF_4)_2,6H_2O$; $Tl(BF_4),H_2O$; $Ag(BF_4),AgF,HF,5H_2O$; $Pb(BF_4)_2,PbF_2,5H_2O$ (also the corresponding *stannous* salt, which was too unstable to give a satisfactory analysis), N_2H_4,HBF_4, and *benzenediazonium fluoborate*. The fluoborates of the heavy metals are characterised by their great solubility, deliquescence, and instability at higher temperatures. The hydrazine and diazonium salts may be included among the alkali salts; they give anhydrous crystals and are not hygroscopic.

M. Carlton.

Recovery of alumina from natural silicates. H. Kassler.—See B., 1927, 105.

Reaction of "aluminon" with hydroxides of scandium, gallium, indium, thallium, and germanium. R. B. Corey and H. W. Rogers (J. Amer. Chem. Soc., 1927, 49, 216—217).—Scandium produces a red lake with "aluminon" (cf. Middleton, A., 1926, 930) which is insoluble in ammonia solution, but is readily soluble in ammonium carbonate solution. Gallium lake forms slowly, but otherwise resembles the aluminium lake. Indium gives a red solution, which is fairly stable in presence of ammonia, but is decolorised by ammonium carbonate. The lake of tervalent thallium forms with difficulty and is unstable both in ammonia and ammonium carbonate solutions. Germanium forms no stable lake, although the solution becomes distinctly turbid on keeping. S. K. Tweedy.

Fixation of nitrogen as aluminium nitride. H. J. Krase, J. G. Thompson, and J. Y. Yee.—See B., 1927, 73.

Constitution of N_2O_4 and N_2O_3; additive compounds of nitro- and nitroso-compounds with tin and titanium tetrachlorides. H. Reihlen and A. Hake (Annalen, 1927, 452, 47—67).—Experiments on the structure of nitrogen tetroxide which involve fission (*e.g.*, Wieland, A., 1921, i, 778) can give no satisfactory results. The N_2O_4 molecule has now been studied as a whole in additive compounds, in which it behaves as $(O{:})_2N{\cdot}O{\cdot}N{:}O$. Co-ordination compounds of nitro-compounds are first investigated; those with aluminium halides are unsuitable, owing to the variability of the co-ordination valency, and hence stannic chloride and titanic chloride, in which it is always six, were used. The following compounds were obtained as crystalline solids: *nitrobenzene stannic chloride*, $Ph{\cdot}NO_2,SnCl_4$, m. p. 11°, and *titanic chloride*, m. p. 77·5°; m-*dinitrobenzene dititanic chloride*, $C_6H_4(NO_2)_2,2TiCl_4$, m. p. 64°; p-*dinitrobenzene titanic chloride*, $C_6H_4(NO_2)_2,TiCl_4$. The titanic compounds are all yellow, as are *nitromethane titanic chloride*, m. p. 48°, and *nitroethane titanic chloride*, m. p. 51°, which can be sublimed without decomposition, and must be derivatives of the true nitro-forms of nitromethane and nitroethane; they show that the nitro-group, and not the aromatic nucleus, is responsible for co-ordination in the other compounds. In preparing the nitromethane compound, a white solid was always obtained, $CH_3O_4NCl_4Ti_2$, regarded as *nitromethane di-titanic oxychloride*, $NMe[{:}O\ .\ .\ .\ TiOCl_2]_2$. The above compounds show that the nitro-group can combine with 1 mol. of stannic or titanic chloride, and thus supplies two co-ordination valencies.

The nitroso-group behaves differently. Nitrosobenzene yields an amorphous *di-nitrosobenzene stannic chloride*, and with titanic chloride, yellow and red amorphous products. Nitrosyl chloride gives dinitrosyl stannic chloride or titanic chloride (cf. Weber, Annalen, 1863, 118, 476). The latter is also obtained by the action of tetranitromethane on titanic chloride, in which titanic carbonato-chloride and nitric oxide are formed, or very slowly by the action of chlorotrinitromethane. These compounds indicate that the nitroso-group supplies one co-ordination valency. Accordingly, if nitrogen tetroxide is symmetrical, it should give a complex, $Cl_4M{<}\substack{O\\O}{\gg}N{-}N{\ll}\substack{O\\O}{>}MCl_4$; if it is nitronitrite, $Cl_4M[.\ .\ .\ O{:}N{\cdot}O{\cdot}N{\ll}\substack{O\\O}{>}MCl_4]_2$. It is found that at 0° in carbon disulphide a brown *bis(nitrogen tetroxide) tri-stannic chloride*, $O_8N_4Cl_{12}Sn_3$, is obtained, showing that nitrogen tetroxide reacts in the second, nitronitrite form. If excess of solid nitrogen tetroxide is added to stannic chloride at −60° and the mixture is allowed to warm up in a freezing mixture, a yellow *tri(nitrogen tetroxide) bis-stannic chloride*, $O_{12}N_6Cl_8Sn_2$, is obtained. A titanic analogue of the latter is apparently formed, but this decomposes in the presence of nitrogen tetroxide to give *titanic* (*tetra*)*nitrate*, $Ti(NO_3)_4$, stable yellow crystals, decomposed by water.

Nitric oxide and nitrous oxide do not combine with stannic or titanic chloride, even at −25° (cf. Kuhlmann, Annalen, 1841, 39, 319; carbon monoxide is similarly inert). Nitrogen pentoxide is decomposed by stannic and titanic chlorides.

Nitrogen trioxide reacts at −40° with stannic chloride in carbon tetrachloride to give an almost colourless product, which may be derived from a colourless tautomeric form of the oxide, $O{:}N{\cdot}O{\cdot}N{:}O$.

E. W. Wignall.

Addition of nitrosyl chloride to metallic salts. H. Gall and H. Mengdehl (Ber., 1927, 60, [*B*], 86—91).—The action of nitrosyl chloride on metallic halides consists in the primary formation of an additive product, which may be stable or may become transformed into the compound of nitric oxide and the higher chloride by transference of the chlorine atom from the nitrosyl chloride to the metal. If the latter compound is unstable, nitric oxide is evolved, and the residual higher chloride may unite with nitrosyl chloride. The *compound*, $MnCl_3NO$, obtained from manganous chloride and nitrosyl chloride at −10°, is immediately decomposed by water with evolution of nitrous fumes, and, when heated, affords nitric oxide, chlorine, and manganous chloride. Under similar conditions, cuprous chloride gives the compound $CuCl_2,NO$, decomposing when heated with evolution of pure nitric oxide and yielding a dark blue solution in a little acetone or alcohol (cf. Manchot, A., 1914, ii, 567). Sublimed ferrous chloride yields the substance $FeCl_3,NOCl$ (cf. Sudborough, J.C.S., 1891, 59, 655), which is a secondary product, since evidence of the existence of the substance $FeCl_3,NO$ is also adduced. Antimony trichloride affords the *compound*, $SbCl_5,NOCl$, whereas the substance $AlCl_3,NOCl$ is obtained from aluminium chloride. Mercurous chloride is slowly converted into the *compound* $HgCl_2,NOCl$, which is also derived from mercuric chloride. The individual nature of the compounds is established by measurement of the vapour tension at a constant temperature. H. Wren.

Ammonium monometaphosphate. Phosphate. III. S. J. Kiehl and T. M. Hill (J. Amer. Chem. Soc., 1927, **49**, 123—132).—*Ammonium monometaphosphate* was prepared as white, monoclinic crystals, *d* 2·2084, from the sodium salt by way of the lead salt. The procedure is described in detail. The solubility of the salt is 25—30 g. per 100 c.c. of water at the ordinary temperature, the solution being neutral to litmus and precipitating insoluble monometaphosphates of some heavy metals from solutions of their salts. The conductivities at 25° of solutions of ammonium and sodium monometaphosphates are recorded. S. K. Tweedy.

Formation of polythionates. E. Josephy and E. H. Riesenfeld (Ber., 1927, **60**, [*B*], 252—254).—The reaction between thiosulphate and sulphur dioxide, which with the potassium salt gives pure potassium trithionate, with the aniline salt affords homogeneous aniline tetrathionate, thus giving a simple method for the preparation of the latter substance. The possibility of separating tri- or tetrathionate from the same solution according to the nature of the cation is due to the presence of all three polythionates and crystallisation of the most sparingly soluble salt. *Aniline pentathionate* is prepared from its components. H. Wren.

Colour of selenium dioxide. J. Meyer and M. Langner (Ber., 1927, **60**, [*B*], 285).—Selenium dioxide melts to an orange-yellow liquid when heated and gives a yellowish-green vapour. The change is reversible and not attributable to dissociation into selenium and oxygen. Solutions of the oxide in warm, concentrated sulphuric or selenic acid are distinctly yellow, but become lighter in colour when cooled. H. Wren.

Heterotri-acids and heterotri-salts. IV. G. Canneri (Gazzetta, 1926, **56**, 871—889; cf. A., 1926, 258; this vol., 33).—Most of the analytical data for salts of complex tri-acids are too complicated for deductions of structure to be made; this is due to mixed crystal formation. Crystallographic study shows that ammonium tungstovanado-phosphates and -arsenates retain an isomorphous tetragonal structure under considerable variations in composition; variations in density are continuous. Ammonium tungstovanadophosphate gives an insoluble, red, crystalline *barium* salt from which the free *acid* is obtained in red, tetragonal crystals, in which the ratio $WO_3 : V_2O_5$ varies roughly between 2 and 5 by weight. Correspondingly, preparations of *tungstovanadoarsenic acid* are made. These two acids form mixed crystals among one another, as do their ammonium salts. Similar mixed crystals of tungstovanado- with the corresponding molybdovanado-phosphates or -arsenates, and of all four salts together, are obtained; the general type is thus

$$R_6H[(P,As)(Mo_2O_7,W_2O_7)_x(V_2O_6)_y],nH_2O.$$

E. W. Wignall.

Univalent manganese. W. Manchot and H. Gall (Ber., 1927, **60**, [*B*], 191—194).—Potassium manganocyanide is reduced by aluminium filings or Devarda's alloy in aqueous-alkaline solution under definite conditions of temperature to the *compound* $K_2Mn(CN)_3$. The new compound is oxidised with extraordinary ease, and decomposes water, rapidly in boiling, slowly in cold solution, with evolution of hydrogen. It is distinguished from the manganocyanide, itself a powerful reducing agent, by its ability to bleach litmus, its intensely blue colour with hydrogen peroxide, red colour with anthraquinone and alcohol, precipitation of lead and cadmium from solutions of their salts, and reduction of Nylander's bismuth reagent. H. Wren.

Action of high temperatures on some metallic sulphides. Picon (Compt. rend., 1927, **184**, 98—99).—Metallic sulphides having the formulæ FeS, MnS, and $CrS_{1\cdot35}$ were heated in a furnace in a carbon tube under a vacuum of 0·001 mm. of mercury. The iron sulphide dissociated into its elements between 1100° and 1600°; manganese sulphide volatilised without decomposition at 1375°; chromium sulphide gradually lost its sulphur from 1350°, and melted at 1550° (the m. p. of the monosulphide). The composition then corresponded with the formula $CrS_{1\cdot06}$. The sulphides are thus more stable than the corresponding oxides. J. Grant.

Nickel carbide. G. Meyer and F. E. C. Scheffer (Rec. trav. chim., 1927, **46**, 1—7; cf. this vol., 29).—A mixture of nickel oxide and asbestos was treated with hydrogen at 270° and after reduction the hydrogen was replaced by carbon monoxide, which was passed for some hours at 250°. The resulting product contained one or more carbides of nickel and gave a mixture of hydrogen and hydrocarbons when treated with hydrochloric acid. No perceptible amount of nickel carbonyl was present. Previous work (*loc. cit.*) indicated that nickel carbide should have a dissociation temperature of about 420°, in agreement with which the above treatment at high temperatures (700°) gives a mixture of nickel and carbon only, the product being unaffected by hydrochloric acid owing to envelopment of the nickel grains by carbon. The formation of the carbide may be represented $x\mathrm{Ni}+2\mathrm{CO}=\mathrm{Ni}_x\mathrm{C}+\mathrm{CO}_2$, whilst at high temperatures the nickel acts as a catalyst for the action $2\mathrm{CO} \rightleftharpoons \mathrm{CO}_2+\mathrm{C}$. The gases evolved when the carbide is treated with acid are complex and contain both methane and unsaturated hydrocarbons.

W. Hume-Rothery.

Sources of error in quantitative chemical analysis by means of *X*-ray emission spectra. H. Stintzing (Physikal. Z., 1926, 27, 844).—The technique is described. R. A. Morton.

Method of micro-titration. E. Schilov [in part with Z. A. Ossennova] (Z. anal. Chem., 1927, 70, 23—34).—A burette for micro-titrations comprises a 1 c.c. calibrated pipette without stopcock, but connected at its upper end by means of a piece of rubber tubing with a manometer filled with a 50% solution of barium bromide. By raising one arm of the manometer, liquid is delivered from the pipette in any desired quantity; conversely, by lowering this arm with the tip of the pipette in the titrating solution, the pipette may be refilled. Arrangements for cleaning the pipette and for filling it directly from the stock bottle are described and illustrated, and examples of its use in volumetric analysis are given.

A. R. Powell.

Rapid calibration of micro-burettes. E. Schilov (Z. anal. Chem., 1927, 70, 35—38).—Microburettes may be calibrated in a similar way to capillary tubes by displacement of a column of mercury supported between two columns of water, provided that the bore of the burette is less than 3 mm. in diameter. The mercury column is caused to move by adjusting the manometer (cf. preceding abstract). For details of the actual procedure and method of calculating the results, the original must be consulted.

A. R. Powell.

Colorimetric determination of hydrogen-ion concentration. J. H. Shaxby and O. M. Jones (J. Physiol., 1926, 61, Proc., xxvi—xxvii).—Dale and Evans' method of the determination of hydrogen-ion concentration is liable to error resulting from the use of unequal depths of liquid in the two tubes. A. A. Eldridge.

Determination of hydrogen-ion concentration with colloid membranes containing indicators. P. Wulff (Kolloid-Z., 1926, 40, 341—342).—A method is described in which the indicator is adsorbed by a colloid membrane, which is dipped in the solution to be examined. On withdrawal, the colour is compared with a series of standard colours.

E. S. Hedges.

Use of the quinhydrone electrode in electrometric titrations. A. J. Rabinowitsch and V. A. Kargin (Z. Elektrochem., 1927, 33, 11—14).—Limits to the accuracy of electrometric titrations of acids with alkali hydroxides using the quinhydrone electrode have been investigated. Not only does the quinhydrone electrode always give p_H values which are too low in solutions more alkaline than about p_H 8, but also in insufficiently buffered solutions of weak acids such errors appear at lower p_H values, *e.g.*, around p_H 6. Since the titration curves of such acids do not become vertical until the neutral point is approached and the vertical portion is short, the observed titration values will tend to be high. The weaker is the acid the greater becomes the error. But, since for a given acid the error (in terms of equivalents of alkali) is practically constant, it becomes important only when very small quantities of the acid are being titrated, *e.g.*, it is negligible when 20—50 c.c. of $0{\cdot}1N$-acetic acid are titrated with $0{\cdot}1$—$0{\cdot}5N$-potassium hydroxide. Good results are usually obtained in the titration of animal fluids owing to their being well buffered. No error arises with strong acids, since their titration curves become vertical at relatively low p_H values. The above inaccuracies are attributed to the slightly acidic character of quinol, the ionisation of which not only furnishes hydrogen ions to the solution, but also causes a shift in the quinol–quinone equilibrium on which the potential of the electrode depends. Purity of the quinhydrone is important, since the presence of acid oxidation products may cause errors even in the titration of strong acids. H. J. T. Ellingham.

Correction for the new citrate buffer solutions. I. M. Kolthoff and J. J. Vleeschouwer (Chem. Weekblad, 1927, 24, 78; cf. A., 1926, 1220).—The figures previously given were based on the assumption that the potassium citrate used was anhydrous; it is now found that the monohydrate was employed. Corrected tables are given.

S. I. Levy.

Employment of the quinhydrone electrode in solutions of low buffer capacity. I. M. Kolthoff and W. Bosch (Chem. Weekblad, 1927, 24, 78—80).—Quinhydrone prepared by the oxidation of quinol with ferric alum gives low p_H values with solutions having low buffer capacity; for such solutions more accurate figures are obtained by use of quinhydrone obtained from alcoholic solutions of quinol and quinone. The solution to be examined should be shaken with the quinhydrone, the measurement taken, the liquor poured off and replaced by fresh solution, this being continued until constant values are obtained. S. I. Levy.

Measurement of moisture content. H. Ebert (Physikal. Z., 1926, 27, 869—870).—The aspiration psychrometer of Assmann gives values for moisture which are correct when the moisture content is high, but when it is low the results err on the high side.

R. A. Morton.

Automatic apparatus for the determination of water. R. Kattwinkel.—See B., 1927, 63.

Sensitiveness of some reagents for gaseous hydrogen sulphide. M. Wilmet (Compt. rend., 1927, 184, 287—289).—The sensitiveness towards hydrogen sulphide of lead and cadmium acetates, lead nitrate, and copper sulphate impregnated on filter-papers, and strips of silver or copper polished by various means, has been tested by observing the time elapsing before stains are produced when the reagents are suspended in a still or moving atmosphere of gas. Lead acetate (10% solution) is the best reagent if used on filter-paper 9 sq. mm. in area.

The method may be made roughly quantitative by standardising the conditions, and the dynamic method will then determine the amount of air containing 0·1 mm.^{3} of gas. The sodium nitroprusside, Lauth's violet, and methylene-blue tests are least trustworthy, whilst copper or brass strips respond only for concentrations at which the gas is harmless to man. The odour is detectable for concentrations down to 1 : 700,000. J. Grant.

Reaction between elementary phosphorus and potassium iodate and its utilisation in the volumetric determination of phosphorus. T. F. Buehrer and O. E. Schupp, jun. (J. Amer. Chem. Soc., 1927, 49, 9—15).—The phosphorus is heated in a reflux apparatus for 3—4 hrs. with potassium iodate, dilute sulphuric acid, and a small volume (2 c.c.) of carbon tetrachloride. The liberated iodine is then distilled into slightly insufficient standard sodium thiosulphate solution at 0°, the slight excess of iodine being determined by titration. The result is checked by titration of the excess of iodate remaining in the distillation flask. The accuracy is about 0·3%. The nature of the reactions involved is discussed. S. K. Tweedy.

Separation of phosphoric acid in qualitative analysis by means of zirconium salts. F. Oberhauser (Ber., 1927, 60, [*B*], 36—42; cf. Curtman, Margulies, and Plechner, A., 1925, ii, 68).—Zirconium hydroxide is appreciably soluble in dilute hydrochloric acid in which zirconium phosphate does not dissolve. In the presence of the hydroxide and hydrochloric acid, zirconium phosphate yields a soluble complex salt in which the phosphate radical cannot be detected by ammonium molybdate except after repeated evaporation with much concentrated nitric acid. In qualitative analysis, the separation of phosphate is effected by addition of saturated zirconium nitrate or oxychloride and ammonium chloride to the oxidised solution from which the customary metals and nickel and cobalt have been separated; the solution is heated to incipient boiling, made alkaline with ammonia, boiled for 3 min., and rendered distinctly acid with acetic acid. The precipitate contains all the phosphate as basic zirconium phosphate, excess of the reagent as the hydroxide, and the greater part of the iron, aluminium, and chromium; zinc, manganese, the alkaline-earth metals, magnesium, the alkali metals, and small amounts of iron, aluminium, and chromium are present as acetates in the filtrates. The precipitated zirconium phosphate appears to have the composition $4Zr(OH)PO_4,3Zr(HPO_4)_2$, and to pass when ignited into the *salt*, $2ZrO_2,5ZrP_2O_7$. Zirconium may be determined by means of an excess of phosphate in concentrated hydrochloric acid solution in presence of metals of the ammonium sulphide and carbonate group. The method is not adapted to the determination of phosphate. H. Wren.

Electrolytic determination and separation of arsenic, antimony, and tin. A. Schleicher and L. Toussaint (Z. anorg. Chem., 1927, 159, 319—324).—The mixture of salts is dissolved in concentrated hydrochloric acid, with addition of hydrazine sulphate and a little potassium bromide, and arsenious chloride is distilled off in an air-stream at the temperature of the water-bath. Arsenic is determined in the distillate by direct titration with 0·1*N*-potassium bromate; antimony and tin are determined in the residue electrolytically. The residue is neutralised with sodium hydroxide until a turbidity is produced, and the incipient precipitate is just redissolved in hydrochloric acid. Excess of hydrochloric acid may not be used, or the deposited antimony will contain antimony chloride. A cathode potential of 0·28—0·35 volt (against the calomel electrode) is used for the deposition of antimony, the solution being kept at 60—70°. The deposition of tin commences at a cathode potential of 0·6 volt, and the temperature is lowered to 35°, with addition of a little hydroxylamine hydrochloride. The whole process can be performed in 3 hrs. The separation of antimony and tin can be carried out between the limits Sb : Sn=100 : 1 and 1 : 100. E. S. Hedges.

Iodometric titrations. II. Determination of arsenate. K. Böttger and W. Böttger (Z. anal. Chem., 1927, 70, 97—109; cf. A., 1926, 1221).—By carrying out the iodometric titration of arsenate in concentrated hydrochloric acid solutions, considerable economy may be effected in the amount of iodide required, and disturbing influences caused by the separation of insoluble iodides (*e.g.*, lead iodide) are avoided. For the determination of arsenic acid in commercial lead arsenate preparations, 0·5 g. is shaken in a stoppered flask with 30 c.c. of cold hydrochloric acid (*d* 1·19), 0·5 g. of potassium iodide is added and, after 15 min., the liberated iodine is titrated with 0·1*N*-thiosulphate. When only very small quantities of arsenic acid are being determined, an atmosphere of carbon dioxide is essential for accurate results, as iodine is liberated by the action of the air on strongly acid iodide solutions. A. R. Powell.

Analysis of silicates. A. Lassieur.—See B., 1927, 108.

Analysis of rock salt. W. Toeldte.—See B., 1927, 106.

Analysis of rubidium and cæsium. L. Moser and E. Ritschel (Z. anal. Chem., 1927, 70, 184—189).—The results of a critical examination of the methods of separating rubidium and cæsium from potassium and from each other described by Strecker and Diaz (A., 1926, 261) are recorded. The alcohol separation of potassium and rubidium chlorides gives high and irregular figures for potassium, the chlorostannate method good results only when little rubidium is present with much potassium, and the antimony chloride precipitation of cæsium very erratic results even under carefully controlled conditions. A. R. Powell.

Volumetric determination of calcium by precipitation as oxalate and titration with permanganate. F. L. Hahn and G. Weiler (Z. anal. Chem., 1927, 70, 1—22).—Precipitation of calcium oxalate with an excess of ammonium oxalate in neutral or ammoniacal solution yields a precipitate which may contain a certain amount of a basic salt, of a double salt, or of mixed crystals, so that, whether the precipitate is titrated directly with permanganate or the excess of ammonium oxalate in the filtrate is determined, incorrect results are obtained for calcium. Pure calcium oxalate may, however, be precipitated from a solution containing 5 c.c. of 0·1*N*-hydrochloric acid and 10 c.c. of 2*N*-ammonium chloride per 100 c.c. by the addition of a slight excess of ammonium oxalate to the boiling solution, followed by ammonia to neutrality. Ammonium acetate may replace the ammonium chloride and 10 c.c. of glacial acetic acid the hydrochloric acid. Better results are obtained by using a known volume of ammonium oxalate solution and titrating the excess in an aliquot part of the filtrate, as calcium oxalate has a tendency to hydrolyse on washing. A. R. Powell.

Determination [and separation] of calcium, strontium, and barium. L. Szebellédy (Z. anal. Chem., 1927, 70, 39—55).—The accuracy of Winkler's methods for the determination of calcium as CaC_2O_4,H_2O (A., 1919, ii, 34), strontium as SrC_2O_4,H_2O (*ibid.*, 1918, ii, 241), and barium as chromate (Z. angew. Chem., 1917, 30, 301) and as sulphate (A., 1921, ii, 62) has been tested and his correction factors have been confirmed. For the separation of calcium from barium and strontium, the nitrate solution is evaporated to dryness and the residue heated for 30 min. at 132°, then for the same time at 180°. The mass is extracted twice with 2·5 c.c. of absolute alcohol, then once with 5 c.c. of *iso*butyl alcohol, the residue is dissolved in water, and evaporation, heating, and extraction are repeated, and, finally, the insoluble portion is redissolved in water for the separation of barium and strontium. The alcoholic filtrates are evaporated in a tared crucible and the residual calcium nitrate is converted into sulphate by heating with five times its weight of ammonium sulphate. Barium is separated from strontium by adding 15 c.c. of *N*-acetic acid and 5 g. of ammonium chloride to the nitrate solution, heating to boiling, and adding slowly 10 c.c. of 10% potassium chromate solution. The precipitate is collected next day on a Gooch crucible, washed with hot water, dried at 132°, and weighed as barium chromate. Strontium is recovered from the filtrate by adding 10 c.c. of *N*-ammonia solution, followed by 10 c.c. of 10% potassium oxalate solution. The latter salt, being more soluble than ammonium oxalate, is more suitable for precipitation of calcium or strontium oxalates. A. R. Powell.

Titration of barium ions. R. F. Le Guyon (Bull. Soc. chim., 1927, [iv], 41, 99—101; cf. A., 1926, 927).—Neutral solutions of barium salts may be determined volumetrically by titration with a standard chromate solution, using silver nitrate as an internal indicator. S. K. Tweedy.

Determination of lead by oxidation with persulphate. P. Ekwall (Z. anal. Chem., 1927, 70, 161—179).—A critical examination of Samter's method of determining lead by oxidation with persulphate in ammoniacal solution ("Analytische Schnellmethoden," Halle, 1911). Under no modification of the conditions could a better conversion to peroxide be obtained than 97%, the precipitate invariably containing small amounts of sulphate and monoxide. The use of potassium persulphate in sodium hydroxide solution gave no better results. A. R. Powell.

Spot method of qualitative analysis. N. A. Tananaiev (J. Russ. Phys. Chem. Soc., 1926, 58, 219—222).—A rapid and simple systematic method is described for the detection of metals which give colour reactions, in presence of each other. A drop of a solution containing aluminium, chromium, iron, cobalt, nickel, zinc, manganese, mercury, lead, silver, bismuth, cadmium, or copper is brought in contact with suitably prepared filter-paper and further treated with appropriate reagents; *e.g.*, for aluminium, the paper is saturated with ferricyanide solution, and the spot of solution to be tested is treated with ammonia and an alcoholic solution of alizarin. A pink ring on a violet background is obtained. For nickel, the paper is saturated with sodium phosphate solution, and the spot moistened with dimethylglyoxime in alcohol, a pink ring being developed.

The method, which is sensitive and accurate, has been extended to other elements (cf. Feigl, A., 1921, ii, 278; 1923, ii, 508). M. Zvegintzov.

Determination of ferrous iron. E. Dittler (Z. anorg. Chem., 1926, 158, 264—276).—The hydrogen sulphide, evolved by decomposition of minerals and meteorites containing sulphur with mineral acid, is collected and, after oxidation by nitric acid, determined as sulphate and the ferrous salt present calculated from the relation $FeS+H_2SO_4=FeSO_4+H_2S$. During the decomposition a brisk stream of carbon dioxide passed through the apparatus prevents any small amount of magnetic pyrites from being attacked and inhibits any reduction which may otherwise result from the reaction $Fe_2(SO_4)_3+H_2S=2FeSO_4+H_2SO_4+S$. A. S. Corbet.

Electrometric study of tungstic acid. H. T. S. Britton (J.C.S., 1927, 147—150).—A solution of tungstic oxide in excess of sodium hydroxide was titrated with hydrochloric acid. A sharp diminution in hydrogen-ion concentration occurred when the amount of hydrochloric acid necessary to react with the alkali in excess of that required to form the normal sodium tungstate (Na_2WO_4) was added. This explains the successful use of phenolphthalein as an indicator for the titration of the oxide. The inflexion in the hydrogen-ion concentration curve indicates that tungstic acid is not an ordinary dibasic acid. Meta- and para-tungstates are assumed to contain tungstic acid either in a polymerised form or in a semi-colloidal form. W. Thomas.

Titration of tin with ferric chloride using indigo-carmine [as internal indicator]. W. Schluttig (Z. anal. Chem., 1927, 70, 55—61).—Stannous chloride may be satisfactorily titrated with ferric chloride at the ordinary temperature, using indigo-carmine as indicator, if the solution contains at least half its volume of concentrated hydrochloric acid. The ferric chloride solution is made by dissolving 47 g. of the commercial salt in 160 c.c. of hydrochloric acid (*d* 1·19) and diluting to 1 litre, and for each titration 10 drops of a 0·5% solution of indigo-carmine are used. The yellow colour of the indicator becomes pale green just before the end-point is reached; a further drop or two of the ferric chloride solution produces a sharp change to indigo-blue. Titrations should be carried out in an atmosphere of carbon dioxide, stannic solutions being previously reduced with iron or aluminium to the stannous state. A. R. Powell.

Electrometric titration of dichromate using potassium ferrocyanide. K. Someya (Z. anorg. Chem., 1926, **159**, 158—160).—The usual apparatus for electrometric titration was employed, using as electrodes a bright platinum wire and a calomel half-electrode. For a sharp end-point, the temperature must lie between 40° and 65° and the amount of concentrated hydrochloric acid be between 5 and 10 c.c. per 60 c.c. of the total volume. Under these conditions, a sharp fall in potential of about 250 millivolts is obtained. M. Carlton.

Separation of minute quantities of gold from ferric oxide. E. Wichers (Ind. Eng. Chem., 1927, **19**, 96).—The approximate determination of gold (of the order 0·005 mg.) in a residue consisting mainly of ferric oxide may be made by separating the ferric oxide by fusion with potassium pyrosulphate. The solution of the sample is absorbed on filter-paper, which is burned off in a porcelain crucible, and the residue fused with about 20 g. of potassium pyrosulphate. The clear mass is dissolved in water acidified with sulphuric acid, filtered through paper treated with paper pulp, and wet with dilute sulphuric acid. A very small amount of ferric oxide may still be present, and the fusion is repeated with a very small quantity of pyrosulphate. The papers are burned off and the slight residue is digested with chlorine water. On the addition of several drops of benzidine reagent, a positive test for gold is obtained, and by using comparative tests with known quantities of gold and comparing the depth of colour, the approximate proportion present may be determined. D. G. Hewer.

Hygrometer employing glycerol. E. Griffiths and J. H. Awbery (Proc. Physical Soc., 1926, **39**, 79—84).—The variation of refractive index of glycerol solutions in equilibrium with air of various humidities has been studied; the time for equilibrium to be reached, when thin films of glycerol are used, has also been investigated. A hygrometer, in which the refractive index of a thin glycerol film is measured, is described. The instrument is robust, and the scale can be engraved directly in humidities. The time-lag is about 15 min. C. J. Smithells.

Clip for securing paper covers on funnels and beakers. N. H. Hartshorne (J.S.C.I., 1927, **46**, 40T).—A description of, and directions for making, a simple wire clip for securing paper covers placed on funnels and beakers to exclude dust or other foreign matter.

Regulating device for pinchcocks of burettes. M. Wikul (Z. anal. Chem., 1927, **70**, 61—62).—A glass rod cut at one end to form a rough wedge is inserted between the arms of the pinchcock on the side remote from the loop. By gently twisting this rod, the solution may be delivered at any desired rate. A. R. Powell.

Device for maintaining a constant level in water-baths. G. Fouque (Bull. Soc. chim., 1927, [iv], **41**, 115—116).—A simple non-siphoning device is described which can readily be constructed from glass tubing. S. K. Tweedy.

Constant-level water-bath using distilled water. R. W. Gerdel (Ind. Eng. Chem., 1927, **19**, 50).—Through the 3-holed cork of a 10- or 15-litre bottle there pass a short tube with stopcock, for filling the bottle and for applying pressure to start the siphon; a tube bent twice at right angles, from the bottom of the bottle to the bottom of the water-bath, and another tube from the bottom of the bottle and connected by rubber tubing (for application of a pinchcock when starting up) to a wider glass tube (diameter at least 1 inch to overcome capillarity) reaching to the desired level in the water-bath. D. G. Hewer.

Gas-tight bearing for rotating laboratory apparatus. C. van Brunt (Ind. Eng. Chem., 1927, **19**, 127).—The rotating horizontal member is in the form of an inner tube fitting as closely as possible into an outer bearing, and the seal is formed by a mercury jacket in a tube (supported against rotation), fixed by rubber tubing, which fits closely enough on the inner tube to hold the mercury under a small head, but not so tightly as to bind. The tubing may be rubbed inside with flake graphite. This bearing has run satisfactorily for days at about 25 r.p.m. D. G. Hewer.

Apparatus for the determination of moisture by distillation with xylene. J. Pritzker and R. Jungkunz.—See B., 1927, 63.

Simple apparatus for the removal of ammonium salts by volatilisation. K. Fischer.—See B., 1927, 73.

Formation of films of lead sulphide on glass surfaces. H. L. Smith (J. Sci. Instru., 1926, **4**, 115—118).—Thin films of lead sulphide can be deposited on the surface of lead glass or zinc crown glass by treatment with a mixture of an alkaline solution of lead tartrate and a solution of thiocarbamide at 50°. Other types of glass and quartz do not give satisfactory results. R. Cuthill.

Apparatus for the purification of gases and the determination of vapour pressures. E. Cardoso (J. Chim. phys., 1926, **23**, 829—840).—A simple and convenient apparatus in which gases can be purified and measurements made of their vapour pressures is described. Complete liquefaction at constant pressure and at two different constant temperatures constitutes the criterion of purity. R. W. Lunt.

Apparatus for the measurement of the speeds of absorption of gases by liquids. P. Riou (Compt. rend., 1927, **184**, 195—197).—An apparatus is described the main feature of which is the gradual drawing of water into a graduated burette by means of the low pressure produced in the absorption tube. The speed is measured by a chronometer, the absorbing liquid in the meantime being automatically stirred.

For high rates of absorption, the absorbing vessel is replaced by a tube drawn out at the absorbing surface. The method gives concordant results and regular curves for a large range of rates of absorption, with or without chemical action. J. GRANT.

Application of eudiometer discharges to the demonstration of the synthesis of nitric oxide and the decomposition of methane. S. PLEŚNIEWICZ (Rocz. Chem., 1926, 6, 741—742).—Two lecture demonstrations are described. R. TRUSZKOWSKI.

Mineralogical Chemistry.

Variations in density of the atmosphere. A. STOCK and G. RITTER.—See B., 1927, 74.

Radioactivity and the heat of the earth. R. W. LAWSON (Nature, 1927, 119, 277—278).—Evans' view that an appreciable proportion of the energy liberated by the radio-elements, when they occur as rock constituents, is absorbed in ways other than raising the temperature of the rocks is contested. A. A. ELDRIDGE.

Walchowite. W. FUCHS and G. LANDSMANN (Ber., 1927, 60, [*B*], 246—249).—Walchowite, an organic mineral from Mähren, *d* 1·1, hardness 1·5—2, acid value 0, saponification value 42·5, iodine value (Hanus) 33·2, is a polymerised resin which gives sesquiterpene alcohols when distilled with zinc dust. When mixed with silver powder and subjected to dry distillation, it yields a mixture of terpenes. It is converted by cold, concentrated sulphuric acid into an amorphous material soluble in chloroform which, according to its colour reactions, is related to the terpenes. H. WREN.

Uranium minerals of Katanga. A. L. HACQUAERT (Natuurwetensch. Tijdschr., 1926, 8, 131—139).—Methods of identifying the minerals are described. Colour is determined by aid of the Ostwald atlas, optical properties with the polarising microscope; for coefficients of refraction, solid mixtures of piperine with arsenic or antimony iodides (n=1·8—2·07) or of sulphur and selenium (2·1—2·7) are required, as the indices of most of the minerals are too high for the ordinary liquids. Dehydration curves are constructed by heating for definite times to definite rising temperatures; the curves so obtained, and physical properties, serve to distinguish different varieties of the same or similar chemical composition. Uranium is best separated in solution as ammonium uranyl carbonate, precipitated and filtered as ammonium uranate, and weighed as U_3O_8. Uranium present as the dioxide is determined by dissolving in 15% sulphuric acid, in a Carius tube filled with carbon dioxide, at 180°, afterwards titrating with permanganate. For determination of the uranium where phosphates are present, the method of Schoep and Steinkuhler (A., 1922, ii, 530) is recommended. S. I. LEVY.

Helium content of some Japanese minerals. J. SASAKI (Bull. Chem. Soc. Japan, 1926, 1, 253—254).—Travers' observation (A., 1899, ii, 769), that nearly half of the helium contained in most minerals is evolved on heating, is used to determine the helium content of fergusonite, monazite, and beryl. From the data thus obtained, the geological age of the two first-named minerals is discussed. A. S. CORBET.

Three South African meteorites. G. T. PRIOR (Min. Mag., 1926, 21, 188—193)—A mass of iron weighing about 26 lb. was found in 1918 on the Vaalbult farm, Prieska Division, Cape Province. The structure is that of a coarse octahedrite. Analysis gave Fe 92·18, Ni 6·99, Co 0·68, Cu 0·02, P 0·19, S trace, insoluble 0·02, total 100·08; *d* 7·62. On May 26, 1918, a stone fell near Witklip, Caroline District, Transvaal. It is a grey bronzite-chondrite. Two or more stones were seen to fall on April 30, 1925, near Queen's Mercy, Matatiele, Griqualand East. The material is classed as a veined grey bronzite-chondrite. Analysis gave Fe(+Co) (14·26), Ni 1·35, FeS 5·42, insoluble silicate 44·48, soluble silicate 34·49%. The insoluble silicate (pyroxene) gave SiO_2 53·98, Al_2O_3 4·78, Cr_2O_3 0·36, FeO 9·28, MnO trace, CaO 2·03, MgO 25·19, Na_2O and loss (4·38)%. L. J. SPENCER.

Aramayoite, a new mineral, from Bolivia. L. J. SPENCER (Min. Mag., 1926, 21, 156—162).—This was found in 1925 in a silver–tin vein in the Animas mine at Chocaya. It shows a confused aggregate of cleavage plates with iron-black colour and brilliant metallic lustre. In addition to the perfect basal cleavage, there are also good cleavages following a steep tetragonal pyramid. The mineral is pseudotetragonal. Streak black, *d* 5·602, *H* 2½. The powdered mineral is slowly decomposed by hot concentrated nitric acid with separation of a white precipitate, but hot concentrated hydrochloric acid has no action. Analysis by E. D. MOUNTAIN gave S 20·87, Sb 29·95, Bi 13·75, Ag 34·74, Cu 0·53, Fe trace, total 99·84, agreeing with the formula $Ag(Sb,Bi)S_2$. L. J. SPENCER.

Schultenite, a new mineral, from South-West Africa. L. J. SPENCER (Min. Mag., 1926, 21, 149—155; cf. A., 1926, 1022).—Colourless platy crystals were found on balydonite pseudomorphous after mimetite and anglesite from Tsumeb. They are monoclinic ($a:b:c$ =0·8643 : 1 : 0·7181, β=84° 36′) and flattened parallel to the plane of symmetry, which is also the direction of good cleavage. Many crystal forms are present, and the table of angles gives the angles from each face to the three axial planes. (This method combines the advantages of both the arrangement of interfacial angles in zones and the latitude and longitude angles of two-circle goniometry.) The crystals are optically positive, with the optic axial plane perpendicular to the plane of symmetry; 2V 58°14′, n_α 1·8903, n_β 1·9097, n_γ 1·9765 (Na); *d* 5·943, *H* 2½. Analysis by E. D. MOUNTAIN gave PbO 63·97, As_2O_5 32·18, H_2O 2·88, total 99·03, corresponding with the formula $PbHAsO_4$. L. J. SPENCER.

Organic Chemistry.

Indirect interatomic effects in organic compounds. F. Swarts (2me. Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 199—236).—A review and discussion of steric hindrance and of various theories advanced to explain the effects of certain atoms or radicals when present in a molecule on the remaining portion of the molecule. Chemical Abstracts.

Exceptional instances of stereoisomerism. J. K. Senior (Ber., 1927, **60**, [*B*], 73—81).—The number of stereoisomeric forms of a carbon compound of given structure is generally assumed to be 2^k (where k is the number of asymmetric carbon atoms), provided the development of the full number of forms is not impeded by internal compensation or by the strain set up by the production of condensed ring systems. It is, however, possible to synthesise saturated non-cyclic compounds which contain a clearly-defined number of asymmetric carbon atoms and exist in optically active forms in number less than 2^k, although the molecules are free from strain and incapable of internal compensation (cf. the ethyl α-bromo-ββ-dibromodimethylpropanetricarboxylate of Beesley and Thorpe, J.C.S., 1920, **117**, 619). It is shown that if a is a symmetrical, saturated, non-cyclic substituent and x, y, z, and v are four structurally different non-cyclic substituents in which n, m, p, and q asymmetric carbon atoms are present in straight chains, the number of isomerides of the given types is given by the formulæ: C*axxx*, $(2^{3n}+2^{n+1})/3$; C*axxy*, 2^{2n+m}; C*axyz*, $2^{n+m+p+1}$; N*xxx*, $2^n(2^n+1)(2^n+2)/6$; N*xxy*, $(2^{2n+m}+2^{n+m})/2$; N*xyz*, 2^{n+m+p}; C*xxxx*, $(2^{4n}+11\times 2^{2n})/12$ (including 2^{n-1} non-divisible *meso*-forms; C*xxxy*, $(2^{3n+m}+2\times 2^{n+m})/3$; C*xxyy*, $(2^{2n+2m}+2^{n+m})/2$; C*xxyz*, 2^{2n+m+p}; C*xxzv*, $2^{n+m+p+q+1}$. If k is the total number of asymmetric carbon atoms in the substituents, the number of isomerides is smaller than 2^k in the types, C*axxx*, N*xxx*, N*xxy*, C*xxxy*, and C*xxyy*, although none of these types permits the existence of non-divisible *meso*-forms and the molecules are free from strain in all cases. H. Wren.

Crystalline, blue ψ-nitrole. H. Rheinboldt and M. Dewald (Ber., 1927, **60**, [*B*], 249—251).—β-ψ-*Nitrole-αγ-diphenylpropane*, $(CH_2Ph)_2C{:}N_2O_3$, m. p. 88° (decomp.), is prepared by the action of ethyl nitrite and nitric acid (d 1·4) on an ethereal solution of dibenzyl ketoxime or from the latter substance and an excess of nitrogen tetroxide. The blue crystals retain their colour at the temperature of liquid air; in hydrocyanic acid at −10°, they are unimolecular. Although stable in the dark, they rapidly decompose on exposure to light, with production of ββ-*dinitro-αγ-diphenylpropane*, m. p. 132°, also prepared by oxidation of the ψ-nitrole with nitric acid in glacial acetic acid solution.

H. Wren.

Decomposition of ethyl alcohol at the surface of thoria. I. II. G. I. Hoover and E. K. Rideal.—See this vol., 215.

An erythritol of the acetylenic series. J. Salkind and E. Komarowskaja (Ber., 1927, **60**, [*B*], 182—184).—Benzoin is converted by the magnesium derivative of dibromoacetylene into αβεζ-*tetrahydroxy-αβεζ-tetraphenyl-Δ^γ-hexinene*, m. p. 218—219°. The substance is acetylated with difficulty to the *triacetate*, m. p. 83—85°. Bromine is added very slowly. The constitution is established by its conversion by solid potassium hydroxide at 100° into acetylene and benzoic acid. It is oxidised by permanganate in acetone solution to carbon dioxide, benzaldehyde, and benzoic acid. H. Wren.

Mutual transformations of alkyl phosphites. M. Janczak (Rocz. Chem., 1926, **6**, 774—793).—Sodium diethyl, dipropyl, and di*iso*butyl phosphites are converted by the action of silver nitrate into the corresponding silver salts, which are also produced, although in smaller yield, from the corresponding acids. This supports the view that phosphorus is tervalent in the ester salts, but quinquevalent in the acid esters. Sodium ethoxide reacts with diethyl hydrogen phosphite to yield diethyl sodium phosphite, ethyl sodium hydrogen phosphite, $EtO\cdot PH(O)\cdot ONa$, ethyl ether, and alcohol. With diethyl ethylphosphite, it reacts as follows: $(EtO)_2PEt{:}O+Et\cdot ONa\longrightarrow EtO\cdot PEt(O)\cdot ONa+Et_2O$, whilst no reaction takes place with triethyl phosphite, sodium ethyl hydrogen phosphite, or sodium ethyl hydrogen ethylphosphite, $EtO\cdot PEt(O)\cdot ONa$. R. Truszkowski.

Resolution of asymmetric glycerides into their antipodes. I. Optically active glyceride sulphuric acids and the thermolability of the optical activity of their salts. II. Optically active glyceride phosphoric acids and the thermolability of the optical activity of their salts. A. Grün and R. Limpächer (Ber., 1927, **60**, [*B*], 255—265, 266—272).—I. αβ-Distearin is converted by cautious treatment with chlorosulphonic acid in the presence of light petroleum into αβ-distearin hydrogen sulphate (cf. Grün and Corelli, A., 1912, i, 409), from which the brucine and strychnine salts are readily obtained in quantitative yield. Under definite conditions, decomposition of the salts into alkaloid hydrogen sulphate and free diglyceride can be effected, but it is very difficult to prevent the conversion of a considerable proportion of the diglyceride into its structural isomeride. This greatly complicates the fractional crystallisation of the alkaloidal salts, but it has been found possible to separate l-*strychnine* dl-αβ-*distearin sulphate* into fractions exhibiting marked differences in solubility. The distearin preparations isolated from the individual fractions are practically inactive, and latent activity cannot be detected when they are examined in thionyl chloride solution. The result is, however, not unexpected, since activity has not been detected in preparations of α-monostearin etc. which are undoubtedly asymmetric and derived from initially active material. The potassium salts of *d*- and *l*-αβ-distearin sulphate, prepared by treating the separate fractions of the strychnine salt dissolved in acetone with alcoholic potassium hydroxide, are almost or completely inactive in solvents at temperatures of 40° and above. If, however, they are cooled below 35°, whereby they assume the properties of typical colloidal solutions, great activity is observed. If the observations of the minimal activity at higher temperature are trustworthy, cooling causes first a diminution in specific rotation, which passes through zero and then increases with time to a constant maximum (up to about $[\alpha]_D$ 10,000° in very dilute solution) in the other direction. The process is reversible, since the cold, highly-active solution passes into an inactive (apparently true) solution when warmed, which again becomes active when cooled. The phenomenon is shown to be due to the optical activity of the potassium salt, and not to a physical cause such as the double refraction of the solution, since it is not exhibited by the potassium salt of the corresponding racemic compound or of the non-resolvable αγ-distearin sulphate.

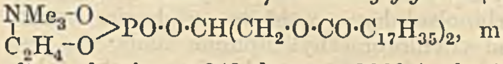
Strychnine αγ-distearin sulphate, $[\alpha]_D^{17\cdot5}$ —10·2 to 10·7° in chloroform, is described. Elimination of strychnine sulphate from it gives a product containing 93% of αγ-distearin and 7% of the αβ-isomeride. Fractional crystallisation of the strychnine salt and conversion of the individual fractions into the potassium salts yields optically inactive products in all cases except one, in which the activity is doubtless due to the αβ-compound formed by isomerisation.

II. The production of αβ-distearin hydrogen phosphate from αβ-distearin and phosphoric anhydride proceeds less smoothly than the analogous preparation of αβ-distearin hydrogen sulphate, since the primary ester readily becomes converted into secondary ester and phosphoric acid, $2(OH)_2PO{\cdot}OR = OH{\cdot}PO(OR)_2 + PO(OH)_3$. Although this change involves about a half of the primary ester, it does not cause serious further difficulty, since the salts of the two series differ widely in solubility. The αβ-ester and its salts, however, show a pronounced tendency towards isomerisation to the αγ-compound. Nevertheless, it has been found possible to separate the strychnine salt into fractions which, after transformation into the corresponding potassium salts, behave as optical antipodes. The thermolability of the specific rotation of these salts resembles that of the corresponding sulphates, but is less marked. The warm solutions do not exhibit appreciable activity, but become active when cooled to an extent which is very considerable in comparison with the activity of glycerides synthesised from optically active materials. The following substances are incidentally described: *strychnine* r-αβ-*distearin γ-phosphate*, m. p. about 195°, decomp. 200°, $[\alpha]_D^{17\cdot5}$ —14·7° in chloroform, and the corresponding *potassium* salt; *strychnine di*-αβ-*distearin phosphate*, $[C_3H_5(O{\cdot}CO{\cdot}C_{17}H_{35})_2O]_2PO{\cdot}OH,C_{21}H_{22}O_2N_2$, m. p. 63—65° after softening at 59°, and the *potassium* salt.

H. WREN.

Glycerolphosphoric acids. P. KARRER and P. BENZ (Helv. Chim. Acta, 1927, 10, 87—91).—The *diacetate*, $[\alpha]_D$ +2·0° (±0·1°), of barium *d*-glycerol-α-phosphate is hydrolysed by barium hydroxide to barium *d*-glycerol-α-phosphate (cf. A., 1926, 818). This is optically inactive, but when reacetylated yields a diacetate having $[\alpha]_D$ +1·8° (±0·2°). The hydrolysis is therefore not accompanied by a displacement of the phosphate radical to the β-position. Lecithin, which is hydrolysed by an exactly similar method, giving principally glycerol-β-phosphoric acid (*ibid.*, 384), must, accordingly, be for the most part a derivative of the latter (cf. Grün and Limpächer, preceding abstract).

H. E. F. NOTTON.

Synthesis of lecithins. II. A. GRÜN and R. LIMPÄCHER (Ber., 1927, 60, [*B*], 147—150; cf. A., 1926, 827).—αγ-Distearin, heated somewhat above its m. p., is treated successively with phosphoric oxide and choline hydrogen carbonate, whereby the *endo*-salt of *choline αγ-distearoylglycerol*-β-*phosphate*,  $\begin{matrix} NMe_3{-}O \\ | \\ C_2H_4{-}O \end{matrix}{>}PO{\cdot}O{\cdot}CH(CH_2{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35})_2$, m. p. 195° after softening at 84°, decomp. 198°, is obtained. The new lecithin so closely resembles that derived from αβ-distearin (*loc. cit.*) that possible identity is not excluded. Two by-products, m. p. 166° after softening at 77° and m. p. 167° after softening at 82°, possibly choline salts of the composition $OH{\cdot}C_2H_4{\cdot}NMe_3{\cdot}O{\cdot}PO[O{\cdot}C_3H_5(O{\cdot}CO{\cdot}C_{17}H_{35})_2]_2$, are described.

H. WREN.

Syntheses of kephalins. A. GRÜN and R. LIMPÄCHER (Ber., 1927, 60, [*B*], 151—156).—αβ-Distearin is treated successively at 71—72° with phosphoric oxide and β-hydroxyethylamine carbonate, whereby a mixture of β-aminoethyl phosphate and β-*aminoethyl hydrogen* αβ-*distearoylglycerol-γ-phosphate*, $C_2H_3(O{\cdot}CO{\cdot}C_{17}H_{35})_2{\cdot}CH_2{\cdot}O{\cdot}PO(OH){\cdot}O{\cdot}C_2H_4{\cdot}NH_2$ (possibly formulated as the *endo*-salt), m. p. 176° after softening at 78—80°, decomp. above 185°, is produced. The kephalin is neutral towards lacmoid, acidic towards phenolphthalein. It is very readily hydrolysed by alkali hydroxide and rapidly suffers ester transformation in presence of alcoholic hydrogen chloride. αγ-Distearin similarly yields β′-*aminoethyl hydrogen αγ-distearoylglycerol*-β-*phosphate*, m. p. 177° after softening at 80°, decomp. 185°. The properties of the two kephalins are so nearly identical that it is regarded as possible that the same kephalin or mixture of symmetrical and unsymmetrical kephalins is obtained from both distearins. Indications of the presence of isomerides have not been obtained.

H. WREN.

Simple reaction for the thiol group. H. RHEINBOLDT (Ber., 1927, 60, [*B*], 184—186).—Solid sodium nitrite is covered with a solution of the substance under investigation in ether, alcohol, light petroleum, chloroform, carbon tetrachloride, benzene, or other solvent, and dilute sulphuric acid is added so that a rapid stream of nitrous gases passes through the liquid; if glacial acetic acid is the solvent, sodium nitrite crystals are cautiously added. The colours are developed immediately (cf. Rheinboldt, A., 1926, 819). Alternatively, if possible, the alcoholic solution of the substance is mixed with an aqueous-alcoholic solution of sodium nitrite and acidified with acetic acid; the colours develop gradually and are stable in concentrated but evanescent in exceedingly dilute solution. The limits of sensitiveness are ethylmercaptan (1 : 7500), thiophenol (1 : 25,000), triphenylthiocarbinol (1 : 7500). The method is more delicate than that of Lecher and Siefken (this vol., 39).

H. WREN.

Lengthened chain compounds of sulphur. P. C. Rây (Nature, 1927, 119, 124).—Polemical (cf. Bennett, A., 1926, 1123). A. A. Eldridge.

Trichloromethylsulphonyl chloride. M. Battegay and W. Kern (Bull. Soc. chim., 1927, [iv], 41, 34—47).—Trichloromethylsulphonyl chloride is slowly decomposed by cold water, the rate of decomposition being rather greater than in the case of *p*-toluenesulphonyl chloride. Sulphurous acid appears to be formed first, $CCl_3{\cdot}SO_2Cl \longrightarrow CCl_3{\cdot}SO_3H \longrightarrow CCl_2(OH){\cdot}SO_3H \rightarrow CCl(OH)_2{\cdot}SO_3H \rightarrow CO(OH){\cdot}SO_3H \rightarrow CO_2+SO_2+H_2O$, but is immediately oxidised by the dichlorocarbinolsulphonic acid to sulphuric, hydrochloric, and trichloromethylsulphinic acids, the last ultimately decomposing into chloroform and sulphur dioxide. With ethyl alcohol, trichloromethylsulphinic acid is formed directly, the alcohol undergoing reduction to acetaldehyde, the sulphinic acid as before affording finally chloroform and sulphur dioxide. A similar reaction occurs with ammonia or with primary amines, the corresponding sulphinate being formed, accompanied by the evolution of nitrogen in the case of ammonia, and of sulphur dioxide in the case of amines, the amine being partly oxidised to indulines (cf. McGowan, A., 1884, 1126). The *aniline*, m. p. 145°, and m-*toluidine*, m. p. 140°, salts of trichloromethylsulphinic acid are described. *o*-Phenylenediamine in alcohol affords 2 : 3-diaminophenazine. No reaction was obtained with 2-aminoanthraquinone in solvents other than nitrobenzene, in which the trichloromethylsulphonyl chloride attacked the solvent, liberating carbonyl chloride, which afforded 2 : 2′-dianthraquinonylcarbamide. Aluminium chloride and benzene yield triphenylcarbinol, with evolution of sulphur dioxide and hydrogen chloride. Keten was not obtained by the action of zinc, or of a mixture of zinc and copper, or of iron in dry ether, the reaction product, m. p. 180°, being contaminated with unchanged sulphonyl chloride. R. Brightman.

Organic molecular compounds with co-ordination centres. I. H. Rheinboldt.—See this vol., 242.

Addition of alkali alkoxide to esters. III. Addition of alkali alkoxide to ethyl formate. F. Adickes (Ber., 1927, 60, [*B*], 272—277; cf. A., 1925, i, 1378; this vol., 41).—Contrary to the observations of Scheibler (A., 1926, 711), the addition of sodium ethoxide to ethyl formate leads to the production, not of sodiumoxyethoxymethylene, but of *sodiumoxydiethoxymethane*, $CH(ONa)(OEt)_2$, the composition of which is deduced from analyses and is in harmony with the insolubility of the compound in ether or light petroleum and its free solubility in alcohol. Unlike other additive compounds, it is decomposed by water thus: $CH(ONa)(OEt)_2+H_2O \longrightarrow NaOH+CH(OH)(OEt)_2 \longrightarrow H_2O+C(OEt)_2$. Scheibler's conception of the hydrolysis, $C(ONa)(OEt)+H_2O \longrightarrow NaOH+CO+Et{\cdot}OH$, cannot be maintained, since carbon monoxide is evolved only in minimal amounts. The production of sodium hydroxide by the hydrolysis is not quite quantitative, since a small proportion of the metal is found as sodium formate. Sodiumoxydiethoxymethane is transformed by phosphoryl chloride and sodium ethoxide into diethoxymethylene (carbon monoxide diethylacetal) thus: $2CH(ONa)(OEt)_2+POCl_3 \longrightarrow CHCl(OEt)_2+NaCl$; $CHCl(OEt)_2=C(OEt)_2+HCl$; $HCl+Na{\cdot}OEt \longrightarrow NaCl+EtOH$. H. Wren.

Mechanism of the catalytic decomposition of esters by nickel. J. N. Pearce and C. N. Ott.—See this vol., 215.

Preparation of ethoxalyl chloride. R. Barré (Bull. Soc. chim., 1927, [iv], 41, 47—49).—Yields of 84% of ethoxalyl chloride are obtained by mechanical agitation of the mixture of phosphorus pentachloride and ethyl oxalate at 110—115°, and decomposition of the dichloride, $CO_2Et{\cdot}CCl_2{\cdot}OEt$, with reduced platinum. At 125—135°, the yield is only 55%. R. Brightman.

Velocity of autocatalytic decomposition of bromosuccinic acid in aqueous solutions. J. Zawidzki and W. Wyczalkowska.—See this vol., 214.

Penthian series. I. Action of sodium ethoxide on ethyl β-thiodipropionate. G. M. Bennett and L. V. D. Scorah (J.C.S., 1927, 194—200).—Ethyl β-thiodipropionate undergoes the Dieckmann reaction with sodium ethoxide, forming the enolic ester *ethyl* Δ^3-*penthien-4-ol-3-carboxylate*, b. p. 150—151°/16 mm., d_4^{20} (vac.) 1·2011, n_{α}^{20} 1·51574, n_{β}^{20} 1·52938 (*phenylpyrazolone*, m. p. 219°; p-*bromophenylpyrazolone*, m. p. 221·5°; p-*nitrophenylpyrazolone*, m. p. 210·5°). The enolic ester, on keeping, deposits crystals of the keto-tautomeride *ethyl penthian-4-one-3-carboxylate*, m. p. 59°; *barium* salt (from either ester). Hydrolysis of the cyclic ester yields *penthian-4-one*, m. p. 65—66°; *oxime*, m. p. 84—85°; *semicarbazone*, m. p. 151°; 2 : 4-*dinitrophenylhydrazone*, m. p. 186°; *dibenzylidene* derivative, m. p. 149—151°; *dipiperonylidene* derivative, m. p. 181°; *chloroplatinate*; *sulphonium methiodide*, m. p. 112—113° (decomp.). B. W. Anderson.

Alkali and alkaline-earth salts of bismuthotartaric acid. C. Pradel (Anal. Fís. Quím., 1926, 24, 600—610; cf. Portillo, A., 1926, 1025).—The preparation of *salts* of the composition $[Bi_3(C_4H_4O_6)_7]R'_4,xH_2O$ or $[Bi_3(C_4H_4O_6)_7]R''_2,xH_2O$, where R′=potassium, sodium, or ammonium, and R″=barium or calcium, is described. In addition, new *compounds*, $K_2[BiO(C_4H_3O_6)],5H_2O$, $(NH_4)_2[BiO(C_4H_3O_6)],2H_2O$, $Na[BiO(C_4H_4O_6)]$, and $NH_4[BiO(C_4H_4O_6)]$, are described. G. W. Robinson.

Double citrates of quadrivalent vanadium. G. Canneri (Gazzetta, 1926, 56, 901—902).—A correction (cf. this vol., 42); to the formula of each citrate described there should be added one oxygen atom, through which the two vanadium atoms are joined. E. W. Wignall.

Mechanism of the formation of citric and oxalic acids from sugars by *Aspergillus niger*. I. F. Challenger, V. Subramaniam, and T. K. Walker (J.C.S., 1927, 200—208).—When the sugar in Molliard's culture medium is replaced by citric acid, *Aspergillus niger* produces malonic acid, glyoxylic acid, and acetone. With calcium acetate, glyoxylic and oxalic acids are formed, and with dipotassium saccharate there are strong indications of citric acid being produced. B. W. Anderson.

d-Galacturonic acid from pectins. K. Smoleński and W. Wlostowska (Rocz. Chem., 1926, 6, 743—746).—A *monohydrate* of d-galacturonic acid, m. p. 116—120°, isolated from beet pulp, is described. R. Truszkowski.

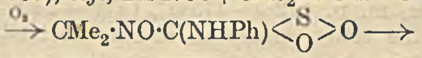
β-Chloroglutaconic anhydride. R. Malachowski and T. Kaliński (Rocz. Chem., 1926, 6, 768—773; cf. A., 1926, 732).—*β-Chloroglutaconic anhydride*, m. p. 113—114°, is obtained from the corresponding acid. From it are prepared, by condensation with cinnamaldehyde, 4-*chloro*-6-*hydroxy*-5-*cinnamylidene*-α-*pyrone*, m. p. 171—172°, with diazobenzene, 4-*chloro*-6-*hydroxy*-α-*pyrone*-5-*phenylhydrazone*, m. p. 204°, and by bromination 3-*chloro*-2-*bromo*-6-*hydroxy*-α-*pyrone*, m. p. 107·5°, which on hydrolysis yields β-*chloro*-α-*bromoglutaconic acid*, m. p. 131—132°. R. Truszkowski.

Optical superposition. VIII. l-Menthylamine, brucine, and strychnine salts of mucic and *allo*mucic acid. T. S. Patterson and J. D. Fulton (J.C.S., 1927, 50—53).—The preparation and optical examination of the following salts were carried out in duplicate: *menthylamine mucate*, m. p. 198° (decomp.), $[\alpha]_{5461}^{19\cdot5}$ $-32\cdot25°$ and $-31\cdot75°$; *menthylamine* allo*mucate*, m. p. 173° (decomp.), $[\alpha]_{5461}^{19\cdot5}$ $-31\cdot50°$ and $-31\cdot00°$; *brucine mucate*, decomp. 150°, $[\alpha]_{5461}^{17}$ $+1\cdot35°$, $[\alpha]_{5461}^{20}$ $+1\cdot15°$; *brucine* allo*mucate*, decomp. 170°, $[\alpha]_{5461}^{17}$ $-1\cdot10°$, $[\alpha]_{5461}^{20}$ $-0\cdot95°$; strychnine mucate, decomp. 273°, $[\alpha]_{5461}^{17\cdot5}$ $+7\cdot93°$, $[\alpha]_{5461}^{20}$ $+7\cdot57°$; *strychnine* allo*mucate*, decomp. 269°, $[\alpha]_{5461}^{17\cdot5}$ $+7\cdot07°$, $[\alpha]_{5461}^{21\cdot5}$ $+6\cdot86°$. These results, in opposition to the principle of optical superposition, show that mucic and *allo*mucic acids differ in their effect in determining the rotation of compounds formed from these acids and the same active base. B. W. Anderson.

Preparation and properties of arabono- and ribono-lactones. V. Hasenfratz (Compt. rend., 1927, 184, 210—213).—Arabono- and ribono-lactones are obtained by modifications of the methods of Bauer (A., 1886, 869) and of Fischer and Piloty (*ibid.*, 1892, 437), respectively. An aqueous solution of arabinose is oxidised by bromine, the solution neutralised with potassium hydroxide, and treated with crystalline calcium chloride. The syrup of the arabonolactone (*dibenzoate*, m. p. 200°; *tribenzoate*, m. p. 120°) obtained by decomposition of the calcium arabonate with oxalic acid and concentration in a vacuum crystallises spontaneously. To convert it into ribonolactone, the arabonolactone (500 g.) is heated under reflux with 280 g. of pyridine and 65 g. of water for 3 hrs., neutralised with milk of lime, and the pyridine distilled off in a vacuum. Calcium arabonate is removed from the filtrate by crystallisation, the lactone freed from its calcium salt by oxalic acid, the solution of ribonic acid boiled with cadmium oxide, filtered, and the cadmium salt caused to crystallise by the addition of one fifth the volume of alcohol. Decomposition of the cadmium salt in aqueous solution with hydrogen sulphide and concentration of the solution of the lactone yields a syrup which readily crystallises. Crystallised from alcohol, ribonolactone has m. p. 84—86° (Fischer and Piloty, *loc. cit.*, give 72—74°) (*tribenzoate*, $[\alpha]_D$ $+11\cdot1°$). On distillation, either lactone gives a 35% yield of a mixture of pyromucic and *iso*pyromucic acids. J. W. Baker.

Reactions of nitrosyl chloride. III. Action of nitrosyl chloride on aliphatic aldoximes. H. Rheinboldt and M. Dewald (Annalen, 1927, 451, 273—281).—The chloronitroso-derivatives formed by the action of nitrosyl chloride on aliphatic aldoximes in ethereal solution, unlike the corresponding aromatic derivatives (this vol., 245), are comparatively stable, crystalline, colourless bimolecular solids of penetrating odour, which dissociate when heated alone, or in solution, into deep blue, unimolecular liquids, the change being reversible. On keeping, they pass more or less rapidly into the corresponding chloro*iso*nitroso-derivatives. Liebermann's and other nitroso-reactions are positive. The αα-*chloronitroso*-derivatives of methane, m. p. 62°, with previous sintering; ethane (cf. Piloty and Steinbock, A., 1902, i, 735); propane, m. p. 56—57°; n-butane, m. p. 41—42°; *iso*butane, $CHMe_2{\cdot}CH_2{\cdot}CHCl{\cdot}NO$, m. p. 36—38°, and n-heptane, m. p. 43°, are described. The compounds prepared analogously from n-octylaldoxime, *iso*valeraldoxime, and phenylacetaldoxime could not be obtained crystalline. H. E. F. Notton.

Condensation of oximes with thiocarbimides. Autoxidation of the additive compounds from oximes and thiocarbimides. C. V. Gheorghiu (Bull. Soc. chim., 1927, [iv], 41, 50—53; cf. Pawlewski, A., 1904, i, 237).—The additive compounds of oximes with thiocarbimides are unstable; those derived from aldoximes (*syn*- and *anti*-) decompose spontaneously into a nitrile, a thiocarbanilide, and carbonyl sulphide. The mechanism is probably $[R{\cdot}CH{:}NO{\cdot}CS{\cdot}NHR'] \longrightarrow R{\cdot}CN+[R'{\cdot}NH{\cdot}CS{\cdot}OH]$: $2[R'{\cdot}NH{\cdot}CS{\cdot}OH]=CS(NHR')_2+COS+H_2O$. There is also some separation of sulphur, probably from autoxidation. Ketoximes afford additive compounds which undergo autoxidation to products identical with those obtained by Goldschmidt from the condensation of oximes with carbimides (cf. A., 1893, i, 707), *e.g.*, $Ph{\cdot}NCS+CMe_2{:}N{\cdot}OH=CMe_2{:}NO{\cdot}CS{\cdot}NHPh$



$$\xrightarrow{O_2} CMe_2{\cdot}NO{\cdot}C(NHPh){<}\overset{S}{\underset{O}{}}{>}O \longrightarrow$$

$CMe_2{:}NO{\cdot}CO{\cdot}NHPh+[SO]$; the thiosulphuric anhydride decomposes into sulphur and sulphur dioxide, and the latter is finally oxidised to sulphuric acid, the separation of sulphur affording an indication of the extent of the reaction. The autoxidation is not inhibited by iodine, ether, acetaldehyde, or quinol, these substances exerting a positive instead of their usual negative catalytic action. Solvents do not affect the autoxidation, but the reaction is slower in hydrocarbons than in alcohol or ether. The oximes of diketones, phenylhydroxamic acid, oximinolævulic acid, and tetramethyldiaminobenzophenoneoxime do not react with thiocarbimides. Resacetophenoneoxime does not react with o-tolylthiocarbimide. The behaviour of α- and β-benzaldoximes, acetaldoxime, heptaldoxime, salicylaldoxime, α- and β-anisaldoxime, and α- and β-furfuraldoxime with phenylthiocarbimide, and, in the first three cases, with *o*- and *p*-tolylthiocarbimides; the reactions of these three thiocarbimides with the oximes of acetone, acetophenone, methyl ethyl ketone, and methyl *iso*butyl ketone, and of phenyl thiocarbimide with those of resacetophenone, benzophenone, methyl *p*-tolyl ketone, methyl propyl ketone, and camphor were also examined. The O-*phenylcarbamates* of methyl ethyl ketoxime (m. p. 135°), diethyl ketoxime (m. p. 96—98°), methyl propyl ketoxime (m. p. 146°), methyl *iso*butyl ketoxime (m. p. 117°), resacetophenoneoxime (m. p. 126°), *p*-tolyl methyl ketoxime (m. p. 112°), and camphoroxime (?) (m. p. 148°) are described, together with the O-*o*-*tolylcarbamates* of methyl ethyl ketoxime (m. p. 80°), acetoxime (m. p. 146—147°), methyl *iso*butyl ketoxime (m. p. 184°), and acetophenoneoxime (m. p. 108—109°), and the O-*p*-*tolylcarbamates* of methyl ethyl ketoxime (m. p. 146—147°), acetoxime (m. p. 105—106°), and acetophenoneoxime (m. p. 126°). R. Brightman.

Relation between rotatory power and structure in sugar group. I. C. S. Hudson (U.S. Bur. Standards Sci. Paper 533, 1926, 21, 241—384).—A summary of the author's earlier work, and a collection of 10 papers published during 1924—1925. A table of the rotatory powers of 104 pure substances examined during the course of the work is given.

H. Burton.

Degradation of *d*-glucose and *d*-α-glucoheptose. G. Zemplén and D. Kiss (Ber., 1927, 60, [*B*], 165—170).—Penta-acetylgluconontrile, m. p. 84°, $[\alpha]_D^{22}$ +46·2° in chloroform, is prepared in 56·8% yield by the action of acetic anhydride and sodium acetate on crude *d*-glucoseoxime freed as far as possible from water. It is converted by sodium methoxide in presence of chloroform into *d*-arabinose in 71·5% yield. Deacetylation of the nitrile previous to degradation causes somewhat poorer yields of *d*-arabinose.

d-α-Glucoheptonolactone is converted by alcoholic ammonia into d-α-*glucoheptonamide*, m. p. 129°, $[\alpha]_D^{22}$ +9·1° in water, which is transformed into its *acetate*, m. p. 165°, $[\alpha]_D^{20}$ +17·4° in chloroform, and thence by phosphoryl chloride into d-α-*hexa-acetylglucoheptononitrile*, m. p. 112·5—113·5°, $[\alpha]_D^{21}$ +24·6° in chloroform; the latter substance is also derived from α-glucoheptose by successive oximation and acetylation. When degraded in the usual manner, it affords dextrose, identified as *d*-β-penta-acetyl glucose.

Penta-acetyl-d-*gluconamide*, m. p. 183·5—184°, $[\alpha]_D^{21\cdot5}$ +20·8° in pyridine, is prepared from the corresponding nitrile by the action of glacial acetic acid and hydrogen bromide. H. Wren.

Deamination of γ-aminohexoses. P. A. Levene and H. Sobotka (J. Biol. Chem., 1926, 71, 181—185).—After deamination of epiglucosamine, and treatment of the resulting solution with phenylhydrazine acetate, there was obtained an *osazone*, m. p. 160°, decomp. 185—190°, $[\alpha]_D^{20}$ −24° to −44°, mutarotating to −8° in methyl alcohol. This osazone appears to be different from that of the γζ-anhydroglucose of Fischer and Zach (A., 1912, i, 239), indicating the possibility that the product of deamination of epiglucosamine is γζ-anhydroallose.

C. R. Harington.

Acetone sugars. XI. Synthesis of a ζ-glucosidogalactose. K. Freudenberg, A. Noë, and E. Knopf (Ber., 1927, 60, [*B*], 238—241; cf. following abstract).—Di*iso*propylidenegalactose is converted by acetobromoglucose and silver oxide in the presence of carbon tetrachloride into *tetra-acetylglucosidodi*iso*propylidenegalactose*, m. p. 141°, $[\alpha]_D^{22}$ −52·6° in *s*-tetrachloroethane, which is hydrolysed by barium hydroxide to *ζ-glucosidodi*iso*propylidenegalactose*, m. p. 84—88°, $[\alpha]_D^{20}$ −67·5° in water. The latter compound is transformed by very dilute acid mainly into *ζ-glucosidogalactose*, $[\alpha]_D^{19}$ +8·2° to +20·6° in water (*osazone*, m. p. 200°).

Amended instructions are given for the preparation of di*iso*propylidenegalactose and acetobromoglucose.

H. Wren.

Acetone sugars. X. γ-Thioglucose. K. Freudenberg and A. Wolf (Ber., 1927, 60, [*B*], 232—238; cf. A., 1926, 601).—Di*iso*propylideneglucose is converted by successive treatment with sodium, carbon disulphide, and methyl iodide into *methyl di*iso*propylideneglucose-γ-xanthate*, b. p. 156—162°/1 mm., m. p. 61°, $[\alpha]_{578}^{16}$ −12·82° in *s*-tetrachloroethane, which is transformed at 290—300° into *methyl di*iso*propylideneglucose-γ-dithiocarbonate*, m. p. 142°, $[\alpha]_{578}^{16}$ −59·91° in *s*-tetrachloroethane. The latter ester is converted by methyl-alcoholic ammonia in the absence of air into methylmercaptan, carbamide, and the non-crystalline *γ-thioglucose di*iso*propylidene ether*, which when treated successively with sodium and methyl iodide affords *γ-methylthioglucose di*iso*propylidene ether*, m. p. 43°, $[\alpha]_{578}^{22}$ −26·5° in *s*-tetrachloroethane. The non-crystalline *γ-methylthioglucose*, obtained by hydrolysis of the di*iso*propylidene ether with dilute sulphuric acid, gives a *tetra-acetate*, m. p. 94°, $[\alpha]_{578}^{21}$ + 24·65° in *s*-tetrachloroethane. *Bisdi*iso*propylideneglucosyl disulphide*, m. p. 163°, $[\alpha]_{578}^{21}$ −330·1° in *s*-tetrachloroethane, is described; it is hydrolysed to *diglucosyl disulphide*, $[\alpha]_{578}^{20}$ +29·85° in water.

In an analogous manner, mannose di*iso*propylidene ether yields *methyl di*iso*propylidenemannosexanthate*, m. p. 80—82°, $[\alpha]_{578}^{16}$ +69·30° in *s*-tetrachloroethane, and the corresponding *thiocarbonate*, m. p. 158—159°. Mannose di*iso*propylidene ether is converted by oxalyl chloride and pyridine in the presence of chloroform into the corresponding *oxalate*, m. p. 138°, $[\alpha]_{578}^{19}$ +83·44° in *s*-tetrachloroethane, which when heated gives small yields of the *carbonate*, m. p. 186—187°. *Methyl di*iso*propylidenegalactosexanthate*, m. p. 162—163°, $[\alpha]_{578}^{16}$ −67·3° in *s*-tetrachloroethane, is described. A modified method is given for the preparation of mannose di*iso*propylidene ether, which is transformed by phosphorus pentachloride into *di*iso*propylidenemannose-α-chlorohydrin*, b. p. 119°/1 mm., $[\alpha]_D^{21}$ + 85·7°. H. Wren.

Constitution of disaccharides. R. Weidenhagen (Z. Ver. Deuts. Zucker-Ind., 1927, 73—85).—An account of recent work on the constitution of disaccharides. H. Burton.

Position of the sugar nucleus in the quercitin glucosides. G. F. Atree and A. G. Perkin (J.C.S., 1927, 234—240).—Rutin (quercetin in union with rutinose), xanthorhamnin (rhamnetin in union with rhamninose) and *iso*quercitrin (quercetin in union with glucose) were methylated with diazomethane and the products hydrolysed, forming, in each case, 5 : 7 : 3′ : 4′-tetramethoxyflavonol. Thus all contain the sugar nucleus in the 3 position. Using less diazomethane, xanthorhamnin yielded a trimethyl ether (?), m. p. 175—178°. Quercimeritrin, on methylation, forms a pentamethyl ether(?), m. p. 203—205° (sinters 197°), which yields, on hydrolysis, 5 : 3 : 3′ : 4′-*tetramethoxyflavonol*, m. p. 284—285° (*acetyl* derivative, m. p. 174—176°); the sugar nucleus in quercimeritrin therefore has the 7 position.

B. W. Anderson.

[Constitution of cellulose.] H. Pringsheim (Annalen, 1927, **451**, 308—312).—Polemical against Schultze and Hess (cf. A., 1926, 942; this vol., 44).

H. E. F. Notton.

Synthesis of γ-ketoalkylamines from β-ketonic acids, amines, and formaldehyde. C. Mannich and K. Curtaz (Arch. Pharm., 1926, **264**, 741—751).—The reaction described by Mannich and Bauroth (A., 1924, i, 947) appears to be general for substituted β-ketonic acids and secondary amines. The yields vary from 40 to 60% of the theoretical. When a primary amine or ammonia is used, a complicated interaction takes place, and the products have not been identified. With unsubstituted β-ketonic acids, both hydrogen atoms of the methylene group may be replaced; acetoacetic acid, for example, yields a mixture of monoamine and diamine, $\mathrm{Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}NR'R''}$ and $\mathrm{Me{\cdot}CO{\cdot}CH[CH_2{\cdot}NR'R'']_2}$.

In these preparations, it is not necessary to isolate the ketonic acid; the potassium salt is obtained in solution by dissolving the ethyl ester in a slight excess of cold 2·5% aqueous potassium hydroxide and keeping the solution for about 2 days. This solution is then exactly neutralised and the amine hydrochloride is added, followed by the formaldehyde. The cold solution is stirred while hydrochloric acid is added to keep it from becoming alkaline; carbon dioxide is evolved. In subsequently isolating the base, sodium hydrogen sulphite is added if necessary, to render inactive any excess of formaldehyde. Ethyl benzylacetoacetate, piperidine, and formaldehyde yield δ-*phenyl-γ-piperidinomethylbutan*-β-*one*, b. p. 180—183°/14 mm. The *hydrochloride*, m. p. 145°, and *oxime hydrochloride*, m. p. 216—217°, are described. When reduced by aluminium amalgam in moist ether, the ketone affords the corresponding *alcohol* (a mixture of stereoisomerides), which has m. p. 62°. The *hydrochloride*, m. p. 187·5°, of the *benzoyl* derivative is an anæsthetic. δ-*Phenyl-γ-diethylaminomethylbutan*-β-*one*, b. p. 157—162°/16 mm., yields a deliquescent *hydrochloride*. The *alcohol* (mixture) has b. p. 164—174°/16 mm.; its *benzoyl* derivative (*hydrochloride*, m. p. 187—190°) possesses pronounced anæsthetic properties. The p-*nitrobenzoyl* derivative (*hydrochloride*, m. p. 191—193°) yields by reduction with hydrogen and palladised charcoal the p-*aminobenzoyl* derivative (*hydrochloride*, m. p. 211—213°), which also is an anæsthetic. γ-*Dimethylaminomethyl*-Δ^{ϵ}-*hexen*-β-*one*, b. p. 75—78°/14 mm., is obtained from allylacetoacetic esters. The salts are deliquescent, with the exception of the *picrate*, m. p. 110°. The *oxime hydrochloride* has m. p. 154°. γ-*Piperidinomethyl*-Δ^{ϵ}-*hexen*-β-*one*, b. p. 121°/12 mm., is somewhat unstable. The *hydrobromide*, m. p. 118°, and *oxime hydrochloride*, m. p. 192—193°, are described. Reduction affords the corresponding *alcohol*, b. p. 131°/13 mm., a mixture, from the crude *benzoyl* derivative, b. p. 208—210° (*hydrochloride*, m. p. about 122°), of which can be separated a purer *hydrochloride*, m. p. 149°, or *hydrobromide*, m. p. 168°. This compound is a strong anæsthetic. γ-*Dipropylaminomethylpentan*-β-*one* has b. p. 119—120° (*chloroaurate* and *oxime hydrochloride*, m. p. 155°). γ-*Piperidinomethylbutan*-β-*one* has b. p. 101—102°/13 mm. (*hydrochloride*, very hygroscopic, m. p. 146°; *picrate*, m. p. 128°). γ-*Dimethylaminomethylbutan*-β-*one*, b. p. 56—58°/15 mm. (*chloroaurate*, m. p. 102°; *picrate*, m. p. 135°), is the parent of "Tutocaine." When dimethylammonium acetoacetate interacts with formaldehyde, the product consists of δ-dimethylaminobutan-β-one and δ-*dimethylamino-γ-dimethylaminomethylbutan*-β-*one*, b. p. 85—90°/12 mm. (*picrate*, m. p. 136·5°; *chloroplatinate*, m. p. 181°), in almost equal amounts. ω-Piperidinopropiophenone (Mannich and Lammerling, A., 1923, i, 43) and ω-dimethylaminopropiophenone (Mannich and Heilner, *ibid.*, 1922, i, 351) are obtained when the appropriate amine benzoylacetate is treated with formaldehyde.

W. A. Silvester.

Imide chlorides and imide bromides of aliphatic acids. I. J. von Braun, F. Jostes, and A. Heymons (Ber., 1927, **60**, [*B*], 92—102).—The statement that the imide chlorides of aliphatic acids are readily transformed by loss of hydrogen chloride into complex bases is too general, since the compounds derived from di- and tri-chloroacetethylamide are relatively or completely stable at high temperatures. The base, $C_{16}H_{15}N_2Cl$, obtained from acetphenylimide chloride, is identified as *diphenylchlorovinylacetamidine*, $\mathrm{NPh{:}CMe{\cdot}NPh{\cdot}CCl{:}CH_2}$, since when catalytically reduced it passes into diphenylethylacetamidine, b. p. 189—192°/15 mm., characterised by the *picrate*, m. p. 162°, by hydrolysis to acetic acid, aniline, and ethylaniline, and by comparison with the compound obtained from ethylaniline and acetphenylimide chloride (which, contrary to the literature, could not be caused to crystallise). During hydrogenation, acetaldehyde, ethyl alcohol, and aniline are produced in small amount. The production of the compound is attributed to the migration of a hydrogen atom in the chloride, $\mathrm{CH_3{\cdot}CCl{:}NPh \longrightarrow CH_2{:}Cl{\cdot}NHPh}$. This possibility is established on lines similar to those used with acyl bromides. Thus, iso*butyrethylamide*, b. p. 105—107°/14 mm., m. p. 68°, is converted by the successive action of phosphorus pentachloride and bromine into a mixture of the compounds $\mathrm{CMe_2Br{\cdot}CCl{:}NEt}$ and $\mathrm{CMe_2Br{\cdot}CBr{:}NEt}$, from which α-*bromo*iso*butyrethylamide*, m. p. 57°, is derived by the action of water. α-*Bromopropionethylamide*, b. p. 114—115°/16 mm., m. p. 60°, with somewhat greater difficulty gives the expected mixture of chlorinated and brominated compounds from which αα-*dibromo*-

propionethylamide, m. p. 61°, is obtained. Dichloroacetethylamide, after treatment with phosphorus pentachloride, reacts very readily with bromine, giving a mixture of substances from which *dichlorobromoacetethylamide*, m. p. 65—66°, is derived by treatment with warm water. α-Bromo*iso*butyrethylamide, αα-dibromopropionethylamide, and dichlorobromoacetethylamide, which do not contain hydrogen attached to the α-carbon atom, are completely stable to bromine after treatment with phosphorus pentachloride. Similarly, α-*chloro*iso*butyrethylamide*, b. p. 80°/15 mm., m. p. 38—39°, is converted by phosphorus pentachloride into α-*chloro*iso*butyrethylimide chloride*, b. p. 160°/atmos. pressure, which is indifferent to bromine, and *fencholethylamide*, b. p. 152°/11 mm., gives the corresponding stable *imide chloride*, b. p. 109—111°/13 mm. If the ethyl group of dichloroacet-, α-bromopropion-, or *iso*butyr-ethylamide is replaced by a phenyl, tolyl, or naphthyl residue, bromination of the nucleus cannot be avoided during the course of the changes; *dichloroacet*-p-*bromoanilide*, m. p. 147—148°, is incidentally described.

Propionethylamide, b. p. 100°/10 mm., is very readily converted by the successive action of phosphorus pentachloride and bromine (2 mols.) into a mixture of the dibrominated imide chloride and bromide, from which αα-dibromopropionethylamide, m. p. 61°, is derived by action of water; if, however, only 1 mol. of halogen is used and the product is treated with water, an inseparable mixture of propionethylamide and its mono- and di-bromo-derivatives is produced. Somewhat similar difficulties are encountered with acetethylamide; *dibromoacetethylamide*, m. p. 96°, is described. Chloroacetethylamide is converted by treatment with phosphorus pentachloride and bromine (1 mol.), followed by water, into *chlorodibromoacetethylamide*, m. p. 46°. H. Wren.

Structure of hydroxyureas [hydroxycarbamides] and of carbamazides. C. D. Hurd and L. U. Spence (J. Amer. Chem. Soc., 1927, 49, 266—274).—When the aqueous solution of *N*-hydroxy-*N'N'*-diethylcarbamide (cf. Hantzsch and Sauer, A., 1898, i, 171) is treated with benzoyl chloride and alkali, a *product*, m. p. 101—102°, is obtained, which is not the expected benzoyl ester, together with dibenzhydroxamic acid, m. p. 156—157°, and a *product*, m. p. above 270°. *N*-Hydroxy-*N'N'*-diethylcarbamide was obtained as an oil by the action of hydroxylamine on diethylcarbamyl chloride in ethyl acetate solution. When heated at 150—160°/25 mm., it decomposes with formation of a charred residue and an oil which, on distillation with alkali, yields diethylhydrazine, and is therefore probably carbonyldiethylhydrazine, $NEt_2\cdot NCO$, formed by rearrangement of the hydroxydiethylcarbamide. Treatment of the hydroxydiethylcarbamide with excess of cold acetic anhydride affords the *acetyl* derivative as an oil which, on treatment with alkali, yields diethylhydrazine. *Phenylcarbimidediethylhydrazone*, m. p. 125·5—126°, is obtained by the action of diethylhydrazine on phenylcarbimide in dry ether. As carbamazide and hydroxycarbamide and their monosubstituted derivatives, $NHR\cdot CO\cdot N_3$ and $NHR\cdot CO\cdot NH\cdot OH$, do not undergo the rearrangement typical of the $\cdot CO\cdot N_3$ and $\cdot CO\cdot NH\cdot OH$ groups, it is concluded that these compounds have the structures $NR{:}C(OH)\cdot N_3$ and $NR{:}C(OH)\cdot NH\cdot OH$.

F. G. Willson.

Reactions of carbohydrazide. I. A. C. Brown, E. C. Pickering, and F. J. Wilson (J.C.S., 1927, 107—112).—The following were prepared from carbohydrazide and the appropriate ketone or aldehyde: *diacetonecarbohydrazone*, m. p. 156°; *di(methyl ethyl ketone)carbohydrazone*, m. p. 113°; *diacetophenonecarbohydrazone*, m. p. 204°; *acetophenone-δ-aminosemicarbazone*, m. p. 188° (benzaldehyde reacts with this compound to form *benzaldehyde acetophenone carbohydrazone*, m. p. 160°); *benzophenone-δ-aminosemicarbazone*, m. p. 223—224° (decomp.); *benzaldehyde-δ-aminosemicarbazone*, m. p. 173°; *benzilmono-δ-aminosemicarbazone*, m. p. 172—174°; and *diacetylmono-δ-aminosemicarbazone*, m. p. 260°. Acetylacetone and carbohydrazide gave 3 : 5-dimethylpyrazole. Dibenzaldehydecarbohydrazone decomposed in boiling alcoholic solution, giving dibenzaldehydehydrazicarbohydrazone and benzylideneazine; similarly, diacetophenonecarbohydrazone gave *diacetophenonehydrazidicarbohydrazone*, m. p. 239—240°, and phenyl methyl ketazine. When heated without solvent, these carbohydrazones gave 4-aminourazole and azine. Benzaldehyde-δ-aminosemicarbazone in boiling toluene decomposed into hydrazidicarbohydrazide and benzylideneazine, and heated alone above the m. p. it gave 4-aminoaurazole, hydrazine, and benzylideneazine, the first two compounds evidently resulting from the hydrazidicarbohydrazide.

B. W. Anderson.

Complex compound of biuret with copper and nickel. W. Traube and W. Wolff (Ber., 1927, 60, [*B*], 43—50; cf. A., 1922, i, 718).—The following complex *derivatives* of biuret are obtained by evaporating an aqueous solution of the substance, treated with an excess of organic alkali and saturated with copper or nickel hydroxide, in a vacuum over sulphuric acid at the atmospheric temperature. The compounds, when freed from mother-liquor, are generally unstable, absorbing carbon dioxide from the air and depositing the metallic hydroxide:

$[(C_2H_3O_2N_3)Cu](NMe_4)_2,4H_2O$;
$[(C_2H_3O_2N_3)Cu](SEt_3)_2,4H_2O$;
$[(C_2H_3O_2N_3)_2Cu](PEt_4)_2,4H_2O$;
$[(C_2H_3O_2N_3)_2Cu][CH_6N_3]_4,2H_2O$;
$(?)[C_2H_3O_2N_3][Cu(CH_5N_3)_2],2H_2O$;
$[(C_2H_3O_2N_2)_2Cu][Ni\,en_3],4H_2O$;
$[(C_2H_3O_2N_3)_2Cu][Zn\,en_3],4H_2O$;
$[(C_2H_3O_2N_3)_2Cu][Cd\,en_3],4H_2O$;
$[(C_2H_3O_2N_3)_2Cu][Co\,en_3],4H_2O$;
$[(C_2H_3O_2N_3)_2Ni][NMe_4]_2,4H_2O$;
$[(C_2H_3O_2N_3)_2Ni][CH_6N_3]_2,2H_2O$;
$[(C_2H_3O_2N_3)_2Ni][Ni\,en_2],4H_2O$;
$[(C_2H_3O_2N_3)_2Ni][Cd\,en_2],4H_2O$;
$[(C_2H_3O_2N_3)_2Ni][Ag(NH_3)_2]_2,6H_2O$.

H. Wren.

[Thiocyanogen chloride.] H. P. Kaufmann (Ber., 1927, 60, [*B*], 58—59; cf. Kaufmann and Liepe, A., 1924, i, 209).—A reply to Lecher and Joseph (this vol., 46). H. Wren.

Free, crystalline gluconoitrile. G. Zemplén (Ber., 1927, 60, [*B*], 171—173).—*Gluconitrile*, m. p.

about 115—120° (decomp.), $[\alpha]_D^{21}$ +8·8° in water, is prepared by hydrolysing its penta-acetate with aqueous-alcoholic sulphuric acid under definite conditions. Separation of the crystalline substance from solutions shown analytically to contain the greatest quantity of it is not easy, whereas little difficulty is experienced when hydrolysis is continued until about 50% of the nitrile has been transformed into ammonium gluconate. H. WREN.

Prussian blue and complex metallic cyanides. H. REIHLEN and W. ZIMMERMANN (Annalen, 1926, **451**, 75—107).—The properties of a number of complex metallic cyanides and ammonium compounds are reviewed, and the conclusion is reached that the cyanides are better represented as complex polynuclear structures than as salts of hydroferrocyanic acid. Such a conception offers an explanation for the structure, conductivity, colour, and general reactions of the complex cyanides, and for the fundamental difference between these substances and the complex ammonium compounds. Whilst the decomposition of the ammonium compounds would be independent of the nature of the central atom, the formation of polynuclear structures by the complex cyanides will depend on the relative ionic volumes of the metals concerned, and the character of the complex formed will depend on the nature of the central atom. The properties of the complex cyanides seem to be directly opposed to the co-ordination theory of valency. R. W. WEST.

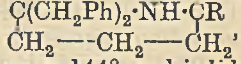
Carbylamines. XV. Reactions with aliphatic carbylamines. M. PASSERINI.—See this vol., 149.

Grignard synthesis of certain organic arsenic derivatives. E. GRYSZKIEWICZ-TROCHIMOWSKI and E. ZAMBRZYCKI (Rocz. Chem., 1926, **6**, 794—803).—Arsenious oxide added to ethereal solutions of various magnesium organic derivatives yields with magnesium aryl salts partly oxidised products, whilst alkyl salts produce trialkylarsines. Thus the following compounds are prepared: diphenylarsine oxide, dibenzylarsenious acid, di-α-naphthylarsine oxide, trimethylarsine, b. p. 48—51°, triethylarsine (whence *chlorodiethylarsine*, b. p. 155°, is prepared), tri-*n*-propylarsine, and *triallylarsine*, b. p. 104°/37 mm. R. TRUSZKOWSKI.

Synthesis of bromovinylarsines. E. SCHMIDT (Bull. Soc. chim., 1927, [iv], **41**, 49—50).—The action of acetylene at 31—35° on a mixture of 2 mols. of aluminium bromide or chloride and 1 mol. of arsenious bromide affords *ββ′β″-tribromotrivinylarsine*, m. p. 65·5—67° (odour of geranium), in addition to the primary and secondary arsines described by Lewis and Stiegler (A., 1925, i, 1470). R. BRIGHTMAN.

Constitution of organo-magnesium derivatives. P. JOLIBOIS (Compt. rend., 1926, **183**, 971—973).—Reasons are stated for adopting the bimolecular formula $MgR_2{\cdot}MgX_2$ for organo-magnesium compounds. The argument is based primarily on the work of Terentjev (A., 1926, 1130). L. F. HEWITT.

Constitution of magnesium organo-compounds. A. JOB and M. DUBIEN (Compt. rend., 1926, **184**, 155—157).—A criticism of the argument advanced by Jolibois (preceding abstract). W. ROBSON.

Reaction of organomagnesium compounds on nitriles. Glutaronitrile and magnesium benzyl chloride. P. BRUYLANTS and A. DEWAEL (Bull. Acad. roy. Belg., 1927, [v], **12**, 464—476).—The action of magnesium benzyl chloride on glutaronitrile yields the *hydrochloride*, m. p. 246° (*chloroplatinate*, decomp. 270°), of the cyclic *base*  $\begin{array}{l}\text{C(CH}_2\text{Ph)}_2\cdot\text{NH}\cdot\text{CR}\\ \text{CH}_2\text{—CH}_2\text{—CH}_2\end{array}$, m. p. 172° (R=NH). The *nitrite*, m. p. 144°, and *iodide* are described. With phenylthiocarbimide, it yields the *phenylthiocarbamate*, m. p. 147—149°. On boiling with 10% sodium hydroxide solution for several hours, the base is converted into the cyclic *amide* (R=O), m. p. 159—160°, which does not exhibit basic properties, but when treated in alcohol-ether solution with dry hydrogen chloride gives a *hydrochloride*, m. p. 205—207° (decomp.), completely hydrolysed in aqueous solution. When heated with excess of fuming hydrochloric acid in a sealed tube at 170° for 6 hrs., the amide yields a small quantity of a *hydrochloride*, m. p. 193°, probably derived from the corresponding open-chain amino-acid; on treatment with ammonia, the original lactam is regenerated. J. W. BAKER.

Action of organomagnesium compounds on *cyclo*heptene oxide. M. GODCHOT and P. BEDOS (Compt. rend., 1927, **184**, 208—210).—*cyclo*Heptene oxide (cf. Böeseken and Derx, A., 1921, i, 663), when treated with magnesium methyl iodide, yields 1-methyl*cyclo*heptan-1-ol, identical with the product obtained from suberone itself. The seven-ring oxide therefore behaves differently from the analogous five- and six-ring compounds (cf. Godchot and Bédos, *ibid.*, 1922, i, 334), isomerisation to *cyclo*heptanone preceding the addition of the Grignard reagent. J. W. BAKER.

Organometallic derivative of gold. A. LUMIÈRE and F. PERRIN (Compt. rend., 1927, **184**, 289—291).—Addition of a concentrated solution of gold chloride to sodium thiopropanolsulphonate yields the amorphous *gold* salt, $CH_2SAu{\cdot}CH(OH){\cdot}CH_2{\cdot}SO_3Na$, which is stable in 2% aqueous solution and has but feeble toxicity. Hence intramuscular injections are free from the disadvantages which accompany the use of sodium gold thiosulphate. J. W. BAKER.

Optical activity and the polarity of substituent groups. VI. Optically active acids and bases. H. G. RULE (J.C.S., 1927, 54—59).—In the polar series corresponding with the relative influence of substituents on benzene substitution and the rotatory power of optically active compounds, the ionic complex $-NH_3^{\bullet}$ ranges itself with the positive substituents, and the complex $-CO{\cdot}O'$ with the negative substituents. The polar influence may be intramolecular, and sudden changes of activity may take place as the chain attached to the asymmetric atom attains a length of 5, 10, or 15 atoms, due to the close proximity of the end of the chain to the asymmetric atom. Further, the influence of polar groups on neighbouring molecules leads to changes in rotatory power. B. W. ANDERSON.

Nitration of decahydronaphthalene. S. S. Nametkin and O. S. Madajeva-Sitscheva (J. Russ. Phys. Chem. Soc., 1926, 57, 382—389).—Decahydronaphthalene is slowly converted by boiling nitric acid (d 1·2) into tert.-*nitrodecahydronaphthalene*, b. p. 96—97°/2 mm., d_4^{20} 1·0847, n_D^{20} 1·4944; from the residue, after the fractionation of the tertiary decahydronaphthalene, crystals of *dinitrodecahydronaphthalene*, m. p. 164°, are obtained. The tertiary nitro-compound is reduced with zinc and acetic acid to the corresponding *amine*, b. p. 98°/15 mm., d_4^{20} 0·9435, n_D^{20} 1·4932, *benzoyl* derivative, m. p. 148—149°. The hydrochloride when boiled for 24 hrs. with potassium nitrite yields an *octahydronaphthalene*, b. p. 88—89°/1·4 mm., d_4^{20} 0·9200, n_D^{20} 1·4979, the residue from which yields tert.-*decahydronaphthol*, m. p. 65°. α-*Nitrodecahydronaphthalene*, b. p. 108—109°/14 mm., d_4^{20} 1·0815, n_D^{20} 1·4978, yields on oxidation α-decahydronaphthalone. E. Rothstein.

Reduction of nitro-compounds with iron and soluble chlorides. R. E. Lyons and L. T. Smith (Ber., 1927, 60, [*B*], 173—182).—Sodium chloride or ferric chloride may replace hydrochloric acid in the reduction of nitrobenzene, *p*-nitrotoluene, *m*-dinitrobenzene, *p*-nitrophenol, or picric acid to the corresponding amines or nitroamines by iron. Only a small proportion of the salts is necessary (1·672—2·675 g. of ferric chloride or 1·523—2·9 g. of sodium chloride for 100 g. of nitro-compound). Amines are obtained in 95—100% yield from nitrobenzene, *p*-nitrotoluene, and *m*-dinitrobenzene when the concentration of chlorine as ferric or sodium chloride lies between 0·0183 and 0·035 g. per c.c. of solution. Theoretical yields of amine are obtained from *p*-nitrophenol or picric acid when the corresponding concentrations are 0·009. Iron passed through an 80-mesh sieve gives the best results with reduction extending over a short period; coarser iron is correspondingly less active. Under similar conditions, the activity of sodium chloride is 84% of that of ferric chloride. *p*-Nitrophenol and picric acid are much more readily reduced by iron in presence of the salts named than are nitrobenzene, *p*-nitrotoluene, or *m*-dinitrobenzene. Picric acid is reduced by iron alone. The presence of a hydroxyl group in the *p*-position greatly diminishes the resistance of the nitro-group towards reducing agents. H. Wren.

Additive products of sulphur dioxide and aromatic hydrocarbons. I. II. F. de Carli (Atti R. Accad. Lincei, 1926, [vi], 4, 460—466, 523—530; cf. A., 1926, 944).—I. Sulphur dioxide forms with toluene the *compounds*, $C_6H_5Me,2SO_2$, m. p. −85·5°, and $C_6H_5Me,3SO_2$, m. p. −80°. The f.-p. curve for the system mesitylene–sulphur dioxide exhibits two eutectics, at −72·5° and −76·5°, corresponding with 10% and about 90% SO_2, and a maximum, −49·4°, corresponding with the compound $C_6H_3Me_3,SO_2$. The isomeric *compound* with ψ-cumene has m. p. −60°, and the system shows two eutectics, at −71° and −82°, corresponding with 15% and 68% SO_2, respectively.

II. Sulphur dioxide forms the following additive *compounds*. With ethylbenzene, C_8H_{10},SO_2, m. p. −91°, and $C_8H_{10},2SO_2$, m. p. −78·5°; the system exhibits two eutectics, at −93° (60% SO_2) and −82·5° (about 42% SO_2). With cymene, $C_{10}H_{14},SO_2$, m. p. −89°, $C_{10}H_{14},2SO_2$, m. p. −83°. With tetrahydronaphthalene, $C_{10}H_{12},SO_2$, m. p. −58°, $C_{10}H_{12},2SO_2$, m. p. −66·2°, and $C_{10}H_{12},3SO_2$, m. p. −70°; two eutectics exist, at −64·5° and −76·5°, respectively. T. H. Pope.

Two forms of cobaltous β-naphthalenesulphonate. W. Biltz and E. Birk (Z. anorg. Chem., 1926, 159, 125—128).—Cobaltous β-naphthalenesulphonate hexahydrate gives rise to two forms of the anhydrous salt depending on the method of dehydration: a rose-coloured (α-) form by direct and rapid dehydration at 130—150° in an air-oven, also a blue (β-) form which is the result of slow dehydration by way of the monohydrate. These forms differ in their optical and crystallographic properties. The α-modification is the more stable form. M. Carlton.

Fluorene series. C. Courtot and C. Vignati (Bull. Soc. chim., 1927, [iv], 41, 58—64).—Repeated crystallisation from 90% alcohol raises the m. p. of 2-bromofluorene, prepared by Matthews and Hodgkinson's method (J.C.S., 1883, 43, 163), to 111·5°; dibromofluorene, m. p. 162—163°, has been isolated from the mother-liquors. Diels' 2-aminofluorene (A., 1901, i, 521) with the diazo-reaction affords the same 2-bromofluorene; the reverse transformation is effected with ammonia and cuprous chloride at 180°. On oxidation, 2-bromofluorene affords 2-bromofluorenone, m. p. 142—143° (oxime, m. p. 194—195°), identical with the bromofluorenone, m. p. 134°, obtained by Schmidt and Bauer (*ibid.*, 1906, i, 28). The halogen therefore enters the same position, whether introduced in the fluorene or the fluorenone molecule. Aqueous ammonia in the presence of cuprous chloride at 200° converts 2-bromofluorenone into the aminofluorenone obtained by Diels (*loc. cit.*) from 2-nitrofluorene. On hydrogenation, 2-bromofluorenone affords 2-*bromofluorenol*, m. p. 129—130°, the product, m. p. 101—102°, obtained, but not analysed, by Schmidt and Bauer (*loc. cit.*) being 9-*chloro*-2-*bromofluorene*; the latter is formed on warming the fluorenol with hydrochloric acid. Nitration of 2-bromofluorene with nitric and acetic acids at 100° affords 2-*bromo*-7(?)-*nitrofluorene*, m. p. 236°, reduced by zinc and alcoholic ammonia to 2-*bromo*-7(?)-*aminofluorene*, m. p. 146°. Oxidation of the bromonitrofluorene affords a bromonitrofluorenone, m. p. 230° (oxime, m. p. 249°), identical with that described by Schmidt and Bauer (*loc. cit.*) and regarded by them as 2-bromo-7-nitrofluorenone. Hydrogen sulphide in alcoholic ammonia converts this bromonitrofluorenone into 2-*bromo*-7(?)-*aminofluorenone*, brownish-red, m. p. 233—234°; with zinc dust the pale yellow 2-*bromo*-7(?)-*aminofluorenol*, m. p. 186—187°, is obtained. R. Brightman.

Coloured hydrocarbons. II. Synthesis of ketones, carbinols, hydrocarbons, and halogen derivatives of the fluorenes. A. A. Vanscheidt (J. Russ. Phys. Chem. Soc., 1926, 58, 55—68; cf. this vol., 140).—The ketones can be regarded as the starting points for the syntheses of the whole series. They can often be obtained from the hydrocarbons, however; thus chrysofluorenone is obtained by the oxidation and subsequent distillation with lead oxide of chrysene, whilst di-α-naphthafluorenone is formed in 90% yield by the agitation in air of an acetone solution of the hydrocarbon in the presence of alcoholic potassium hydroxide, m. p. 272° (cf. Schmidlin and Huber, A., 1910, i, 833, impure, 255°). The carbinols are obtained from the ketones by the action of zinc dust in boiling glacial acetic acid. The di-α-naphthafluorenol has m. p. 265° (decomp.), 20° higher than found by Tschitschibabin. Alkaline reduction results largely in autoxidation. The halogen derivatives (or "*meso*halofluorenes") can, with the exception of the iodides, be prepared by Staudinger's method (A., 1906, i, 824) by the action of halogen acid on an acetic acid solution of the carbinol. The following new compounds were synthesised: *chrysofluorenyl chloride*, $\genfrac{}{}{0pt}{}{C_6H_4}{C_{10}H_6}\!>\!CHCl$, m. p. 146° (decomp.); *bromide*, m. p. 142° (decomp.); *di-α-naphthafluorenyl chloride*, $\genfrac{}{}{0pt}{}{C_{10}H_6}{C_{10}H_6}\!>\!CHCl$, m. p. 224°, *bromide*, m. p. 234°. The iodides were obtained by double decomposition in acetone solution of the bromo-compounds with sodium iodide. *Fluorenyl iodide* decomposes at 98° with evolution of iodine; *chrysofluorenyl iodide*, decomp. 130°; *di-α-naphthafluorenyl iodide*, decomp. 160°. The chlorides and bromides decompose on fusion, with formation of the coloured hydrocarbons and evolution of halogen acid: $2{<}Ar_2{>}CHX \longrightarrow {<}Ar_2C{:}CAr_2{>}$. They all dissolve in sulphuric acid, giving blue solutions for the chrysofluorenes, and green for the others, probably due to halochromism: ${<}Ar_2CHX+H_2SO_4 \rightleftharpoons {<}Ar_2CH{\cdot}SO_3H+HX$. They are coloured, the chloride lemon-yellow, bromide yellow, and iodide orange. The colour deepens with the introduction of naphthalene nuclei. By the action of hydrogen iodide on the carbinols in glacial acetic acid and boiling, instead of the iodide, the hydrocarbon is formed quantitatively and with great ease. This simple method seems never to have been previously employed. M. Zvegintzov.

Arylamine salts of some sulphonic acids of the benzene series. II. *m*-Nitrobenzenesulphonic acid. C. M. Keyworth (J.S.C.I., 1927, 46, 20T).—The preparation of *m*-nitrobenzenesulphonic acid is briefly discussed. The arylamine salts of *m*-nitrobenzenesulphonic acid are similar in properties to those of benzenemonosulphonic acid, except that they are much less soluble in water. They are also much less soluble in water than the inorganic salts of *m*-nitrobenzenesulphonic acid. The benzidine salt is very sparingly soluble and may be used for determining *m*-nitrobenzenesulphonic acid in absence of sulphuric acid or sulphates. A table is given showing the principal properties of the commoner arylamine salts, together with a comparison of the corresponding salts of benzenesulphonic acid. The m. p. of the m-*nitrobenzenesulphonates* prepared are: aniline, 222°; *o*-toluidine, 193°; *m*-toluidine, 195°; *p*-toluidine, 222°; α-naphthylamine, 221°; β-naphthylamine, 250°; benzidine and tolidine, above 300°; dianisidine, 279—281°; *m*-xylidine, 185°; *o*-chloroaniline, 204°; *p*-chloroaniline, 234°.

Complex-isomerism. E. Hertel and J. Mischnat (Annalen, 1926, **451**, 179—208).—Existing data are reviewed and it is shown that the predictions of Pfeiffer ("Organische Molekülverbindungen," 1922, 226) are fulfilled with regard to the existence of two types of additive compounds of aromatic substances with polynitrophenols. With picric acid and an aromatic amine, type I is the "true picrate" in which the hydroxylic hydrogen atom is united by a subsidiary valency to the basic nitrogen atom, and in type II the subsidiary valency of the nitro-groups of picric acid is saturated by the residual valency field of the aromatic nucleus of the base, $OH{\cdot}C_6H_2(NO_2)_3 \ldots\ldots R{\cdot}NH_2$. With a strong phenol (picric acid) and a strong base (α-naphthylamine), only type I is obtained, whilst weak components (2 : 6-dinitrophenol and 2 : 4-dichloro-α-naphthylamine) yield only type II. Between these limits, it is possible with suitable components (2 : 6-dinitrophenol and 4-bromo-α-naphthylamine) to obtain both types of the additive compound. Type I compounds are much lighter in colour and of lower m. p. than the type II isomerides. Hydroxyl groups in the *o*-position to the nitro-groups have a deepening effect on the colour of the type II compounds, the colour of molecular compounds with picric acid being darker than those with trinitrobenzene, although the m. p. of the two series of compounds are of the same order.

Although in general type I is the stable isomeride (cf. Skraup and Eisemann, A., 1926, 999), it sometimes happens, as with 1 : 6-dibromo-β-naphthylamine picrate, that type I is obtained only at low temperatures and readily passes into type II, which is stable at all temperatures from 0° to its m. p. In the system 4-bromo-α-naphthylamine–2 : 6-dinitrophenol the compound of type I is stable, whilst II is unstable and decomposes rapidly into its components on being isolated, but may be preserved under its solution in bromobenzene.

Comprehensive tables are included illustrating the difference in colour and m. p. of the two types of molecular compounds. R. W. West.

Acetylation of aniline in anhydrous glycerol. E. Sakellarios (Ber., 1927, 60, [*B*], 218—219; cf. Gasopoulos, A., 1926, 1131).—The use of glycerol in the acetylation of aniline with glacial acetic acid is disadvantageous, since a portion of the acid is consumed in converting the glycerol into acetin and the liberated water dilutes the acid. The disadvantage is more pronounced in the case of *o*-toluidine. A 50% economy of acid is effected by addition of xylene. Aniline is converted into acetanilide by monoacetin at 200°, but not to an appreciable extent at 130°. H. Wren.

Sulphonation of *o*-toluidine and preparation of sodium 6-chloro-5-nitro-*m*-toluenesulphonate. M. N. Schultz and H. J. Lucas (J. Amer. Chem. Soc., 1927, 49, 298—302).—Sulphonation of *o*-toluidine to the 5-sulphonic acid is best effected by heating the base with 2 mols. of fuming sulphuric acid (20% SO_3) for 10 hrs. at 180° (yield, 77%). The presence of iodine is detrimental, as it increases charring (cf. Rây and Dey, J.C.S., 1920, **117**, 1405). Treatment of the diazotised sulphonic acid with cuprous chloride gives a 98·2% yield of 6-chloro-*m*-toluenesulphonic acid, most of which separates out direct, the remainder being obtained on evaporating the solution, removal of copper being unnecessary (cf. Davies, *ibid.*, 1922, **121**, 785). Treatment of the dried sulphonic acid with phosphorus pentachloride affords the sulphochloride in 85% yield, nitration of which according to Davies' method (*loc. cit.*) gives a 75% yield of the 5-nitro-derivative. Subsequent hydrolysis to sodium 6-chloro-5-nitro-*m*-toluenesulphonate, also by Davies' method, gives a yield of 80%. F. G. Willson.

M. p. of pure *s*-*p*-bromophenyl-*n*-hexylthiocarbamide. R. F. Hunter and C. Soyka (Chem. News, 1927, **134**, 13).—The m. p. of *s*-*p*-bromophenyl-*n*-hexylthiocarbamide was erroneously given in a recent paper (cf. this vol., 263) as 189°. The correct m. p. is 106°. W. J. Powell.

Rearrangement of alkylanilines. W. J. Hickinbottom (J.C.S., 1927, 64—67; cf. *ibid.*, 1920, **117**, 103).—Ethyl- and butyl-anilines, when heated at 220—290° in open tubes in presence of cobalt, zinc, cadmium, or manganese chlorides, silver sulphate, or copper phosphate, rearrange, giving *p*-aminoethyl- and *p*-aminobutyl-benzenes. The presence of water has no effect on the change. Ethylaniline hydrochloride heated at 220—290° gave chiefly aniline, with a small amount of an unidentified amine, whereas dry butylaniline hydrochloride gave *p*-amino-*n*-butylbenzene. These results do not support the view that the reaction takes place with intermediate formation of alkyl chloride, according to the scheme: $2NHR{\cdot}C_6H_5+MCl_2+H_2O \longrightarrow 2RCl+2C_6H_5{\cdot}NH_2+MO \longrightarrow 2R{\cdot}C_6H_4{\cdot}NH_2+MCl_2+H_2O$. H. Burton.

Alternating effect in carbon chains. XI. Substitution of benzylamine salts. J. W. Baker and C. K. Ingold (J.C.S., 1927, 261—264; cf. A., 1926, 1131).—Nitration of (*a*) α-phenylethylamine, (*b*) α-phenyl*iso*propylamine, (*c*) α-nitro-α-phenylethane, gave the following amounts of *meta*-substituted product: (*a*) 40%, (*b*) 26%, (*c*) 43%. These results are in agreement with those previously obtained (*loc. cit.*), confirming the view that phenylnitromethane derivatives are nitrated in the *meta*-position to approximately the same extent as substituted benzylamines. H. Burton.

Alternating effect in carbon chains. X. Nitration of some derivatives of β-phenylethylamine. F. R. Goss, W. Hanhart, and C. K. Ingold (J.C.S., 1927, 250—261; cf. A., 1926, 1132).—Nitration of (*a*) β-phenylethylamine, (*b*) methyl-β-phenylethylamine, (*c*) dimethyl-β-phenylethylamine picrate, (*d*) trimethyl-β-phenylethylammonium picrate, gives the following amounts of *m*-nitro-derivative, isolated as a suitable salt, or by oxidation to the corresponding nitrobenzoic acids with subsequent analysis: (*a*) 12%, (*b*) 15%, (*c*) 13%, (*d*) 19%. Nitration of *trimethylbenzylammonium picrate*, m. p. 168—169°, yields 88% of the *m*-nitro-derivative. These results show that the directive effect of an ionic centre situated in a side-chain of saturated carbon atoms does not alternate, but diminishes with increasing distance from the nucleus. The following salts have been isolated during the investigation: β-o-*nitrophenylethylammonium chloride*, m. p. 162—163°; β-m-*nitrophenylethylammonium oxalate*, m. p. 200° (decomp.), and *chloride*, m. p. 204—205°; *dimethyl*-β-o-*nitrophenylethylammonium picrate*, m. p. 160—161°; *dimethyl*-β-m-*nitrophenylethylammonium oxalate*, m. p. 186°, and *picrate*, m. p. 166—167°; *dimethyl*-β-p-*nitrophenylethylammonium picrate*, m. p. 162°; *trimethyl*-β-o-*nitrophenylethylammonium picrate*, m. p. 146—147°; *trimethyl*-β-m-*nitrophenylethylammonium picrate*, m. p. 147—148°; *trimethyl*-β-p-*nitrophenylethylammonium iodide*, m. p. 206°, and *picrate*, m. p. 144—145°; m-*nitrobenzyltrimethylammonium picrate*, m. p. 180—180·5°; and p-*nitrobenzyltrimethylammonium picrate*, m. p. 194°. The quaternary ammonium picrates were made usually by treating the tertiary base with a solution of trinitroanisole. H. Burton.

Preparation of α-naphthylthiocarbimide from α-naphthylamine and thiocarbonyl chloride. G. Dyson and R. F. Hunter (Chem. News, 1927, **134**, 4—5).—See A., 1926, 718.

Substitution products of 2-aminodiphenyl. H. A. Scarborough and W. A. Waters (J.C.S., 1927, 89—97).—2-Nitrodiphenyl on reduction with tin and hydrochloric acid (cf. Blanksma, A., 1906, i, 345) gives 5-chloro-2-aminodiphenyl (60%) and 2-aminodiphenyl (cf. Hübner, *ibid.*, 1882, 180). Chlorination of 2-aminodiphenyl in carbon tetrachloride solution yields 3 : 5-*dichloro*-2-*aminodiphenyl hydrochloride*, m. p. 140—145° (all m. p. are corr.). 3 : 5-*Dichloro*-2-*aminodiphenyl*, m. p. 51° (*benzoyl* derivative, m. p. 207°), on deamination gives 3 : 5-*dichlorodiphenyl*, b. p. 180°/15 mm. Sodium hypochlorite converts 2-acetamidodiphenyl into N-*chloro*-2-*acetamidodiphenyl*, m. p. 86°, which when treated with acetic acid gives a mixture of substances. Further treatment of this mixture with sodium hypochlorite followed by acetic acid gives 5-*chloro*-2-*acetamidodiphenyl*, m. p. 122·5° (*benzamido*-derivative, m. p. 142—143°). 2 : 5-*Dichlorodiphenyl* has b. p. 171°/15 mm. Monobromination of 2-aminodiphenyl in carbon tetrachloride furnishes 5-*bromo*-2-*aminodiphenyl hydrobromide*, m. p. 226°, whilst dibromination in acetic acid in presence of sodium acetate gives 3 : 5-*dibromo*-2-*aminodiphenyl*, m. p. 51—52° (*benzoyl* derivative, m. p. 218°). Deamination of this base yields 3 : 5-dibromodiphenyl, b. p. 208°/15 mm. 2-Acetamidodiphenyl furnishes 5-*bromo*-2-*acetamidodiphenyl*, m. p. 130°, which on hydrolysis with alcoholic hydrobromic acid gives 5-*bromo*-2-*aminodiphenyl*, m. p. 57·5° (*benzoyl* derivative, m. p. 162°). 2 : 5-*Dibromodiphenyl* has b. p. 209°/15 mm. *N*-Bromo-2-acetamidodiphenyl was not obtained pure, and the crude substance on treatment with acetic acid gives 5-bromo-2-acetamidodiphenyl and 2-acetamidodiphenyl.

Nitration of the last substance gives 4′-*nitro*-2-*acetamidodiphenyl*, m. p. 199°, and 5(or 3) : 4′-*dinitro*-2-*acetamidodiphenyl*, m. p. 211°. Hydrolysis of these compounds furnishes 4′-*nitro*-2-*aminodiphenyl*, m. p. 158°, and 5(or 3) : 4′-*dinitro*-2-*aminodiphenyl*, m. p. 238°, deamination of the latter giving 3 : 4′-dinitrodiphenyl. 2-*Bromo*-4′-*nitrodiphenyl*, m. p. 82·5°, on oxidation with chromic acid gives *p*-nitrobenzoic acid, whilst oxidation of the dihalogenodiphenyls gives the dihalogenobenzoic acids. H. BURTON.

Occurrence of free radicals in chemical reactions. V. H. WIELAND, A. HINTERMAIER, and I. DENNSTEDT [with J. LORENZO] (Annalen, 1927, 452, 1—34; cf. A., 1926, 61).—p-*Phenylbenzoyl chloride*, m. p. 113°, gives with hydrazine s-*di*-p-*phenylbenzoylhydrazine*, m. p. 260—270° (decomp.), but *ethyl* p-*phenylbenzoate*, m. p. 46°, b. p. 178°/10 mm., gives p-*phenylbenzhydrazide*, m. p. 189°. This condenses with triphenylmethyl chloride to give p-*phenylbenzoylhydrazotriphenylmethane*, m. p. 183° (decomp.). The p-*phenylbenzoylazotriphenylmethane*, m. p. 82° (decomp.), obtained from this by oxidation is very unstable, decomposing to p-*phenylbenzoyltriphenylmethane*, m. p. 178°, or in a stream of oxygen to *p*-phenylbenzoic acid and triphenylmethyl peroxide, which is also obtained from all the azo-compounds mentioned below.

Acetylazotriphenylmethane decomposes vigorously at 70°, or in xylene at 40°, to *acetyltriphenylmethane*; in oxygen to diacetyl peroxide. iso*Butyrylazotriphenylmethane*, m. p. 60—61° (decomp.), obtained from the *hydrazo*-compound, m. p. 170—172°, by the action of hypochlorous acid (potassium ferricyanide or bromine in chloroform having no action), is extremely unstable, evolving nitrogen from a chloroform solution at $-7°$. In oxygen, *diisobutyryl peroxide* is obtained; in nitrogen a syrup, from which, by distillation, triphenylmethane, and, by aërial oxidation, *iso*butyric acid are obtained. The pinacolin (*iso*butyryltriphenylmethane) cannot be isolated, nor can it be obtained from magnesium triphenylmethyl chloride and an alkyl *iso*butyrate. Pivalyl chloride gives with hydrazine *dipivalylhydrazine*, but by heating ethyl pivalate with hydrazine hydrate at 140°, *trimethylacethydrazide*, m. p. 65°, b. p. 113°/12 mm., is obtained; *trimethylacetylazotriphenylmethane*, m. p. 71° (decomp.), obtained from the *hydrazo*-compound, m. p. 123°, decomposes readily, evolving nitrogen and carbon monoxide to form ααα-triphenyl-ββ-dimethylpropane, m. p. 189·5°; in oxygen, *tert.*-butyl peroxide is formed.

The above three acylazotriphenylmethanes show during decomposition in an indifferent solvent the carmine-red colour associated with free acyl radicals. The *iso*butyryl compound on decomposition gives in ether an intense red colour, which fades on cooling and reappears on warming again, indicating an association and deassociation of free radicals. An ethereal solution of the trimethylacetyl compound shows an absorption spectrum with two bands between 580 and 590 μμ, as well as the triphenylmethyl band at 520 μμ.

Phenylacetylazotriphenylmethane, m. p. 68° (decomp.), obtained from the *hydrazo*-compound, m. p. 181—183° (decomp.), forms moderately stable yellow crystals, but in light petroleum solution turns red and then yellow, forming *as*-tetraphenylethane; with oxygen, the peroxide of phenylacetic acid is formed. *Diphenylacetylazotriphenylmethane*, m. p. 76° (decomp.), is obtained by oxidation of the *hydrazo*-compound, m. p. 184—186° (decomp.), by calcium hypochlorite (potassium ferricyanide not reacting); it decomposes much more slowly than the phenylacetyl compound, giving a solution with an absorption band at 580 μμ, and evolving 70% of the theoretical carbon monoxide to give pentaphenylethane, with some pentaphenylacetone, isolated only from the product of decomposition in oxygen. *Triphenylacethydrazide*, m. p. 196° (decomp.), formed, with some *bistriphenylacetylhydrazine*, decomp. 253°, from the acid chloride, gives, with triphenylmethyl chloride, *triphenylacetylhydrazotriphenylmethane*, m. p. 170—172° (decomp.), oxidised by calcium hypochlorite to the *azo*-compound, which decomposes at 53—54°, or immediately in solution, giving carbon monoxide and triphenylmethyl, which when shaken with air or oxygen gives its peroxide. The triphenylacetyl radical is thus very unstable, and no hexaphenylacetone is formed. An attempt to obtain this by another method has also failed. Carbohydrazide with triphenylmethyl chloride gives s-*bistriphenylcarbohydrazide*, m. p. 178—181° (decomp.), after drying in a vacuum, 200—202°, which is oxidised by bromine water to *bis*-ββ′-*triphenylmethylcarbazone*, $CPh_3\cdot NH\cdot NH\cdot CO\cdot N{:}N\cdot CPh_3$, m. p. 96—97° (decomp.). This cannot be oxidised to the bisazo-compound, decomposition always occurring. It is the most stable of these azo-compounds, not decomposing in petroleum until heated to 80°, when the orange colour of triphenylmethyl is observed, and triphenylacetylhydrazotriphenylmethane (see above) is obtained. *Triphenylmethylsemicarbazide*, m. p. 190—192°, when oxidised by bromine water, gives *triphenylmethylazoformamide*, $CPh_3\cdot N{:}N\cdot CO\cdot NH_2$, m. p. 200—225° (decomp.), which decomposes in solution to triphenylacetamide; in oxygen, no peroxide, $[NH_2\cdot CO\cdot]_2O$, can be obtained. *Triphenylmethylhydrazoformanilide*, m. p. 198° (decomp.), is not sufficiently soluble to be oxidised.

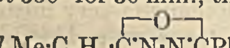
Benzenesulphonazotriphenylmethane is not obtainable: the *hydrazo*-compound decomposes on oxidation, giving *benzenesulphontriphenylmethane*; the dibenzenesulphonylhydrazine also decomposes, giving diphenylsulphone.

The hydrazo-compound from benzylhydrazine and triphenylmethyl chloride cannot be isolated, undergoing autoxidation in air to *as*-tetraphenylethane; it is concluded that benzylazotriphenylmethane is very unstable. p-*Anisylhydrazotriphenylmethane*, m. p. 114° (decomp.), is also very susceptible to autoxidation; it yields the *azo*-compound, m. p. 114° (decomp.), which decomposes in xylene at 70—80° to a product from which no *p*-methoxytetraphenylmethane can be isolated, but only triphenylmethane. E. W. WIGNALL.

Metallic derivatives of *o*-amino- and *o*-hydroxy-azo-compounds. G. CHARRIER and A. BERETTA [with I. PAPPOFF] (Gazzetta, 1926, 56, 865—871).—Cupric, nickelous, and cobaltous ammonium hydroxides react with *o*-amino- and *o*-hydroxy-azo-compounds to give crystalline compounds, which were at first thought to be salts in which the azo-compound had replaced the ammonia, but which proved to have the general formula $M[Az]_2$, where M is the metal and Az the azo-compound. These compounds, especially those of copper, are readily converted on heating into triazoles, and may be intermediate products in the formation of the latter by way of metal ammonia derivatives. They are stable to alkali, but are decomposed by acid. The following are described: *Copper bisbenzeneazo*-β-*naphthylamine*, red, m. p. about 130°, soluble in benzene, and the corresponding *nickel*, green, m. p. 260—265° (decomp.), and *cobalt*, dark brown, sinters 215—220°, m. p. about 265°, compounds; *copper bis*-o-*tolueneazo*-β-*naphthylamine*, decomp. below m. p.; *copper bisbenzeneazo*-β-*naphthol*, m. p. about 278°, and the corresponding *nickel* and *cobalt* compounds, which decompose below m. p.; *copper bis*-p-*tolueneazo*-β-*naphthol*, m. p. 285—290° (decomp.), and the corresponding *nickel* compound. E. W. WIGNALL.

Spectrochemical studies of hydroxyazo-compounds. I. T. UEMURA, N. YOKOJIMA, and C. TAN (Bull. Chem. Soc. Japan, 1926, **1**, 260—266).—The relation between the colour and constitution of hydroxyazo-compounds has been studied spectrochemically. The colour change from yellow, through red, to bluish-violet, observed on addition of alkali to *p*-nitrobenzeneazo-β-naphthol, and considered by Suitsu and Okuma (J. Soc. Chem. Ind. Japan, 1926, **29**, 132) to be due to the azo-, mono- and diquinonoid forms, respectively, has now been observed in simpler compounds.

p-Hydroxyazobenzene, benzeneazoresorcinol, benzeneazo-*p*-cresol, *p*-nitrobenzeneazophenol, and *m*-nitrobenzeneazoresorcinol all show the first colour change on addition of alkali, whilst the violet diquinonoid forms of *p*-nitrobenzeneazoresorcinol and *p*-nitrobenzeneazo-*p*-cresol are obtained on further addition of alkali. These results are in agreement with the curves obtained by plotting the oscillation frequencies against the relative thicknesses of 0·0001*N*-solutions of the hydroxyazo-compounds. A. S. CORBET.

Molecular rearrangement of some new unsymmetrical hydrazines. E. C. GILBERT (J. Amer. Chem. Soc., 1927, **49**, 286—292).—α-*Benzoyl*-β-p-*toluoylhydrazine*, m. p. 220—221°, is obtained by the action of *p*-toluoyl chloride on benzoylhydrazine in suspension in benzene. When heated at 450° for 5 min., it yields a mixture of aniline (80%) and *p*-toluidine (20%). When heated at 350° for 30 min., the product contained the *compound*  $\mathrm{Me{\cdot}C_6H_4{\cdot}\overset{\frown O \frown}{C{:}N{\cdot}N{:}C}Ph}$, m. p. 114—115°, which forms an additive *compound* with silver nitrate (1 : 1), m. p. 260° (decomp.). α-*Benzoyl*-β-p-*chlorobenzoylhydrazine*, m. p. 222—223°, obtained by the action of *p*-chlorobenzoyl chloride on benzoylhydrazine in aqueous alkaline solution, yields aniline and *p*-chloroaniline, when heated at 410° for 3 min., in the proportion of 1 : 3. The results obtained are in accordance with the Stieglitz theory of the rearrangement (A., 1922, i, 778). F. G. WILLSON.

Organic salts of hydrofluoboric acid. E. WILKE-DÖRFURT and G. BALZ (Ber., 1927, **60**, [*B*], 115—118).—Attention is directed to the striking resemblance between perchloric and hydrofluoboric acids in their salts. The following *fluoborates* are described: *benzenediazonium*, volatile at 100°, and o-*toluenediazonium*, characterised by unusual stability, *tetramethylammonium*; *tetraethylammonium*; *neurine*, $C_2H_3{\cdot}NMe_3,BF_4$; *brucine*, not molten below 250°; *strychnine*, not molten below 280°; *morphine*; *cocaine*. *Brucine persulphate* and the corresponding *fluorosulphonate* are described. H. WREN.

Stereochemistry of dicyclic ring systems. II. Decahydronaphthalene and its derivatives. II. β-Substituted decahydronaphthalenes. W. HÜCKEL, R. MENTZEL, E. BRINKMANN, and E. KAMENZ (Annalen, 1926, **451**, 109—132).—The previous investigation (A., 1925, i, 258) has been extended, and second *cis*- and *trans*-forms of 2-hydroxydecahydronaphthalene (β-decalol) and 2-aminodecahydronaphthalene (β-decalylamine) have been isolated. That each of these compounds should exist in four isomeric forms supports the views of Mohr (*ibid.*, 1922, i, 243).

Hydrogenation by Skita's method of β-naphthol and *ar*-tetrahydro-β-naphthol yields 33% of decahydronaphthalene (75% *cis*- and 25% *trans*-) and 67% of β-decalol (mainly the *cis*-form, m. p. 105°), whilst with *ac*-tetrahydro-β-naphthol the relative quantities of the products are reversed. Separation of the mixture of β-decalols may be effected by crystallisation of the hydrogen phthalates and yields *cis*-β-decalol, m. p. 105°, *trans*-β-decalol, m. p. 75° (*hydrogen phthalate*, m. p. 180°), and a new *cis*-form (*hydrogen phthalate*, m. p. 153°; *phenylurethane*, m. p. 102°), which after further purification through its *oxalate*, m. p. 131—132°, has m. p. 17°.

Catalytic reduction of β-naphthyl methyl ether yields only the tetrahydro-derivative, whilst β-naphthyl benzoate gives a mixture which, after hydrolysis, yields mainly decahydronaphthalene and 20% of *cis*-β-decalol, m. p. 105°.

Reduction of *cis*-β-decalone (*cis*-2-ketodecahydronaphthalene) by sodium and alcohol yields a mixture of the two *cis*-β-decalols, mainly m. p. 105°, whilst the *trans*-ketone on reduction by Willstätter's and Skita's methods gives a mixture of *trans*-β-decalol, m. p. 75°, and a new *trans*-form (*phenylurethane*, m. p. 99°), which after further purification through the *oxalate*, m. p. 143°, has m. p. 53°.

Technical β-decalol may be separated into the four isomerides by fractional distillation followed by fractional crystallisation of the hydrogen phthalates and further purification through the oxalates.

Hydrogenation of *cis*-β-decaloneoxime yields only the known *cis*-β-decalylamine (*acetyl* derivative, m. p. 154°; *benzoyl* derivative, m. p. 202°; *benzoate*, m. p. 218°), but reduction by sodium and alcohol yields a mixture from which a second *cis*-β-decalylamine (*benzoyl* derivative, m. p. 127°) can be isolated. Similarly, *trans*-β-decaloneoxime yields two *trans*-β-decalylamines, the known form with acetyl derivative, m. p. 130° (*benzoyl* derivative, m. p. 177°; *benzoate*, m. p. 217°), and the new form (*acetyl* derivative, m. p. 163°; *benzoyl* derivative, m. p. 174°).

Experiments with decahydronaphthalene and β-decalone show that the *cis*-form has a slightly higher heat of combustion than the *trans*-form in each case. R. W. WEST.

Stereochemistry of dicyclic ring systems. III. Hexahydrohydrindene and its derivatives. W.

Hückel and H. Friedrich (Annalen, 1926, **451**, 132—160).—Models constructed similarly to those of Mohr (A., 1922, i, 243) suggest that *cis*-hexahydrohydrindol should exist in two *meso*-forms, whilst the *trans*- should exist in one racemic form. These isomerides have now been isolated.

When *cis*- and *trans*-β-decalols are heated with potassium hydrogen sulphate, they yield *cis*- and *trans*-Δ^2-octahydronaphthalenes (cf. Borsche and Lange, A., 1924, i, 32), which, on oxidation with alkaline potassium permanganate, give good yields of *cis-cyclo*hexane-1 : 2-diacetic acid (*dianilide*, m. p. 212—214°; *diethyl* ester, b. p. 187°/24 mm., d_4^{20} 1·030, n_D^{20} 1·4581), and the *trans*-acid (*monoanilide*, m. p. 179°; *dianilide*, m. p. 283°; *diethyl* ester, b. p. 182°/21 mm., d_4^{20} 1·0246, n_D^{20} 1·4566). The *trans*-acid, m. p. 167°, may be resolved through its cinchonidine salt into enantiomorphs having m. p. 148—150°. This favours the view that the *trans*-hexahydrohydrindol should be a racemic form. Ethyl *cis-cyclo*hexane-1 : 2-diacetate by the Dieckmann reaction yields ethyl *cis*-hexahydro-β-hydrindone-α-carboxylate, b. p. 170—173°/21 mm., which by acid hydrolysis gives *cis*-hexahydro-β-hydrindone, m. p. 10°, b. p. 109°/23 mm., d_4^{20} 0·998, $n_D^{16\cdot7}$ 1·48457 (semicarbazone, m. p. 215—216°; oxime, m. p. 80°), which is also obtained by heating the *cis*-diacetic acid with acetic anhydride. Similarly, the *trans*-compounds yield ethyl *trans*-hexahydro-β-hydrindone-α-carboxylate, b. p. 160—163°/20 mm., and *trans*-hexahydro-β-hydrindone, m. p. −12°, b. p. 98°/19 mm., d_4^{20} 0·978, n_D^{17} 1·47687 (semicarbazone, m. p. 243°; oxime, m. p. 161°).

Reduction of hexahydro-β-indone by Willstätter's method yields mainly hexahydrohydrindene with some hexahydro-β-hydrindol, which can be partly separated through the *hydrogen phthalates*, m. p. 109—110° and m. p. 80—85° (still impure) (*phenylurethanes*, m. p. 102—103° and m. p. 82°), and a small quantity of *cis*-hexahydro-β-hydrindone. Reduction by Skita's method in neutral solution gives a 50% yield of mixed ketone and alcohol. By reduction, *cis*-hexahydro-β-hydrindone yields a mixture of the two *cis*-hexahydro-β-hydrindols, whilst the *trans*-ketone yields *trans*-hexahydro-β-hydrindol, m. p. 17°, b. p. 102°/13 mm. (*phenylurethane*, m. p. 114°).

Oxidation of *cis*-hexahydro-β-hydrindol by chromic acid in acetic acid solution yields *cis*-hexahydro-β-hydrindone and *cis-cyclo*hexane-1-acetic-2-propionic acid. The *trans*-isomeride of the latter acid is obtained by oxidising *trans*-hexahydro-β-hydrindone with alkaline potassium permanganate solution.

The heat of combustion of *cis*-hexahydro-β-hydrindone is slightly higher than that of the *trans*-isomeride. R. W. West.

Action of methyl alcohol on phenol at high temperature and pressures; formation of xanthen. W. Ipatiev, N. Orlov, and A. Petrov (Ber., 1927, **60**, [*B*], 130—133; cf. A., 1926, 281).—Methyl alcohol and phenol in presence of aluminium hydroxide at 440° and 220 atm. (maximum) afford *o*-cresol, anisole, xanthen, and smaller amounts of ethylene, carbon monoxide, hydrogen, carbon, and traces of benzene. The isomeric cresols are not produced. The formation of hexamethylbenzene could not be established. Anisole is doubtless formed by direct etherification of phenol under the influence of the catalyst. The production of *o*-cresol appears due to isomerisation of anisole and that of xanthen to the action of phenol on *o*-cresol with loss of water and hydrogen. Phenol when heated in the presence of aluminium hydroxide yields diphenylene oxide and small amounts of diphenyl ether. H. Wren.

Substituted diaryl ethers. I. Di-*p*-tolyl ether. J. Reilly, P. J. Drumm, and H. S. B. Barrett (J.C.S., 1927, 67—73).—Di-*p*-tolyl ether, prepared from potassium *p*-tolyloxide and *p*-bromotoluene in presence of copper bronze and *p*-cresol, has m. p. 50° (see Gladstone and Tribe, J.C.S., 1882, **41**, 9). Oxidation of the ether with chromic acid gives *di-*p*-carboxydiphenyl ether* (*silver* salt). Nitration of di-*p*-tolyl ether with nitric acid in acetic acid solution yields *2-nitrodi-*p*-tolyl ether*, m. p. 50°; with nitric acid alone, or by treatment with nitrogen peroxide, 2 : 2′-*dinitrodi-*p*-tolyl ether*, m. p. 126°; with nitric acid–sulphuric acid, the 2 : 2′-dinitro-compound and 2 : 6 : 2′(?) : 6′(?)-*tetranitrodi-*p*-tolyl ether*, m. p. 246°, this last substance being obtained also by nitration of 2 : 6-*dinitrodi-*p*-tolyl ether*, m. p. 98—100°. There are produced at the same time varying amounts of nitrated *p*-cresols. The above nitro-derivatives were also synthesised by preparing them from the requisite potassium nitrotolyloxides and bromonitrotoluenes. Di-*p*-tolyl ether condenses with acetyl chloride, benzoyl chloride, and phthalic anhydride in presence of aluminium chloride, giving monoketonic substances.

Di-*p*-tolylene oxide, m.p. 165° (Buch, A., 1885, i, 147, gave this as the m. p. of di-*p*-tolyl ether), is obtained by heating *p*-cresol with litharge. H. Burton.

Reciprocal exchange of aromatically combined hydroxyl and halogen. II. Mechanism of the Ullmann–Nadai reaction. W. Borsche and E. Feske (Ber., 1927, **60**, [*B*], 157—159; cf. A., 1918, i, 11).—Replacement of hydroxyl in polynitrophenols by chlorine (cf. Ullmann and Nádai, A., 1908, i, 525) occurs according to the scheme $(NO_2)_2C_6H_3{\cdot}OH+Cl{\cdot}SO_2{\cdot}C_7H_7=(NO_2)_2C_6H_3{\cdot}O{\cdot}SO_2{\cdot}C_7H_7+HCl$;
$(NO_2)_2C_6H_3{\cdot}O{\cdot}SO_2{\cdot}C_7H_7+NPhEt_2=$
$(NO_2)_2C_6H_3{\cdot}NPhEt_2{\cdot}O{\cdot}SO_2{\cdot}C_7H_7 \xrightarrow{+HCl}$
$(NO_2)_2C_6H_3{\cdot}NPhEt_2Cl \longrightarrow NPhEt_2+(NO_2)_2C_6H_3Cl$.

3 : 5-Dinitro-*o*-tolyl *p*-toluenesulphonate dissolved in nitrobenzene and diethylaniline saturated with hydrogen chloride is converted at 120° into 2-chloro-3 : 5-dinitrotoluene, m. p. 61°, in 53% yield. The sulphonic ester merely becomes hydrolysed when heated with hydrochloric acid in acetic acid solution at 130° or 160°. When the ester is warmed with pyridine, the *compound* $(NO_2)_2C_6H_2Me{\cdot}NC_5H_5{\cdot}O{\cdot}SO_2{\cdot}C_7H_7$, m. p. 196°, is produced, which is converted by 5*N*-hydrochloric acid at 170° into 2-chloro-3 : 5-dinitrotoluene in 80% yield. 4-Chloro-3 : 5-dinitrotoluene is obtained in 10—15% yield from diethylaniline hydrochloride and 3 : 5-dinitro-*p*-tolyl *p*-toluenesulphonate at 110° or from dinitro-*p*-cresol and *p*-toluenesulphonyl chloride in diethylaniline. The yield rises to 70% when the *pyridinium* derivative of the sulphonate, m. p. 179°, is heated with hydrochloric acid. H. Wren.

Some aryl amides. S. Weil (Rocz. Chem., 1926, 6, 756—767) [with (Mlle.) Bomberg].—m-*Nitrobenz-o-phenetidide*, m. p. 113°, yields on reduction m-*aminobenz-o-phenetidide* (I), m. p. 89—90°, which on condensation with *m*-nitrobenzoyl chloride gives m-3-*nitrobenzamidobenz-o-phenetidide*, m. p. 172°, giving by reduction m-3-*aminobenzamidobenz-o-phenetidide*, $NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot OEt$ (II), m. p. 119—120°. The m-*nitrobenzamide* of *aminophenyldimethylpyrazolone*, m. p. 199°, is obtained by the action of *m*-nitrobenzoyl chloride on aminoantipyrine.

[With (Mlle.) Z. Wyszogród.]—*Ethyl* p-3-*nitrobenzamidobenzoate*, m. p. 177—178°, prepared by the action of *m*-nitrobenzoyl chloride on ethyl *p*-aminobenzoate, yields on reduction the corresponding *amine* (III), m. p. 176—177°, which is further condensed with *m*-nitrobenzoyl chloride to yield ethyl p-3-(m-*nitrobenzamido*)*benzamidobenzoate*, m. p. 218°, corresponding *amine*, m. p. 205—206°.

[With (Mlle.) C. Wierzbicka.]—2-*Nitro*-p-*toluoyl chloride*, m. p. 17°, on condensation with ethyl *p*-aminobenzoate yields *ethyl* p-2-*nitro*-4-*toluamidobenzoate*, m. p. 172°, giving the corresponding *amine* (IV), m. p. 173—174°, on reduction. The above condensation is repeated with this amine, yielding *ethyl* p-2-(2'-*nitro*-4'-*toluamido*)-4-*toluamidobenzoate*, m. p. 207—208°, which again, on reduction of the nitro-group, yields an *amine*, m. p. 181—182°.

[With J. Slifirski.]—Certain of the amines prepared as above are converted into carbamide derivatives by the action of carbonyl chloride. The *carbamides* have the following m. p.: from amine I, 224—225°; II, above 200° (decomp.); III, above 210° (decomp.); and IV, 180—181°. These carbamides possess considerable trypanocidal properties.

R. Truszkowski.

2 : 3-Dichloroquinol. E. Gebauer-Fülnegg and E. Malnič (Monatsh., 1926, 47, 403—404; cf. Dimroth, Eber, and Wehr, A., 1926, 296).—Only moderate yields of 2 : 3-dichloroquinol are obtained (1) by the action of sulphuryl chloride on quinol in ether solution, (2) by the action of sulphur dioxide on *p*-benzoquinone dichloride (Peratoner and Genco, A., 1895, i, 362), and (3) by the method of Eckert and Endler (*ibid.*, 1922, i, 932). As stated by Hollander (*ibid.*, 1920, i, 559), this product is not obtained by the action of hydrogen chloride on an ethereal solution of monochlorobenzoquinone. The following derivatives of 2 : 3-dichloroquinol are prepared: *dimethyl ether*, m. p. 124°; 2 : 3-*dichloro*-4 : 5-*dibromo*-p-*benzoquinone*, m. p. 294°.

J. W. Baker.

Bromination of quinol monomethyl ether (*p*-methoxyphenol). F. M. Irvine and J. C. Smith (J.C.S., 1927, 74—77).—Monobromination of quinol monomethyl ether in carbon disulphide solution yields the 2-*bromo*-derivative, m. p. 44—45° (*benzoyl* derivative, m. p. 85°), whereas bromination of 4-*methoxyphenyl benzoate*, m. p. 87°, in formic acid solution gives 3-*bromo*-4-*methoxyphenyl benzoate*, m. p. 105·5°, which on hydrolysis furnishes 3-*bromoquinol monomethyl ether*, m. p. 77—78°. Dibromination of the ether in acetic acid solution yields 30—35% of the 2 : 5-dibromo-derivative, the main product being the 2 : 6-dibromo-isomeride (cf. Kohn and Guttmann, A., 1925, i, 1263). An improved method for the preparation of 2 : 6-dibromoquinol dimethyl ether is given.

H. Burton.

Synthesis of *p*-methoxyephedrine and *p*-hydroxy-*m*-methoxyephedrine. G. Koller (Monatsh., 1926, 47, 397—402).—β-Bromo-α-methoxy-α-*p*-anisylpropane (prepared by the action of methyl alcohol on anethole dibromide) when heated with 2 mols. of a 33% methyl-alcoholic solution of methylamine at 110° for 8 hrs. yields β-*methylamino*-α-*methoxy*-α-p-*anisylpropane*, b. p. 142—143°/13 mm., which, when treated in an atmosphere of carbon dioxide with a solution of hydrogen chloride saturated at 0°, yields β-*methylamino*-α-*hydroxy*-α-p-*anisylpropane* (*p*-methoxyephedrine; cf. Späth and Koller, A., 1925, ii, 1086), m. p. 119—120° (*hydrochloride*, m. p. 169—170° in a vacuum). *iso*Eugenol dibromide treated with absolute methyl alcohol similarly yields β-bromo-α-methoxy-α-(*p*-hydroxy-*m*-methoxyphenyl)propane (β-bromo-α-methoxydihydro*iso*eugenol), m. p. 82—83° (Auwers, *ibid.*, 1902, i, 212, describes it as a syrup), which is added in small successive portions to a 33% alcoholic methylamine solution and the product hydrolysed with hydrochloric acid to remove the α-methoxy-group, when β-*methylamino*-α-*hydroxy*-α-(p-*hydroxy*-m-*methoxyphenyl*)*propane* (amorphous) is obtained. Physiologically, these compounds are much weaker in their action than ephedrine.

J. W. Baker.

Constitution of furoperylene. A. Rollett and L. Bayer (Monatsh., 1926, 47, 447—448).—Dehydration of 1 : 12-dihydroxyperylene with zinc and zinc chloride at 250—320° for 0·4 hr. yields 1 : 12-furoperylene, m. p. 252°, which does not depress the m. p. of a purified specimen prepared from β-dinaphthalene oxide (Weitzenböck and Seer, A., 1913, i, 847), thus confirming the constitution there assigned.

J. W. Baker.

Dehydration of benzyl alcohol. S. S. Nametkin and D. N. Kursanov (J. Russ. Phys. Chem. Soc., 1926, 57, 390—394).—By the xanthate reaction on acyclic hydroxy-compounds, it is possible to convert the latter into unsaturated hydrocarbons. This can occur in three ways. An unsaturated hydrocarbon containing a double linking may be formed (cf. A., 1904, i, 327; 1905, i, 71; 1925, i, 1146), or isomerisation may occur (cf. Qvist, *ibid.*, 1919, i, 165; and Komppa and Roschier, *ibid.*, 1922, i, 1167), or, finally, the dehydration may be 1 : 3 and not 1 : 2 (cf. Tschugaev and Budrick, *ibid.*, 1912, i, 480). None of these courses is possible in benzyl alcohol. Dehydration with vigorous dehydrating agents (Cannizzaro, Annalen, 1854, 92, 114) yielded a compound $C_{14}H_{12}$, m. p. 163°. By the xanthate reaction, the authors find that the main product is stilbene: $2CH_2Ph\cdot O\cdot CS\cdot S\cdot Me \longrightarrow 2COS + 2MeSH + CHPh{:}CHPh$.

Methyl benzyl xanthate, m. p. 29°, is prepared by the action of methyl sulphate on benzyl xanthate. Ethyl sulphate yields the *ethyl* ester, b. p. 170—171°/14 mm., m. p. below 20°. It has the characteristic odour of mercaptan. The methyl ester is converted by ammonia at 0° in the course of two weeks into the *amide*, m. p. 61·5—62°. When the ester is heated a

350° in a flask carrying a condenser, the substance is decomposed with the formation of stilbene on the walls of the condenser. The residue in the flask was a *substance*, m. p. 184—185°, having an empirical formula, $C_{28}H_{26}S$. E. ROTHSTEIN.

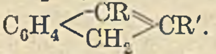
Action of sulphur on organic compounds. IX. L. SZPERL (Rocz. Chem., 1926, 6, 728—737).—*o*-Methylbenzyl alcohol, m. p. 33·7—34·2°, prepared from *o*-methylbenzyl bromide, yields, on heating at 200° with sulphur, *o*-methylbenzaldehyde, *o*-toluic acid, probably 2 : 2′-dimethylstilbene, and a number of unidentified products.

[With I. LIBRACH.]—*m*-Methylbenzyl alcohol when heated with sulphur yields m-*methylbenzyl ether*, b. p. 315—321°, *m*-methylbenzaldehyde, *m*-toluic acid, 3 : 3′-dimethylstilbene, and a number of unidentified products.

[With E. SZPIC.]—*p*-Methylbenzyl alcohol, similarly treated, gives *p*-methylbenzaldehyde, *p*-toluic acid, 4 : 4′-dimethylstilbene, and unidentified products. R. TRUSZKOWSKI.

Molecular transpositions. Preparation and dehydration of some β-phenyl-β-alkylethyl alcohols. (MME.) RAMART-LUCAS and (MLLE.) AMAGAT (Compt. rend., 1927, **184**, 30—32).—β-Phenyl-β-alkylethyl alcohols, on dehydration, yielded chiefly hydrocarbons of the symmetrical type, CHPh:CHR, with small amounts of the $CPhR{:}CH_2$ type, thus differing from *iso*butyl alcohol and the corresponding ββ-diaryl alcohols (cf. A., 1925, i, 658). The following are described: α-*phenyl*-n-*butyramide*, m. p. 84—85°, b. p. 185°/16 mm.; β-*phenyl*-n-*butyl alcohol*, b. p. 120—121°/15 mm.; β-*phenyl*-n-*butylamine*, b. p. 110°/13 mm., *hydrochloride*, m. p. 156°; α-*phenyl*-β-*methylbutyramide*, m. p. 110°; β-*phenyl*-γ-*methylbutyl alcohol*, b. p. 130°/15 mm.; β-*phenyl*-γ-*methyl*-n-*butylamine hydrochloride*, m. p. 128°. B. W. ANDERSON.

Action of Grignard reagents on amino-acids. II. Synthesis of peptide alcohols and their fission by acid and alkali. F. BETTZIECHE and R. MENGER (Z. physiol. Chem., 1926, **161**, 37—65).—Although amino-alcohols of the type $NH_2{\cdot}CHR{\cdot}CR'_2{\cdot}OH$ react almost quantitatively with chloroacetyl chloride, the resulting products are aminated with great difficulty to glycylamino-alcohols. On the other hand, benzoylglycylamino-alcohols are readily prepared by the use of hippuryl chloride. The diphenyl compounds (R′=Ph) are easily hydrolysed by acid, forming benzoic acid, ammonia, and a ketone or an aldehyde, $R{\cdot}CO{\cdot}CHR'_2$. The dibenzyl compounds ($R'{=}CH_2Ph$), on the other hand, give, with greater difficulty, first oxazolines and finally 2-benzylindenes. Hydrolysis of the peptide alcohols with alkali yields first glycine and the amino-alcohol, which then undergoes further fission into amine and ketone.

γ-*Bromoacetamido*-α-*phenyl*-β-*benzyl*iso*propyl alcohol*, m. p. 87—88°, is prepared in 72% yield from the amino-alcohol and bromoacetyl bromide in presence of sodium hydroxide. β-*Chloroacetamido*-ααβ-*triphenylethyl alcohol*, m. p. 218—219°, and β-*chloroacetamido*-αα-*diphenylpropyl alcohol*, m. p. 170—171°, are similarly obtained; the latter, treated with aqueous-alcoholic ammonia at 130°, gives a very small yield of β-*glycylamino*-αα-*diphenylpropyl alcohol*, m. p. 187·5°. γ-Bromoacetamido-α-phenyl-β-benzylbutan-β-ol is converted by ammonia into an oily γ-*glycylamino*-α-*phenyl*-β-*benzylbutan*-β-*ol*, which on benzoylation yields γ-*hippurylamino*-α-*phenyl*-β-*benzylbutan*-β-*ol*, m. p. 183°, more readily prepared from hippuryl chloride and γ-amino-α-phenyl-β-benzylbutan-β-ol. These two methods are also used for the preparation of β-*hippurylamino*-ααβ-*triphenylethyl alcohol*, m. p. 213—214°, γ-*hippurylamino*-αγ-*diphenyl*-β-*benzyl*iso*propyl alcohol*, m. p. 188°, and β-*hippurylamino*-αα-*diphenylpropyl alcohol*, m. p. 188°. Hydrolysis of compounds of the type $X{\cdot}NH{\cdot}CHR{\cdot}CR'_2{\cdot}OH$ with concentrated hydrochloric acid gives the following results. Where X=PhCO, R=Me, and $R'{=}CH_2Ph$, 2-phenyl-5 : 5-dibenzyl-4-methyloxazoline, m. p. 152—153°, and a non-basic *isomeride*, m. p. 90°, are isolated, but no benzoic acid. The non-acylated amino-alcohol is obtained in the case of the benzyl compounds ($X{=}NH_2{\cdot}CH_2{\cdot}CO{\cdot}$ or $NHBz{\cdot}CH_2{\cdot}CO{\cdot}$, R=Me or Ph, $R'{=}CH_2Ph$), and is accompanied by an indene derivative,  $C_6H_4{<}\begin{matrix}CR\\CH_2\end{matrix}{>}CR'$. γ-Glycylamino-α-phenyl-β-benzylbutan-β-ol is also formed from the corresponding β-hippurylamino-alcohol, and where $X{=}NHBz{\cdot}CH_2{\cdot}CO{\cdot}$, R=Ph, $R'{=}CH_2Ph$ there are isolated the benzoylamino-alcohol (X=Bz), and dibenzylacetophenone (β-benzoyl-αγ-diphenylpropane), m. p. 78°. The phenyl compounds (R′=Ph) give ketones, viz., αα-diphenylacetone, m. p. 45—46° (oxime, m. p. 164°), from $X{=}NH_2{\cdot}CH_2{\cdot}CO$ or $NHBz{\cdot}CH_2{\cdot}CO$ and R=Me, and diphenylacetophenone, m. p. 135—136° (R=Ph). β-Glycylamino-αα-diphenylethyl alcohol with hydrochloric acid gives diphenylacetaldehyde, but with 40% sulphuric acid at 120—128° deoxybenzoin. During the hydrolysis of the acylamino-alcohols with 8% or 15% sodium hydroxide, there are obtained, in addition to the corresponding amino-alcohols, from γ-hippurylamino-α-phenyl-β-benzylbutan-β-ol, a *substance*, m. p. 163° (impure), together with an unisolated *compound* which is hydrolysed by acid to γ-amino-α-phenyl-β-benzylbutan-β-ol, benzoic acid, and glycine, and from γ-hippurylamino-αγ-diphenyl-β-benzylbutan-β-ol, a *substance*, m. p. 173°. In the case of the benzyl (but not the phenyl) compounds containing the hippurylamino-group, a glycylamino-derivative is isolable. No dibenzyl ketone is identified where $R'{=}CH_2Ph$, but benzophenone is isolated where R′=Ph, except in the case of β-glycylamino-αα-diphenylpropyl alcohol. C. HOLLINS.

Formation of chrysene by the dehydrogenation of cholesterol. O. DIELS and W. GÄDKE (Ber., 1927, **60**, [*B*], 140—147; cf. A., 1925, i, 1062).—The hydrocarbon, m. p. 246—248°, obtained by the dehydrogenation of cholesterol by palladised charcoal is identified as chrysene. In addition, a hydrocarbon, m. p. about 180°, which is unsaturated towards bromine, and a hydrocarbon, m. p. about 325°, stable towards bromine, are also produced. H. WREN.

Yeast ergosterol. I. F. REINDEL, E. WALTER, and H. RAUCH (Annalen, 1927, **452**, 34—46).—The ergosterol used had m. p. 160—161°, $[\alpha]_D$ −117° (all rotations in chloroform); acetate, m. p. 172—173°

(cf. Windaus and Grosskopf, A., 1923, i, 75); benzoate, m. p. 163—165°. Attempts to obtain the corresponding ketone by oxidation led to breakdown products, whether chromic acid, potassium permanganate, lead tetra-acetate, or fuming nitric acid at −20°, each in acetic acid, was used. Attempts to obtain ergosteryl chloride also failed, owing to an isomerisation which readily occurs. Thus when ergosteryl acetate was dissolved in chloroform and treated at 0° with hydrogen chloride, iso*ergosteryl acetate*, m. p. 129—131°, $[\alpha]_D$ −62·5°, was obtained, which was hydrolysed by potassium methoxide to iso*ergosterol*, $C_{27}H_{41}$·OH, m. p. 135—136°, $[\alpha]_D$ −86·9° (*benzoate*, m. p. 135°). This is presumably a valency isomerism, since catalytic hydrogenation of the original and of the *iso*ergosteryl acetates gave the same α-ergostanyl acetate, $C_{27}H_{47}$·OAc, m. p. 110°, $[\alpha]_D$ +5·18° in chloroform, hydrolysed to α-ergostanol, m. p. 130—131°, $[\alpha]_D$ +17·86° (*benzoate*, m. p. 130—131°), from which ergostanyl chloride, $C_{27}H_{47}Cl$, was obtained crystalline, m. p. 104—105°, by the action of phosphorus pentachloride. The α-ergostanyl acetate is further capable of isomerisation to β-*ergostanyl acetate*, m. p. 94—95°, $[\alpha]_D$ +3·0°, 95%, with 5% of a new *acetate*, m. p. 110—111°, of a *sterol*, m. p. 141—142°. Hydrolysis of the β-acetate gave β-*ergostanol*, m. p. 114—118°, also obtained by isomerisation of α-ergostanol. Either ergostanol gave with chloroacetyl chloride a β-*ergostanyl chloroacetate*, m. p. 166—167°. When β-ergostanyl acetate was subjected to catalytic hydrogenation, a small amount of hydrogen only was absorbed, and a γ-*ergostanyl acetate*, m. p. 144—145°, $[\alpha]_D$ +5·95°, was formed in 80% yield, with an acetate, m. p. 109°, possibly α-ergostanyl acetate. γ-*Ergostanol* obtained by hydrolysis has m. p. 144—145°, $[\alpha]_D$ +15·94° (*benzoate*, m. p. 163—165°; *chloroacetate*, m. p. 200—201°). E. W. Wignall.

Organic molecular compounds with co-ordination centres. I. H. Rheinboldt [with H. Pieper and P. Zervas] (Annalen, 1927, **451**, 256—273).—Examination of a series of complex acids similar to those obtained by Wieland and Sorge (A., 1916, i, 710) from deoxycholic acid, and by Boedecker (*ibid.*, 1920, i, 848) from *apo*cholic acid, shows that the number of mols. of bile acid combined with the central fatty acid molecule depends on the number of carbon atoms in the latter, but not on saturation or on the presence of a free carboxyl group. Fatty acids containing 4 to 8 carbon atoms combine with 4 mols., those containing 9 to 14 with 6 mols., and those containing more than 15 with 8 mols. of bile acid. It is suggested, in accordance with the theoretical considerations of Hüttig (*ibid.*, 1921, ii, 193), that these compounds represent a new type of organic molecular compound, in which the whole fatty acid molecule acts as a co-ordination centre. New *choleic acids* have been prepared from the following compounds and deoxycholic acid, the number of mols. of the latter being given in parentheses: tiglic acid (4), m. p. 171·5—172°; sorbic acid (4), m. p. 171—172°; *n*-heptoic acid (4), m. p. 169°; *n*-octoic acid (4), m. p. 170°; pelargonic acid (6), m. p. 173°; *n*-decoic acid (6), m. p. 174—175°; *n*-undecoic acid (6), m. p. 176°; undecenoic acid (6), m. p. 174°; lauric acid (6), m. p. 176—177°; tridecoic acid (6), m. p. 177—178°; myristic acid (6), m. p. 181—182°; *n*-pentadecoic acid (8), m. p. 183·5—184°; cetyl palmitate (8), m. p. 195°; *n*-heptadecoic acid (8), m. p. 185·5—186·5°; stearolic acid (8), m. p. 174°; arachidic acid (8), m. p. 188—189°; behenic acid (8), m. p. 189—189·5°; ethyl behenate (8), m. p. 191·5°; brassidic acid (8), m. p. 184°; dibromobehenic acid (8), m. p. 177°; behenolic acid (8), m. p. 183—183·5°; lignoceric acid (8), m. p. 193—193·5°; cerotic acid (8), m. p. 193—194°; octylcetylacetic acid (8), m. p. 188—188·5°; cerylformic acid (8), m. p. 194·5°; montanic acid (?), m. p. 196°; ethyl montanate (8), m. p. 197—198°; and from the following compounds and *apo*cholic acid: tiglic acid (4), m. p. 168—168·5°; sorbic acid (4), m. p. 170—171°; ethyl behenate (8), m. p. 190°, and montanic acid, m. p. 190°. The great stability of the last-named compound is shown by means of a m.-p. curve. H. E. F. Notton.

Sulphonation of cinnamic acid: proof that the secondary product is *m*-sulphocinnamic acid; synthesis of *o*-sulphocinnamic acid; action of sodium hydrogen sulphite on cinnamic acid derivatives. F. J. Moore and G. R. Tucker (J. Amer. Chem. Soc., 1927, 49, 258—266; cf. A., 1922, i, 454).—Contrary to the statement of van Duin (*ibid.*, 737), sulphonation of cinnamic acid with fuming sulphuric acid (18% free SO_3) at below 35° yields *p*- and *m*-sulphocinnamic acids, the *o*-isomeride not being produced. At higher temperatures, a disulphonic acid is formed, but the *o*-sulphocinnamic acid is again not produced. The *m*-sulphocinnamic acid was characterised by mixed m. p. of the following salts, obtained both from the sulphonation product and from synthetic *m*-sulphocinnamic acid: p-*toluidine hydrogen* salt, m. p. 227—230°; p-*anisidine hydrogen* salt, m. p. 238—239°. The o-*toluidine* (? hydrogen) salt was not obtained crystalline. *Barium hydrogen* o-*sulphocinnamate* was prepared by treating sodium *o*-bromocinnamate with sodium hydrogen sulphite in boiling aqueous solution until acidification caused no appreciable precipitation, and heating the product with sodium sulphite and a small proportion of copper sulphate for 40 hrs. at 170°. From it, the following salts of o-*sulphocinnamic acid* (+$2H_2O$) were prepared: *aniline hydrogen* salt, m. p. 208—209°; p-*toluidine hydrogen* salt (H_2O), m. p. 225—227°; o-*toluidine hydrogen* salt, m. p. 234—235°; and p-*anisidine hydrogen* salt, m. p. 205—207°. The *monochloride*, obtained by the action of phosphorus pentachloride on the sodium salt, has m. p. 179—182°. Oxidation of the potassium salt with aqueous permanganate affords salicylic acid. The action of aqueous sodium hydrogen sulphite on bromocinnamic acids yields products formed by addition of the sodium hydrogen sulphite to the double linking, which are transformed into sulphocinnamic acids under the conditions of Rosenmund's reaction (A., 1921, i, 370).

F. G. Willson.

***p*-Methylbenzylallylacetic acid and its cyclisation to tetrahydronaphthalene derivatives. A new dimethylnaphthalene.** G. Darzens and A. Heinz (Compt. rend., 1927, 184, 33—35).—Ethyl sodiomalonate reacts with *p*-methylbenzyl chloride in toluene to form *ethyl* p-*methylbenzylmalonate*, b. p. 179—180°/20 mm., and the sodium derivative of this forms with allyl bromide *ethyl* p-*methylbenzylallylmalonate*. The corresponding *acid*, on warming, gives p-*methylbenzylallylacetic acid*, b. p. 180°/20 mm., *methyl* ester, b. p. 146—150°/15 mm. This acid is converted by sulphuric acid into 1 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-3-*carboxylic acid*, m. p. 142—144° (*methyl* ester, b. p. 172°/15 mm.), and p-*methylbenzylvalerolactone*, b. p. 187°/15 mm. Dehydrogenation of the former by heating with sulphur gives rise to 1 : 7-*dimethylnaphthalene*-3-*carboxylic acid*, m. p. 217° (*methyl* ester, m. p. 68—69°, b. p. 199—201°/15 mm.), from which 1 : 7-*dimethylnaphthalene*, b. p. 147—149°/15 mm., *picrate*, m. p. 123—124°, is obtained (cf. J.C.S., 1907, 91, 1149). B. W. Anderson.

Preparation and analysis of methylation products of thiosalicyclic (*o*-thiolbenzoic) acid. G. Sachs and M. Ott (Monatsh., 1926, 47, 415—418).—*o*-Methylthiolbenzoic acid (Meister, Lucius, & Brüning, E.P. 593/07; B., 1907, 1003) when treated with an aqueous or alcoholic solution of mercuric acetate yields a *mercury* salt, m. p. 158—159°, which when heated with methyl iodide for 2 hrs. at 150° yields o-*carbomethoxyphenyldimethylsulphonium mercuric iodide*, $CO_2Me{\cdot}C_6H_4{\cdot}SMe_2I,HgI_2$, m. p. 123—124·5°, which is also obtained by the action of methyl sulphate on lead *o*-thiolbenzoate, $C_6H_4<\substack{CO_2\\S}>Pb$, and treatment of the product with potassium mercuric iodide. If a concentrated solution of iodine in potassium iodide is added instead of the potassium mercuric iodide, o-*carbomethoxyphenyldimethylsulphonium pentaiodide*, $CO_2Me{\cdot}C_6H_4{\cdot}SMe_2I_5$, is obtained. Determination of the methyl group by the method of Pollak and Spitzer (A., 1922, ii, 789) gives low results, but a value more nearly approaching the theoretical is obtained by the addition of mercuric iodide to the hydriodic acid, the silver iodide being converted into the chloride by a current of chlorine at the ordinary temperature before weighing. J. W. Baker.

Bile acids. XXV. Degradation of [*cyclo*-hexane]dicarboxylic acid. H. Wieland, O. Schlichting, and W. von Langsdorff (Z. physiol. Chem., 1926, **161**, 74—79).—Three methods for the conversion of *cyclo*hexane-1 : 2-dicarboxylic acid into compounds which should be convertible into adipic acid were tried unsuccessfully. Magnesium methyl iodide reacts in warm ether with ethyl *cyclo*hexane-1 : 2-dicarboxylate to give the 2-*hydroxy*iso*propyl*cyclo*hexanecarboxylic lactone*, m. p. 80° (*potassium* and *silver* salts of the hydroxy-acid are described), and oily *anhydro*-1 : 2-*di*(*hydroxy*iso*propyl*)cyclo*hexane* (1 : 1 : 3 : 3-*tetramethylhexahydrophthalan*), b. p. 80—83°/15 mm. In vigorously boiling ether, the product is 1 : 2-*di*(*hydroxy*iso*propyl*)cyclo*hexane*, m. p. 104°, which is converted by aqueous-alcoholic hydrochloric acid into the anhydro-compound. Reduction of ethyl *cyclo*hexane-1 : 2-dicarboxylate by Bouveault's method gives a small yield of ωω-*dihydroxy*-1 : 2-*dimethyl*cyclo*hexane* [1 : 2-*di*(*hydroxymethyl*)cyclo*hexane*], m. p. 57°, and the corresponding anhydro-compound (*hexahydrophthalan*), b. p. 170—175°/730 mm. The formation of the anhydro-compound in each case prevents oxidation of the two glycols to adipic acid.

Ethyl *cyclo*hexane-1 : 2-dicarboxylate is converted by way of the *dihydrazide*, m. p. 245°, *diazide*, and *diurethane*, m. p. 145°, into 1 : 2-diamino*cyclo*hexane dihydrochloride, m. p. 303°, but attempts to prepare from this the dihydroxy-compound failed. C. Hollins.

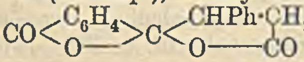
Dependence of rotatory power on chemical constitution. XXXI. Resolution of *m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine. S. G. Clarke, J. Kenyon, and H. Phillips (J.C.S., 1927, 188—194).—Chloramine-T and *m*-methylthiolbenzoic acid react, giving dl-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*, $C_6H_4Me{\cdot}SO_2{\cdot}N{\cdot}SMe)C_6H_4{\cdot}CO_2H$, m. p. 173—175° (cf. Mann and Pope, *ibid.*, 1922, **121**, 1052). Treatment with brucine furnished the l-*brucine*-l-*acid* salt, m. p. 123—125°, $[\alpha]_{5461}$ −144°, $[\alpha]_{4359}$ −279° (in ethyl alcohol), which on decomposition gave l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*, m. p. 172—173°, $[\alpha]_{5461}$ (in ethyl alcohol) −338°. A table of specific rotatory powers of this substance in different solvents for different wave-lengths is given.

d-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*, m. p. 172—173°, $[\alpha]_{5461}$ +338°, $[\alpha]_{4359}$ +627° (in ethyl alcohol), was obtained from its l-*cinchonidine* salt, m. p. 204°, $[\alpha]^{17.5}_{5461}$ (in chloroform) +48·27° (other rotatory powers are given).

The sulphonylimine is decomposed by hydrogen peroxide into *m*-carboxyphenylmethylsulphone and *p*-toluenesulphonamide, and by hydrochloric acid into the sulphonamide together with *m*-carboxyphenyl methyl sulphoxide and *m*-methylthiolbenzoic acid. A review of the constitution of chloramine-T and its reactions with thioethers in the light of the electronic theory of valency is given. H. Burton.

Persistence of optical activity in the elimination of water from optically active glycols. I. A. McKenzie and W. S. Dennler (Ber., 1927, **60**, [*B*], 220—225).—*r*-α-Naphthylglycollic acid is resolved into its optical antipodes by crystallisation of the cinchonine salt from rectified spirit whereby d-α-*naphthylglycollic acid*, m. p. 124—125°, $[\alpha]^{14}_{D}$ +162° in water, $[\alpha]^{14}_{D}$ +194° in ethyl alcohol, is obtained. *Methyl* d-α-*naphthylglycollate*, b. p. 230—232°/36 mm., $[\alpha]^{16}_{5461}$ +115° in acetone, is converted by magnesium benzyl chloride into β-1-*naphthyl*-αα-*dibenzylethylene glycol*, m. p. 195—196°, $[\alpha]^{16}_{D}$ −78° in acetone, which is transformed by cold, concentrated sulphuric acid into r-benzyl β-phenyl-α-1-naphthylethyl ketone, m. p. 58·5—59·5° (cf. A., 1926, 834), and by boiling dilute sulphuric acid into a partly racemised product from which l-*benzyl* β-*phenyl*-α-1-*naphthylethyl ketone*, m. p. 78°, $[\alpha]_D$ −278° in acetone, is isolated by fractional crystallisation. The active ketone is completely racemised by alcoholic alkali, thus proving that the α-naphthyl group exerts an influence similar to that of the phenyl residue. H. Wren.

Smooth extension of the ring from indandione to dihydroxynaphthalene derivatives. I. D. Rădulescu and G. Gheorgiu (Ber., 1927, **60**, [*B*], 186—190).—Ethyl 2-phenylindan-1 : 3-dione-2-acetate, m. p. 105—106° (corresponding *methyl* ester, m. p. 110—112°), is converted by zinc chloride, concentrated sulphuric acid, or, preferably, sodium ethoxide in the absence of air into *ethyl* 1 : 4-*dihydroxy-2-phenylnaphthalene*-3-*carboxylate*, m. p. 153—154°, the yield being almost quantitative. It is transformed by the action of air on its alkaline solution partly into *ethyl* 2-*phenyl*-1 : 4-*naphthaquinone*-3-*carboxylate* ($+0\cdot5H_2O$), m. p. 112°, and partly into 3-hydroxy-2-phenyl-1 : 4-naphthaquinone, m. p. 145—146° [identified further by conversion into the corresponding methyl derivative, m. p. 122—123°, acetate, m. p. 112—113°, and monophenylhydrazone, m. p. 199—200° (decomp.)]. The ester is smoothly converted into 3-hydroxy-2-phenyl-1 : 4-naphthaquinone by boiling alkali in the presence of air. It is transformed by reductive acetylation into *ethyl* 1 : 4-*diacetoxy-2-phenylnaphthalene*-3-*carboxylate*, m. p. 134°. 1 : 3 : 4-*Triacetoxy-2-phenylnaphthalene*, m. p. 166—168°, is described. 2-*Phenylindan*-1 : 3-*dione*-2-*acetic acid*, m. p. 214—215° (*barium* and *sodium* salts), is prepared by hydrolysis of the corresponding ester by acid; the corresponding *chloride*, m. p. 198—200°, and *amide*, m. p. 255—256°, are described. Treatment with concentrated potassium hydroxide converts the acid into β-phthaloyl-β-phenylpropionic acid, m. p. 169—171° (decomp.), readily transformed into the *lactone*,



$\mathrm{CO}<\begin{smallmatrix}C_6H_4\\ O—\end{smallmatrix}>\mathrm{C}<\begin{smallmatrix}CHPh\cdot CH_2\\ O——CO\end{smallmatrix}$, m. p. 175—176°. H. WREN.

Parachor and chemical constitution. IV. Three- and four-membered rings. S. SUGDEN and H. WILKINS (J.C.S., 1927, 139—147).—From measurements of the densities and surface tensions of nine compounds containing a three-membered ring, it is deduced that the parachor for such rings is 17. The *normal* and *labile* esters of 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid give values indicating that each of these compounds contains a three-membered ring and a non-polar double linking. The value 11·6 obtained for four-membered rings from measurements made on three *cyclo*butane derivatives is in good agreement with the value previously obtained (A., 1924, ii, 662).

The hypothesis is put forward that the value of structural parachors depends on the intensity of unsaturation. Thus the ratio between the number of hydrogen atoms required to convert any ring structure into an open-chain saturated compound (latent valencies$=x$), and the number of octets sharing this unsaturation (n), gives the degree of unsaturation. From this value ($x/n=1$ for double linking), and the value for the parachor for the double linking (23·2), the value for ring structures can be calculated. These values are in good agreement with those found experimentally. H. BURTON.

Glutaconic acids. XXI. Non-formation of Δ^2-tetrahydro*iso*phthalic acid by reduction of *iso*phthalic acid. E. H. FARMER and H. L. RICHARDSON (J.C.S., 1927, 59—63; cf. A., 1926, 1039).—The main product of the reduction of *iso*phthalic acid (cf. Perkin and Pickles, J.C.S., 1905, 87, 293), is *cis*-Δ^4-tetrahydro*iso*phthalic acid (formerly described as Δ^2-acid). A small quantity of the Δ^3-tetrahydro*iso*phthalic acid, m. p. 244°, is also formed, probably not as a primary reduction product. The Δ^3-acid is also obtained by the action of boiling alkali on the *cis*-Δ^1-compound, and on oxidation with ozone gives β-carboxyadipic acid. Adipic (or glutaric) acid, the expected oxidation product of the true Δ^2-form, could not be detected when the reduction product, after removal of the Δ^3- and *cis*-Δ^4-acids, was oxidised with ozone. It is concluded that Perkin and Pickles' *cis*-Δ^4-acid (which should be either Δ^2- or *trans*-Δ^4-) is absent. The absence of the *trans*-Δ^4-acid is indicated only by its non-isolation, since the ozone oxidation product of *cis*- and *trans*-forms is the same, tricarballylic acid. H. BURTON.

Oxidation of nitrophenylcyanoacetates. A. FAIRBOURNE and H. R. FAWSON (J.C.S., 1927, 46—50).—Ethyl sodiocyanoacetate condensed with *p*-chloronitrobenzene, chloro-2 : 4-dinitrobenzene, and picryl chloride, yields *ethyl* p-*nitrophenylcyanoacetate* (I) (*sodium* derivative), *ethyl* 2 : 4-*dinitrophenylcyanoacetate*, (II), m. p. 66° (*sodium* and *silver* derivatives), and *ethyl* 2 : 4 : 6-*trinitrophenylcyanoacetate*, m. p. 95°. Hydrolysis of I and II with hot dilute hydrochloric acid gives *p*-nitrophenylacetonitrile and 2 : 4-*dinitrophenylacetonitrile*, m. p. 89°. *Ethyl* 2 : 4-*dinitrophenylethylcyanoacetate*, m. p. 98°, is obtained from the silver derivative of II and ethyl iodide.

Oxidation of I with chromic anhydride in boiling glacial acetic acid gives *ethyl* αβ-*di*-p-*nitrophenyl*-αβ-*dicyanosuccinate*, m. p. 209°, which is also obtained by treating the silver derivative of I with iodine. From II there is obtained by oxidation *ethyl* 2 : 4-*dinitrobenzoylformate*, m. p. 89° (*phenylhydrazone*, m. p. 170°), derived from the intermediate hydroxy-ester $R\cdot C(OH)(CN)\cdot CO_2Et$, by loss of hydrogen cyanide. The sodium derivative of II on treatment with bromine in moist ether gives *ethyl bromo*-2 : 4-*dinitrophenylcyanoacetate*, m. p. 98°, which on oxidation passes into *ethyl bromo*-2 : 4-*dinitrophenylhydroxycyanoacetate*, m. p. 157°, thus showing the bromine to be in the ring. The same sodium derivative when treated with chlorine in aqueous solution gives *ethyl chloro*-2 : 4-*dinitrophenylcyanoacetate*, m. p. 101°. No substituted anthracene derivative was obtained from any of the oxidations. H. BURTON.

3-Nitro-4-amino- and 3 : 4-dihalogeno-benzaldehydes. H. H. HODGSON and H. G. BEARD (J.C.S., 1927, 20—27).—*p*-Acetamidobenzaldehyde (p-*nitrophenylhydrazone*, m. p. 264—265°), on nitration with diacetylorthonitric acid in acetic anhydride solution, gives 3-*nitro*-4-*acetamidobenzylidene diacetate*, m. p. 114°, which on hydrolysis yields 3-nitro-4-acetamidobenzaldehyde (p-*nitrophenylhydrazone*, m. p. 289—290°) and 3-nitro-4-aminobenzaldehyde (p-*nitrophenylhydrazone*, m. p. 270—272°; *oxime*, m. p. 207°). The 4-halogeno-3-nitrobenzaldehydes were obtained in the usual way from the nitroaminoaldehyde, and also by nitration of the 4-halogenobenzaldehydes. 4-Chloro-3-nitrobenzaldehyde (p-*nitrophenylhydrazone*, m. p. 278—279°; *oxime*, m. p. 146°), 4-bromo-3-nitrobenzaldehyde [p-*nitrophenylhydrazone*, m. p. 282—283°; oxime, m. p. 154° (Schöpff, A., 1892, i, 336, gives m. p. 145—146°)], and 4-*iodo*-3-*nitrobenz*-

aldehyde, m. p. 141° (p-*nitrophenylhydrazone*, m. p. 277—278°; *oxime*, m. p. 157°), are described and their structures proved by oxidation to the corresponding benzoic acids. Conversion of these aldehydes into the dihalogeno-compounds was carried out by the method previously described (B., 1926, 511). There were prepared in this way 3 : 4-dichlorobenzaldehyde [p-*nitrophenylhydrazone*, m. p. 276—277°; oxime, m. p. 118—119° (Erdmann and Schwechten, A., 1891, i, 450, give m. p. 114—115°)]; 4-*chloro*-3-*bromobenzaldehyde*, m. p. 70° (p-*nitrophenylhydrazone*, m. p. 273—274°; *oxime*, m. p. 131°); 4-*chloro*-3-*iodobenzaldehyde*, m. p. 117° (p-*nitrophenylhydrazone*, m. p. 277—278°; *oxime*, m. p. 115—116°); 3-*chloro*-4-*bromobenzaldehyde*, m. p. 52° (p-*nitrophenylhydrazone*, m. p. 272—273°; *oxime*, m. p. 104°); 3 : 4-*dibromobenzaldehyde*, m. p. 75° (p-*nitrophenylhydrazone*, m. p. 270—274°; *oxime*, m. p. 129°); 4-*bromo*-3-*iodobenzaldehyde*, m. p. 127° (p-*nitrophenylhydrazone*, m. p. 265°; *oxime*, m. p. 141°); 3-*chloro*-4-*iodobenzaldehyde*, m. p. 70·5° [p-*nitrophenylhydrazone*, m. p. 261—262° (decomp.); *oxime*, m. p. 129°]; 3-*bromo*-4-*iodobenzaldehyde*, m. p. 66° (p-*nitrophenylhydrazone*, m. p. 260—261°; *oxime*, m. p. 157—158°), and 3 : 4-*di-iodobenzaldehyde*, m. p. 118° [p-*nitrophenylhydrazone*, m. p. 245—247° (decomp.); *oxime*, m. p. 177—178°].

Oxidation of the aldehydes gives the corresponding acids, the following being described: 4-*chloro*-3-*iodobenzoic acid*, m. p. 216—217°; 4-*bromo*-3-*iodobenzoic acid*, m. p. 243—244°; 3-*chloro*-4-*iodobenzoic acid*, m. p. 219°; and 3-*bromo*-4-*iodobenzoic acid*, m. p. 242—243°. p-*Acetamidobenzylidene*-p-*toluidine* and 3-*nitrobenzaldehyde*-4-*azo*-β-*naphthol* have m. p. 187—188° and 271°, respectively. H. BURTON.

Action of phosphorus halide on alkylformanilides. Preparation of secondary and tertiary *p*-alkylaminobenzaldehydes. A. VILSMEIER and A. HAACK (Ber., 1927, 60, [*B*], 119—122; cf. Fischer, Müller, and Vilsmeier, A., 1925, i, 439).—Methylformanilide is converted by phosphoryl chloride in presence of benzene into the additive *compound*, $C_6H_5{\cdot}NMe{\cdot}CHCl{\cdot}O{\cdot}POCl_2$, which when heated at 70° (or preferably first converted by phosphorus pentachloride into methyldichloromethylaniline and then heated) yields *p*-methylaminobenzaldehyde, m. p. 56—57°. Treatment of methylformanilide with phosphoryl chloride and subsequently with a tertiary fatty-aromatic amine gives dialkylaminoaldehydes according to the scheme: $C_6H_5{\cdot}NMe{\cdot}CHCl_2+C_6H_5{\cdot}NMe_2 \longrightarrow HCl+C_6H_5{\cdot}NMe{\cdot}CHCl{\cdot}C_6H_4{\cdot}NMe_2$ and $C_6H_5{\cdot}NMe{\cdot}CHCl{\cdot}C_6H_4{\cdot}NMe_2+C_6H_5{\cdot}NMe{\cdot}CHCl_2 \longrightarrow CHCl_2{\cdot}C_6H_4{\cdot}NMe_2+C_6H_5{\cdot}NMe{\cdot}CH{:}NMePhCl$. *p*-Dimethylaminobenzaldehyde, m. p. 73°, *p*-diethylaminobenzaldehyde, *p*-methylbenzylaminobenzaldehyde, m. p. 68°, and p-*dibenzylaminobenzaldehyde*, m. p. 88—90°, are thus prepared. Dimethyl-*m*-toluidine and α-dimethylaminonaphthalene give less satisfactory yields of aldehyde. H. WREN.

Reactions of nitrosyl chloride. II. Action on aromatic aldoximes. H. RHEINBOLDT, M. DEWALD, F. JANSEN, and O. SCHMITZ-DUMONT (Annalen, 1926, 451, 161—178; cf. A., 1925, i, 1131).—Nitrosyl chloride reacts with aromatic aldoximes, yielding chloro-oximes, a nitroso-derivative being probably formed as an intermediate product: $R{\cdot}CH{:}NOH \longrightarrow R{\cdot}CHCl{\cdot}NO \longrightarrow R{\cdot}CCl{:}NOH$. The formation of the nitroso-compound is indicated by the green colour developed in the reaction mixtures, but the intermediate compound could be isolated only in the case of piperonaloxime (*hydrochloride* described). When this oxime is treated with 3 mols. of nitrosyl chloride in ethereal solution, ω-*chloro*-ω-*nitroso*-3 : 4-*methylenedioxytoluene*, $(CH_2O_2{:}C_6H_3{\cdot}CHCl{\cdot}NO)_2$, colourless crystals melting at about 75° to a green liquid, which solidifies and then melts at 125—126°, is deposited. This substance dissolves in organic solvents to a green solution and readily passes into *chloropiperonaloxime*, yellow needles, m. p. 129°, when the solid or its solutions are warmed. With *p*-toluidine in ether solution, the chloro-oxime yields the p-*toluidino*-derivative, $CH_2O_2{:}C_6H_3{\cdot}C({:}NOH){\cdot}NH{\cdot}C_6H_4{\cdot}Me$, m. p. 150—151°.

By the action of nitrosyl chloride in ethereal solution on aromatic aldoximes, the following substances were prepared: ω-*p*-toluidinobenzaldoxime, m. p. 161—162° (decomp.); ω-*chlorofurfuraldoxime*, m. p. 103—104° [*anilino*-derivative, m. p. 126—127° (decomp.)], and *difurylfuroxan*, m. p. 113—114°; ω-*chloroanisaldoxime*, m. p. 120°; ω-*chloro*-p-*tolualdoxime*, m. p. 69—70° [p-*toluidino*-derivative, m. p. 134—135° (decomp.)]; ω-*chlorocuminaldoxime*, oil [*anilino*-derivative, m. p. 145—146° (decomp.)]; ωω′-*dichloroterephthaldialdoxime*, m. p. 188° (decomp.); ω-chloro-*o*-nitrobenzaldoxime, m. p. 99—100°; ω-chloro-*m*-nitrobenzaldoxime, m. p. 99·5—100°; ω-chloro-*p*-nitrobenzaldoxime, m. p. 123·5—124°; ω-*chloro*-o-*nitropiperonaloxime*, m. p. 116—117° (decomp.) [*piperidino*-derivative, m. p. 181—182° (decomp.)]; ω-*chloro*-p-*cyanobenzaldoxime*, m. p. 151—152°; ω-*chloro*-p-*carboxybenzaldoxime*, m. p. 198—199° (decomp.); ω-*chlorocinnamaldoxime*, m. p. 98°.

The *O*-methyl ethers of benzaldoxime and *m*-nitrobenzaldoxime do not react with nitrosyl chloride, as would be expected from the mechanism of the reaction given above. R. W. WEST.

Reducing action of a mixture of magnesium iodide (or bromide) and magnesium on aromatic ketones. Probable formation of magnesium subiodide (or sub-bromide). M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1927, 49, 236—257).—When benzophenone is treated, according to the Grignard procedure, with magnesium and an aryl halide in ether–benzene in presence of iodine, and the product hydrolysed, benzopinacol is obtained in practically theoretical yield. The reduction depends on the simultaneous action of magnesium and magnesium iodide, and does not take place in absence of either of these. It is therefore concluded that the reaction is due to the intermediate formation of magnesium subiodide, MgI, which combines with the benzophenone with formation of a free radical, termed a "halomagnesium ketyl," $Ph_2C(OMgI){\cdot}$, the bimolecular form of which is hydrolysed to benzopinacol. The reduction takes place in benzene solution in presence of a trace of ether, and small amounts of moisture do not inhibit the reaction. The latter proceeds at 0°, and is almost as rapid at 25° as at the b. p. of the solvent, a few minutes sufficing for the complete reduction of 55 g. of ketone. When benzophenone is added to a solution of magnesium iodide in ether–benzene at 25°, the additive *compound* $(\mathrm{Ph_2CO})_3,\mathrm{MgI_2}$ is precipitated, and if the amount of iodine present is insufficient for the quantitative formation of this product, the reduction will not proceed. The presence of the slightest excess of iodine over and above this proportion, however, brings about complete reduction, which supports the view that magnesium and magnesium iodide react under these conditions to form the subiodide, and also indicates that the bimolecular form of the above halomagnesium ketyl continuously loses magnesium iodide, with formation of the magnesium pinacolate. At 60°, a trace of iodine is sufficient to bring about the reduction, as the above additive compound is not precipitated, and is probably dissociated. Benzopinacol can also be obtained in 90—95% yield by the action of magnesium and magnesium bromide, and of beryllium and beryllium iodide, on benzophenone. Negative results were obtained with magnesium metal and chloride, with zinc and its halides, cadmium and its halides, silver and magnesium iodide, and with zinc and mercuric iodide, mercuric chloride, magnesium iodide, or magnesium bromide. Magnesium amalgam does not reduce benzophenone to the pinacol in ether–benzene. Rearrangement of benzopinacol to β-benzopinacolin is effected by warming the former in glacial acetic acid in presence of a trace of iodine. The dissociation of the iodomagnesium pinacolate with formation of the above "ketyl" is shown by the analogy of its behaviour with that of triphenylmethyl. The solid material is colourless, but gives intensely coloured solutions, the colour of which is discharged by a small amount of oxygen and reappears on keeping. The iodomagnesium pinacolate is obtained, together with methane, both in theoretical yield, by the action of magnesium methyl iodide on benzopinacol, and also from magnesium phenyl iodide and benzil. Treatment of the iodomagnesium pinacolate with iodine affords, quantitatively, benzophenone and magnesium iodide, whilst oxygen yields benzophenone and magnesium oxyiodide. The action of magnesium and magnesium iodide on 4-methylbenzophenone yields analogously 4 : 4′-dimethylbenzopinacol, m. p. 173—175°, which, when heated in acetic acid with a trace of iodine, affords a *product*, m. p. 114—116°, probably a pinacolin or a mixture of its structural isomerides. Di-*p*-tolyl ketone affords similarly 4 : 4′ : 4″ : 4‴-tetramethylbenzopinacol, m. p. 183—184°, the additive *product*, $[(\mathrm{C_7H_7})_2\mathrm{CO}]_2,\mathrm{MgI_2},\mathrm{Et_2O}$, being formed intermediately. 4 : 4′ : 4″ : 4‴-*Tetramethylbenzopinacolin*, m. p. 137—138°, obtained from the pinacol as above, is described. *p*-Chlorobenzophenone is converted analogously into 4 : 4′-dichlorobenzopinacol, m. p. 172—178°, whilst phenyl diphenylyl ketone affords in the same way 4 : 4′-*diphenylbenzopinacol* (s-*dihydroxydiphenyldidiphenylylethane*), m. p. 198—199°, in 97% yield (cf. Schlenk, A., 1914, i, 396). When the latter is boiled with acetyl chloride and acetic acid in benzene solution, it yields 92% of the pinacolin *phenyl phenyldidiphenylylmethyl ketone*, $\mathrm{Bz{\cdot}CPh(C_6H_4Ph)_2}$, m. p. 198°, and 8% of the pinacolin, $\mathrm{PhC_6H_4{\cdot}CO{\cdot}CPh_2{\cdot}C_6H_4Ph}$. Didiphenylyl ketone affords similarly 4 : 4′ : 4″ : 4‴-*tetraphenylbenzopinacol*, m. p. about 200° (decomp.). When heated, the latter decomposes into didiphenylyl ketone and didiphenylylcarbinol, whilst it yields 4 : 4′ : 4″ : 4‴-*tetraphenylbenzopinacolin*, m. p. 204—207°, when boiled with acetyl chloride and acetic acid in benzene. Fluorenone yields analogously *fluorenopinacol*, m. p. 190—192° (decomp.), which, when heated with 70% sulphuric acid and acetic acid, yields the corresponding pinacolin, 9-diphenylenephenanthrone, m. p. 255°. An additive *product* of fluorenone and fluorenopinacol (1 : 1) is described. *Xanthopinacol*, m. p. 185—187° (decomp.), is obtained analogously, with intermediate formation of the additive *product* $(\mathrm{C_{13}H_8O_2})_2,\mathrm{MgI_2},\mathrm{Et_2O}$. When heated with 70% sulphuric acid and acetic acid, xanthopinacol yields dixanthylene, m. p. 312—313°. Analogous preparations of the pinacols from anthrone and Michler's ketone are described. It is concluded that the formation of a subhalide may explain many reactions which are effected with "activated" magnesium. F. G. Willson.

Action of magnesium phenyl bromide on trisubstituted acetonitriles. (Mme.) Ramart-Lucas and F. Salmon-Legagneur (Compt. rend., 1927, **184**, 102—104).—By the action of magnesium phenyl bromide in benzene, toluene, or xylene on nitriles, $\mathrm{CR_3{\cdot}CN}$, the ketones, $\mathrm{CR_3{\cdot}COPh}$, are obtained, the hydrobromides of the ketimines, $\mathrm{CR_3{\cdot}CPh{:}NH,HBr}$, being isolable when one or two of the substituent groups, R, are aromatic. Phenyl *tert.*-butyl ketone (oxime, m. p. 167°), *phenyl α-phenyl-α-methylpropyl ketone* (β-*benzoyl*-β-*phenylbutane*), b. p. 187—189°/16 mm., *phenyl α-phenyl-α-ethylpropyl ketone* (γ-*benzoyl*-γ-*phenylpentane*), m. p. 48—49°, b. p. 218°/35 mm. [*oxime*, m. p. 187—188°; *ketimine hydrobromide*, m. p. 208—210° (decomp.)], *phenyl α-phenyl-α-benzylpropyl ketone* (β-*benzoyl*-αβ-*diphenylbutane*), m. p. 112—113° [*oxime*, m. p. 201—202°; *ketimine hydrobromide*, m. p. 227° (decomp.)], and *phenyl αα-diphenyl*-β-*methylpropyl ketone* (α-*benzoyl*-αα-*diphenyl*isobutane), m. p. 98° (*ketimine hydrobromide* hydrolysed with difficulty), are described. C. Hollins.

Action of nitromethane and its homologues on benzil. I. Kasiwagi (Compt. rend., 1927, **184**, 35—37).—Benzil reacts readily with the sodium derivative of nitromethane, forming ethyl benzoate and a white powder, which, on treatment with acid, yields ω-nitrostyrene and β-nitro-α-phenylethyl alcohol. With the sodium derivative of nitroethane, benzil forms ethyl benzoate and a white powder containing nitrogen and 19% of sodium. This, on treatment with acid, is resolved into benzoic acid and acetaldoxime. Presumably in each case a complex intermediate compound is first formed. B. W. Anderson.

Preparation of α-diketones from αβ-unsaturated ketones. C. Dufraisse and H. Moureu (Compt. rend., 1927, **184**, 99—101).—By the successive addition of bromine (1 mol.), piperidine (4 mols.), and excess of acid to a solution of an αβ-unsaturated ketone (1 mol.), the series of five reactions: $\mathrm{{\cdot}CO{\cdot}CH{:}CH{\cdot}} \longrightarrow \mathrm{{\cdot}CO{\cdot}CHBr{\cdot}CHBr{\cdot}} \longrightarrow \mathrm{{\cdot}CO{\cdot}CBr{:}CH{\cdot}} \longrightarrow \mathrm{{\cdot}CO{\cdot}CBr(NC_5H_{10}){\cdot}CH_2} \longrightarrow \mathrm{{\cdot}CO{\cdot}C(NC_5H_{10}){:}CH{\cdot}} \longrightarrow \mathrm{{\cdot}CO{\cdot}C(OH){:}CH}$, may be induced to occur in a single operation, giving 40—80% yields of α-diketones. The following diketones, R·CO·CO·Me, are synthesised: R=methyl, ethyl, *n*-propyl, *iso*propyl (poor yield), phenyl, and benzyl; also phenyl-*p*-methoxybenzylglyoxal, and, in poor yield, α-phenyl-β-ethylglyoxal. No experimental details are given.

C. Hollins.

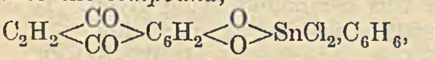
New diketone from phenyl *p*-tolyl ketone. T. W. Jezierski (Rocz. Chem., 1926, 6, 738—740).—The main product of the reaction between phenyl *p*-tolyl ketone and sulphur is *s-di*-pp′-*dibenzoyldiphenylethane*, $(Ph·CO·C_6H_4·CH_2)_2$, m. p. 239—240°.

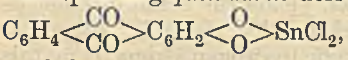
R. Truszkowski.

Condensations of unsaturated substances with diazomethane. II. Condensation of diazomethane with carbon disulphide and xyloquinone. R. Rotter (Monatsh., 1926, 47, 493—495).—Diazomethane reacts with xyloquinone in ether solution at the temperature of a freezing mixture to yield a moderately stable condensation *product*, $C_{10}H_{12}O_2N_4$, which is more stable than the corresponding product obtained from benzoquinone (Pechmann and Seel, A., 1899, i, 947), but which, like the latter, can be converted into a stable secondary product. No pure product could be isolated by the interaction of diazomethane and carbon disulphide.

J. W. Baker.

Naphthazarin. P. Pfeiffer [with H. Oberlin and B. Segall] (Ber., 1926, 60, [*B*], 111—115).—Confirmation of Dimroth and Ruck's conception (A., 1926, 297) of naphthazarin as 5 : 8-dihydroxy-1 : 4-naphthaquinone is found in the observation that it is converted by stannic chloride in presence of benzene into the *compound*,


$C_2H_2{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_2{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}SnCl_2,C_6H_6$, this behaviour being characteristic of hydroxy-ketones containing the hydroxyl group in the *ortho*-position to the carbonyl group (cf. Pfeiffer and others, A., 1913, i, 879); the corresponding *quinizarin* derivative,


$C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_2{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}SnCl_2$, is described. Further, naphthazarin is unable to add pyridine, which is in harmony with the presence of *ortho*- but not of *para*-hydroxy-groups.

The *compound*, $SnCl_3·O·C_6H_3(OMe)·COMe$, from pæonol and the $SnCl_3$ derivative of methyl salicylate (cf. Pfeiffer, *loc. cit.*) appear unimolecular in freezing naphthalene, whereas the mol. wts. of the benzylidene- and *p*-anisylidene-pæonol compounds could not be established. In both compounds, therefore, the tin atom has an unoccupied co-ordination position, unless it be assumed that this position is occupied by a naphthalene molecule. Steric considerations render a unimolecular structure in the usual sense very improbable for these compounds.

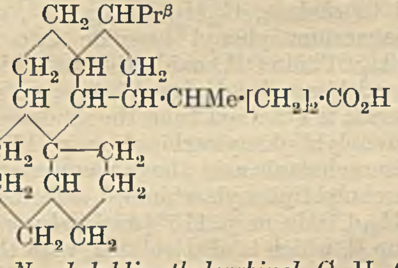
H. Wren.

Action of oxalyl chloride on homologues of naphthalene and 1 : 6-dimethoxynaphthalene. R. Lesser and G. Gad (Ber., 1927, 60, [*B*], 242—245).—The action of oxalyl chloride on various methylnaphthalenes in presence of aluminium chloride gives acenaphthenequinones in satisfactory yield only in the case of 1 : 6-dimethylnaphthalene. 3-*Methylacenaphthenequinone*, m. p. 198—199° (corr.), and 2 : 2′-*dimethylnaphthil*, m. p. 237—238° (corr.) [corresponding *azine*, $C_{30}H_{22}N_{21}$, m. p. 269° (corr.)], are derived from 2-methylnaphthalene. 1 : 6-Dimethylnaphthalene affords 5 : 8-*dimethylacenaphthenequinone*, m. p. 193—194° (corr.), yielding, with *o*-phenylenediamine, the *azine*, $C_{20}H_{14}N_2$, m. p. 198—199° (corr.), and with 3-hydroxythionaphthen the *compound*, $C_{22}H_{14}O_2S$. 3 : 7-*Dimethylacenaphthenequinone*, m. p. 207° (corr.) [*azine*, m. p. 194° (corr.)], and (?) 2 : 6-*dimethylnaphthoic acid* are derived from 2 : 6-dimethylnaphthalene. 2 : 7-Dimethylnaphthalene yields 2 : 7-*dimethyl*-1-*naphthoic acid*, m. p. 173° (corr.), and very little 3 : 8-*dimethylacenaphthenequinone*, m. p. 207—208° (corr.). 1 : 6 - Dimethoxynaphthalene affords 13-*hydroxy*-4 : 5-*benzocoumaranone*-2 : 3-*dione* (5-*hydroxy*-1 : 2-*diketodihydro*-β-*naphthofuran*), m. p. 298—300° (corr. decomp.) after darkening at 275°, 3 : 6-*dimethoxyacenaphthenequinone*, m. p. 227° (corr.) [corresponding *azine*, m. p. 196—197° (corr.)], and a *substance*, m. p. 238—239° (corr.). 2 : 7-Dimethoxynaphthalene is converted into 3 : 8-dimethoxyacenaphthenequinone, m. p. 279° (corr.) [*azine*, m. p. 253° (corr.); *monophenylhydrazone*, m. p. 128° (corr.); *diphenylhydrazone*, m. p. 232—233° (corr.)], and 7-methoxy-1 : 2-diketodihydro-β-naphthofuran, m. p. 204° (corr.) [*quinoxaline* derivative, $C_{19}H_{14}O_3N_2,CH_3·CO_2H$, m. p. 275—276° (corr.)] (cf. Staudinger and others, A., 1921, i, 432, 433).

H. Wren.

Bile acids. XXV. Degradation of [*cyclo*hexane]dicarboxylic acid. H. Wieland, O. Schlichting, and W. von Langsdorff.—See this vol., 243.

Bile acids. XXVI. Nature of the side-chain and of the fourth ring. H. Wieland, O. Schlichting, and R. Jacobi (Z. physiol. Chem., 1926, 161, 80—115; cf. A., 1924, i, 857).—Degradation of cholanic acid by means of alternate Grignard reactions and oxidations shows the side-chain to be $·CHMe·CH_2·CH_2·CO_2H$, and the annexed structure is suggested for cholanic acid. Five bisnorcholanic acids (side-chain $·CHMe·CO_2H$) are described, and their isomerism is discussed.



Norcholyldimethylcarbinol, $C_{26}H_{46}O$, m. p. 96—97°, b. p. 220°/2 mm., prepared from ethyl cholanate, m. p. 92°, and magnesium methyl iodide, is oxidised by chromium trioxide in acetic acid to norcholanic acid, $C_{23}H_{38}O_2$, m. p. 177° (*methyl* ester, m. p. 74°; *ethyl* ester, m. p. 66—67°), the yield being much better than from norcholyldiphenylcarbinol, m. p. 106·5° (cf. Cerecedo, Diss., Munich, 1921; Lunde, Diss., Freiburg, 1925; Cerecedo prepared from the diphenylcarbinol a *hydrocarbon*, $C_{36}H_{48}$, m. p. 121°). Ethyl norcholanate gives with magnesium methyl iodide *bisnorcholyldimethylcarbinol*, m. p. 116°, which is oxidised to α-*bisnorcholanic acid*, m. p. 214°, $[\alpha]_{D}^{17}$ −7·5° (in alcohol). *Bisnorcholyldiphenylcarbinol*,

m. p. 122—123°, gives the same acid in twice the yield. *Ethyl bisnorcholanate*, m. p. 106—107°, reacts less easily with the Grignard agent, giving *trinorcholyldimethylcarbinol*, $C_{21}H_{35}\cdot CMe_2\cdot OH$, m. p. 159—160°, which is converted by oxidation into two stereoisomeric γ- and δ-*bisnorcholanic acids.* The γ-acid, m. p. 210—211° (*methyl* ester, m. p. 117°; *ethyl* ester, m. p. 82—83°), is optically inactive, whilst the δ-acid, m. p. 184° (*methyl* ester, m. p. 99°), has $[\alpha]_D^{18}$ +31·74° (in alcohol). β-*Bisnorcholanic acid*, m. p. 242°, $[\alpha]_D^{18}$ +23·33° (in alcohol) (oily *ethyl* ester), is recovered from unreacted ester which has been treated for a short time with magnesium phenyl bromide; the diphenylcarbinol obtained from the β-ester is oxidised by chromic-acetic acid to ætiocholanic acid, m. p. 218°. A fifth isomeride, ε-*bisnorcholanic acid*, m. p. 181°, $[\alpha]_D^{20}$ +14·30° (*methyl* ester, m. p. 123°), is isolated by means of its insoluble *sodium* salt from the oxidation product of the neutral portion in the preparation of the α-acid.

The diphenylcarbinol, $C_{21}H_{35}\cdot CPh_2\cdot OH$, from ethyl bisnorcholanate, is converted by crystallisation from acetic acid into an unsaturated *hydrocarbon*, $C_{19}H_{31}\cdot CMe{:}CPh_2$, m. p. 175—176°, which on oxidation (without isolation) yields *ætiocholanic acid*, m. p. 219° (*methyl* ester, m. p. 98—99°; *ethyl* ester, m. p. 78—79°). The unsaturated *hydrocarbon*, $C_{32}H_{40}$, m. p. 233°, obtained from ethyl ætiocholanate and magnesium phenyl bromide, is oxidised to *ætiobilianic acid*, $C_{19}H_{30}O_4$, m. p. 228° (*anhydride*, m. p. 206°).

From the neutral products of these various oxidations are isolated the following compounds: (1) From norcholyldimethylcarbinol, an α-*acetoxyketone*, $C_{22}H_{37}\cdot CO\cdot CMe_2\cdot OAc$, m. p. 147°, the corresponding α-*hydroxyketone*, m. p. 96—97°, and *norcholyl methyl ketone*, $C_{22}H_{37}\cdot COMe$, m. p. 113° [*oxime*, m. p. 151° (decomp.); *semicarbazone*, m. p. 232° (decomp.)], the last-mentioned ketone being reduced by Clemmensen's method to *homocholane*, m. p. 75°. (2) From bisnorcholyldimethylcarbinol, *bisnorcholyl methyl ketone*, m. p. 148° [*semicarbazone*, m. p. 223° (decomp.)], which is reduced to *cholane*, $C_{24}H_{42}$, m. p. 90°, or converted by magnesium phenyl bromide into a *carbinol*, $C_{21}H_{35}\cdot CH_2\cdot CPhMe\cdot OH$, oxidisable to α-bisnorcholanic acid and *bisnorcholyl phenyl ketone*, m. p. 140° (a *stereoisomeride* is obtained from the oxidation products of bisnorcholyldiphenylcarbinol, m. p. 130°, together with ε-bisnorcholanic acid above-mentioned). (3) From bisnorcholyldiphenylcarbinol, *ætiocholyl methyl ketone*, $C_{19}H_{31}\cdot COMe$, m. p. 115° [*semicarbazone*, m. p. 236° (decomp.)], which is also isolated, with the cyclic ketone *ætiocholanone*, $C_{19}H_{30}O$, m. p. 105° [*semicarbazone*, m. p. 263 (decomp.)], from the neutral products in the oxidation of norcholyldimethylcarbinol to norcholanic acid. C. HOLLINS.

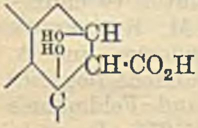
Two sterol-like substances from *Asclepius syriaca*. I. L. SCHMID and R. STOHR (Monatsh., 1926, 47, 433—436).—The sterol-like product $C_{27}H_{46}O$ isolated from *Asclepius syriaca* by the method of Klein and Pirschle (A., 1924, i, 355) in 0·5% yield has m. p. 176° (after sintering at 164°) and sublimes in a vacuum at 180°. When treated with acetic anhydride, it yields an *acetate*, m. p. 206°, which when treated in ethereal solution with a solution of bromine in acetic acid yields a *bromoacetate*, $C_{33}H_{53}O_2Br$, m. p. 265°, and a second *bromoacetate*, $C_{47}H_{75}O_3Br$, m. p. 201°, the latter corresponding with an alcohol, $C_{45}H_{74}O_2$. The second bromoacetate when heated with 10% alcoholic potassium hydroxide solution yields a *bromo-alcohol*, $C_{45}H_{75}O_2Br$, m. p. 170° (*propionate*, m. p. 214°). Phosphorus pentachloride has no action on the hydroxyl group present in the original sterol, and, since it yields no condensation product with digitonin, it is probably similar to amyrin. J. W. BAKER.

β-Amyrin from *Manila elemi* resin. IV. A. ROLLETT (Monatsh., 1926, 47, 437—445; cf. A., 1923, i, 588; 1925, i, 945).—Treatment of the crude amyrin with a slight excess of benzoic anhydride at 150° for 3—5 hrs. yields the mixed α- and β-benzoates in nearly quantitative yield, separation being subsequently effected by the method previously described. When the β-benzoate is heated with copper in an atmosphere of carbon dioxide or hydrogen under reduced pressure, a sublimate giving the reactions of benzoic acid is obtained, together with a small quantity of *di*-β-*amyrin ether*, m. p. 135—136°, probably contaminated with a little β-amyrilene. Treatment of the β-benzoate in a suspension of acetic acid and carbon disulphide with a solution of bromine in acetic acid yields a *substance*, $C_{37}H_{53}O_2Br$, which is obtained in three different crystalline forms (highest m. p. obtained, 202°, mixed m. p. with dibromo-β-amyrin benzoate, 190°), and in one case a *substance* of the same composition, m. p. 234—235°. Hydrolysis of these bromo-products yields only amorphous substances. β-Amyrenone on bromination in acetic acid solution yields *monobromo*-β-*amyrenone*, m. p. 198—199°, detailed crystallographic data for this compound being given. It is unattacked by heating with acetic anhydride.

J. W. BAKER.

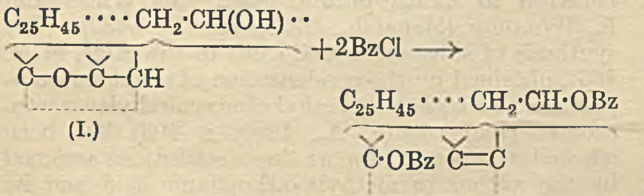
Scoparin. F. HEMMELMAYR and J. STREHLY (Monatsh., 1926, 47, 379—392; cf. A., 1893, i, 601; 1894, i, 542; 1918, i, 503).—Scoparin, heated in methyl-alcoholic solution, yields the same product as that previously obtained in ethyl alcohol. Attempts to replace all the hydroxylic hydrogen atoms by metals or acyl radicals were unsuccessful, but the results are consistent with the formulæ $C_{20}H_{20}O_{10}$ or $C_{22}H_{22}O_{11}$, of which the latter is preferred. The following are described: *heptapotassium* salt; *pentasodium* salt; *barium* salt, $C_{44}H_{36}O_{22}Ba_4$; *pentachloroacetyl* derivative, soluble in alkali with intense yellow colour, and *hexa*- (or *hepta*- ?)*anisoyl* derivative, m. p. 135°. When boiled with dilute sulphuric acid, scoparin is converted into an isomeric *substance* which slowly loses water. Dilute hydrochloric acid, on the other hand, causes the loss of 2 mols. of water to yield a brown *substance*, $C_{22}H_{18}O_9$, m. p. about 240° (*acetyl* derivative, m. p. 210°). G. M. BENNETT.

Saponins and related substances. XVI. Hederagenin. A. W. VAN DER HAAR (Rec. trav. chim., 1926, 46, 28—32; cf. A., 1925, i, 946; Jacobs, *ibid.*, 947, 948; 1926, i, 1250).—The author acknowledges that the so-called hederagenin chloride, methyl ester, and amide (A., 1922, i, 160) are identical with the neutral sulphites of these compounds described by Jacobs. *Hederagenin menthyl ester sulphite* has m. p. 265—266°. The non-recognition of the presence of the sulphite residue was due to the fact that hederagenin methyl ester and its sulphite have the same m. p. Hederagenin monoacetate, m. p. 156—157°, supposed to be formed by the loss of one acetyl group from hederagenin diacetate on heating or in boiling alcohol, is shown to be the diacetate of the same m. p. described by Jacobs, the former description being the result of an analytical error. The view is maintained that the difference in ease of acetylation is best explained by the assumption that the hydroxyl groups are secondary and tertiary, and that the formation of hederagenolic acid and hederagenone requires their location on the β-carbon atoms with reference to the carboxyl group. The formation of the sulphite bridge and acetonyl derivative is possible if the hydroxyl groups are in the *cis*-position (annexed formula). Jacobs' use of chromic acid oxidation, sulphuric acid, and Clemmensen's reduction is criticised.

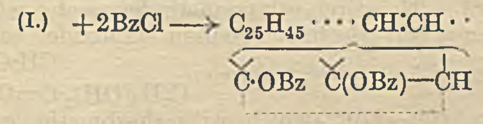


J. M. Gulland.

Phytochemistry. IV. Betulin. III. O. Dischendorfer and H. Grillmayer (Monatsh., 1926, **47**, 419—425; cf. this vol., 59; Schulze and Pieroh, A., 1922, i, 1045).—*allo*Betulin on treatment with benzoyl or *p*-bromobenzoyl chloride at 150—180° for 8 hrs. yields, respectively, *heterobetulin dibenzoate*, m. p. 230°, $[\alpha]_D^{20}$ +35·49°, and the corresponding *di*-p-*bromobenzoate*, m. p. 253° (after sintering at 200°), $[\alpha]_D^{20}$ +40·16°, in which both the acyl groups are attached to oxygen. The former on hydrolysis yields *heterobetulin*, $C_{30}H_{50}O_2$, m. p. 267—268° (after sintering at 260°), $[\alpha]_D^{20}$ +11·59°, which is isomeric but not identical with *allo*betulin, and on re-esterification with benzoyl chloride and pyridine yields the original dibenzoate, and with acetic anhydride the *diacetate*, m. p. 248—249°, $[\alpha]_D^{20}$ +28·29°. When heated with 95% formic acid, heterobetulin yields a *monoformate*, m. p. 284—285° (decomp.), $[\alpha]_D^{19}$ +44·52°, which is isomeric with *allo*betulin formate, the ethereal oxygen linking being ruptured and re-formed in another position. These reactions show that the di-esters obtained from *allo*betulin are the enol esters of the unknown monoketone heterobetulone. The formation of heterobetulin dibenzoate from *allo*betulin is analogous to the formation of terpin diacetate by the acetolysis of cineole, and is represented by the scheme:



the alternative scheme,



analogous to the formation of terpineol acetate, being negatived by the fact that *allo*betulone forms a di- and not a tri-ester with benzoyl chloride.

J. W. Baker.

Action of anhydrous formic acid on *d*-α-pinene. J. Reisman (Bull. Soc. chim., 1927, [iv], 41, 94—98).—Prolonged (2 months') action of anhydrous formic acid on *d*-α-pinene (Aleppo turpentine, α_D +42° per dm.) affords a mixture of limonene, dipentene, terpinene, terpinolene, and diterpilene, together with the formates of terpineol and terpinenol and traces of bornyl formate.

R. Brightman.

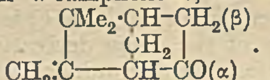
Determination of unsaturated hydrocarbons and formation of tricyclic rings by dehydration of alcohols. S. S. Nametkin and L. J. Brussova (J. Russ. Phys. Chem. Soc., 1926, 57, 372—378).—The authors have used the reaction of perbenzoic acid, with compounds containing a double linking (cf. Prilischaev, A., 1910, i, 86), to determine the amount of such compounds when they are formed by the dehydration of alcohols, in cases when there is the possibility of a tricyclic compound being formed. The latter do not react with perbenzoic acid. The compound is treated with excess of perbenzoic acid, the mixture kept for 3 days at the ordinary temperature, and after adding potassium iodide and sulphuric acid, titrated with sodium thiosulphate. Tricyclene, formed by the oxidation of camphor semicarbazone (A., 1920, i, 855), contains 35% of non-tricyclic compound, probably camphene.

Pure cyclo*fenchene*, b. p. 143—143·5°/754 mm., d_4^{20} 0·86013, n_D^{20} 1·4515, is obtained in an analogous way from fenchone. α-Methylcamphene, obtained by the dehydration of tertiary methylfenchyl alcohol with potassium hydrogen sulphate, contains 2% of saturated hydrocarbon. The method confirms the structure given to this compound. Other terpene compounds have been examined with similar results.

E. Rothstein.

Optical superposition. VII. Bornyl dimethoxysuccinates. T. S. Patterson, J. D. Fulton, and (Mrs.) J. M. MacCulloch [(Miss) J. M. Semple] (J.C.S., 1926, 3224—3230; cf. *ibid.*, 1915, **107**, 142; A., 1924, i, 1041; 1925, i, 115).—The rotatory power of bornyl *i*-dimethoxysuccinate is nearly the same as the mean of the rotatory powers of the *d*- and *l*-esters. The results are not taken as confirming the principle of optical superposition, since the differences from the mean observed are dependent on the temperature, and cannot be due to experimental error. *Bornyl* l-*dimethoxysuccinate*, m. p. 70°, α_g^{14} (1 dm.) −2·28°, *bornyl* d-*dimethoxysuccinate*, m. p. 103°, α_g^{16} (1 dm.) +11·4°, and *bornyl* i-*dimethoxysuccinate*, m. p. 114°, $[\alpha]_g^{12·5}$ +44·79°, are described, together with the rotatory powers of solutions of similar concentrations in different solvents over a range of temperature.

H. Burton.

True camphenone. S. S. Nametkin and A. S. Zabrodina (J. Russ. Phys. Chem. Soc., 1926, **57**, 379—381).—From α-nitrocamphene (cf. A., 1925, i, 416), the authors obtain α-camphenone, to which they assign the structure  $\begin{array}{l} \quad CMe_2{\cdot}CH{-}CH_2(\beta) \\ \quad | \qquad CH_2 \quad | \\ CH_2{:}C{-\!-}CH{-}CO(\alpha) \end{array}$. The potassium salt of secondary α-nitrocamphene, freed from water, was slowly added to a vigorously shaken solution of tin in fuming hydrochloric acid, and the product purified by distillation in steam. By this method 30 g. of nitrocamphene yielded 3 g. of the crude ketone. The residue of the steam distillation also yielded 3 g. of the hydrochloride of the amino-derivative previously described (*loc. cit.*). The *semicarbazone*, m. p. 205°, yields the pure *ketone*, m. p. 77—78°. The latter yields the *oxime*, m. p. 117—118°.

E. ROTHSTEIN.

Constitution of the acid formed by the action of sulphuric acid on camphorquinone. M. B. BHAGVAT and J. L. SIMONSEN (J.C.S., 1927, 77—89).—The keto-acid, $C_{10}H_{16}O_3$, formed by the action of sulphuric acid on camphorquinone and previously described as *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid (A., 1925, i, 919), is *d*-2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid. Bromination of the methyl ester in acetic acid solution gives *methyl* 5 : 5-*dibromo*-2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-*carboxylate*, m. p. 57—58°, which, on treatment with barium hydroxide, yields a mixture of acids (I), (II), (III), and (IV) (below). 4-*Hydroxy*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexen*-5-*one*-1-*carboxylic acid* (I), m. p. 151—152° [*methyl* ester, m. p. 73—74° (*dioxime*, m. p. 138—139°; *disemicarbazone*, m. p. 206—207°); *acetyl* derivative (+0·5H_2O), m. p. 128°], is converted by digestion with 50% potassium hydroxide solution into 1-*hydroxy*-4 : 4 : 5-*trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid* (II) (+0·5H_2O), m. p. 191—192° (*potassium* salt). The *acetyl* derivative of (II) decomposes at 207—208°, resolidifying to 4 : 4 : 5-*trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic* acid (III), m. p. 257—258° [*sodium* salt (inactive in aqueous solution); *dianilide*, m. p. 200—201°], which, on reduction with sodium and amyl alcohol, yields trans-4 : 4 : 5-*trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid*, m. p. 182—183°. Oxidation of (III) or of l-4 : 4 : 5-*trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid* (IV), m. p. 215—216° (*sodium* salt has $[\alpha]_D^{23}$ −62° in water; *dianilide*, m. p. 208—209°), with nitric acid gives γ-methylbutane-αβγ-tricarboxylic acid (V). Oxidation of (III) with potassium permanganate at 0° yields *γ-acetyl-γ-methylbutane-αβ-dicarboxylic acid* (VI), m. p. 125—126°, and a second *keto-dicarboxylic acid* (VII), $C_{10}H_{12}O_5$, m. p. 183—185° [*oxime* (+0·5H_2O), decomp. 214°; *semicarbazone*, decomp. 241°]. Further oxidation of (VI) with sodium hypobromite gives (V), also obtained on oxidation of (VII) with nitric acid.

The structure of the original keto-acid is established by these results, and the presence of a methylene group adjacent to the carbonyl group is confirmed by preparation of an *oximino*-ester by the action of *iso*amyl nitrite on the methyl ester in presence of sodium. Hydrolysis of this non-crystallising oil with formaldehyde and hydrochloric acid, followed by treatment with dilute potassium hydroxide solution, gives the acid (I) and thence the acid (III), identical with that prepared from the dibromo-ester. The suggestion that the keto-acid can exist in keto- and enolic forms (*loc. cit.*) is confirmed by the preparation of the *acetyl* derivative of the enolic form by treating camphorquinone with acetic anhydride and zinc chloride. l-4-*Acetyl*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexene*-1-*carboxylic acid* has m. p. 109—111°, $[\alpha]_D$ −66·3° in chloroform, and does not show mutarotation. Hydrolysis gives the ordinary ketonic form of the acid. Direct acetylation of the latter could not be effected.

M. CLARK.

New terpene alcohol, $C_{10}H_{18}O$. O. ACHMATOWICZ (Rocz. Chem., 1926, 6, 804—814).—Bornyl acetate, prepared in presence of sulphuric acid or zinc chloride, yields on hydrolysis a new alcohol, apparently a space isomeride of borneol, termed endo*borneol*, m. p. 186°, b. p. 203—204°, which on oxidation yields camphor. Its *ethyl ether*, b. p. 83—87°/20 mm., 197—198°/751 mm., *phenylurethane*, m. p. 138—139°, and *benzoate*, b. p. 186—187°/15 mm., are described.

R. TRUSZKOWSKI.

Cadinene. II. Compounds related to cadinene. G. G. HENDERSON and J. M. ROBERTSON (J.C.S., 1926, 2811—2816; cf. Henderson and A. Robertson, A., 1924, i, 1328).—*iso*Cadinene (*loc. cit.*) is probably identical with Tröger and Feldmann's sesquiterpene from cade oil (A., 1899, i, 376; Lepeschkin, *ibid.*, 1908, i, 278) and with Ruzicka and Capato's hexahydrocadalene (*ibid.*, 1925, i, 943). They differ from cadinene in the position of the double linkings. Oil of false cubebs yields on fractionation a mixture of dicyclic alcohols, $C_{15}H_{25}\cdot OH$, consisting mainly of l-*cadinol*, b. p. 153—155°/10 mm., d_4^{16} 0·9727, n_D^{16} 1·508, $[\alpha]_{5461}^{15}$ −54° (cf. *d*-cadinol +22°, other properties identical), which is converted into cadinene dihydrochloride, m. p. 118°, $[\alpha]_{5461}^{16}$ −43·7° (in chloroform). There is also isolated a new dicyclic sesquiterpene alcohol, *cubebol* (*phenylurethane*, m. p. 186°, $[\alpha]_{5461}^{19}$ +58·9°; *α-naphthylurethane*, m. p. 197—198·5°; *dibromide*, oily; *dibromide phenylurethane*, decomp. at 76—80°; no stable hydrochloride), which, regenerated from the phenylurethane by means of alcoholic potassium hydroxide, has m. p. 61—62°.

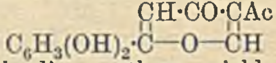
C. HOLLINS.

Furfuraldehyde in industry. D. H. KILLEFFER.—See B., 1927, 92.

5-Hydroxymethylfurfuraldehyde. J. J. BLANKSMA (Helv. Chim. Acta, 1927, 10, 67).—The properties of this compound (Reichstein, this vol., 61, there incorrectly described as 5-hydroxyfurfuraldehyde) had been previously described (Troje, A., 1925, ii, 1210; Middendorp, *ibid.*, 1919, i, 129).

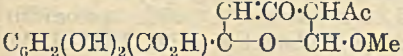
H. E. F. NOTTON.

Condensation of esters of ethoxymethylene-β-ketonic acids with resacetophenone and their relation to xanthophanic acid. R. WEISS and K. WOLDICH (Monatsh., 1926, 47, 427—432).—The synthesis of substances analogous to the ester, m. p. 165°, obtained by the condensation of ethyl resacetophenonecarboxylate and ethyl ethoxymethyleneacetoacetate (Liebermann, A., 1909, i, 403) has been effected in order to support the constitutions assigned by the author to methylxanthophanic acid and its transformation product. Resacetophenone itself condenses with ethyl ethoxymethyleneacetoacetate in presence of alcoholic sodium ethoxide to yield 2-*resorcyl*-5-*acetyl*-1 : 4-*pyrone*,



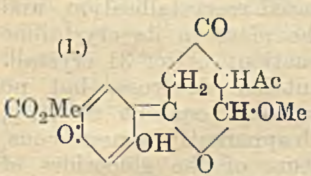
$$\begin{array}{l}\phantom{C_6H_3(OH)_2\cdot{}}CH\cdot CO\cdot CAc\\ C_6H_3(OH)_2\cdot C{—}O{—}CH\end{array}$$

m. p. 169—170° (which with diazomethane yields another *substance*, m. p. 168°); and with *ethyl ethoxymethylenebenzoylacetate* (prepared, mixed with ethyl benzoylacetate, from which it cannot be separated, by the action of this ester on ethyl orthoformate and acetic anhydride) to yield 2-*resorcyl*-5-*benzoyl*-1 : 4-*pyrone*, m. p. 180°. Treatment of the transformation product obtained by the action of magnesium methoxide on ethylxanthophanic acid (*idem*, *ibid.*, 1908, i, 548) with sulphuric acid merely hydrolyses the ester group without eliminating a molecule of alcohol, a *substance*, m. p. 176°, to which the constitution

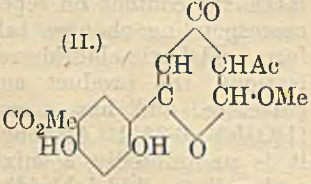


$$\begin{array}{l} \qquad\qquad\qquad\qquad \text{CH:CO·CHAc} \\ C_6H_2(OH)_2(CO_2H)\cdot\overset{|}{C}—O—\overset{|}{C}H\cdot OMe \end{array}$$

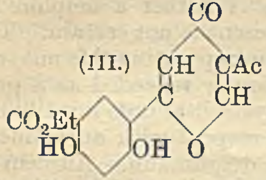
is assigned, being obtained. The following constitutions are therefore assigned to methylxanthophanic acid (I) and its transformation product (II), respectively, the action of magnesium methoxide merely bringing about a tautomeric change. The constitution of the ester,



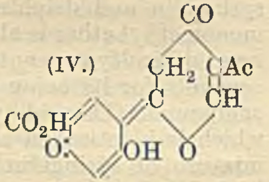
(I.)



(II.)



(III.)



(IV.)

m. p. 165°, obtained by Liebermann and the corresponding acid, m. p. 185°, are therefore represented by the formulæ (III) and (IV), respectively.

J. W. Baker.

Hydrogenation of xanthone and xanthen. V. Ipatiev and N. Orlov (Compt. rend., 1926, 183, 973—975).—Xanthone when hydrogenated in presence of copper oxide yields xanthen, which on further hydrogenation in presence of nickel oxide gives 2-*hydroxydi*cyclo*hexylmethane*, m. p. 40—43°, d_0^{20} 0·9581; this further gives *di*cyclo*hexylmethane*, b. p. 250—252°/763 mm.

L. F. Hewitt.

Tannins and related substances. XXII. Passage from the flavone to the catechin series. K. Freudenberg and A. Kammüller (Annalen, 1927, **451**, 209—213; cf. A., 1926, 73).—Catalytic reduction of quercetin pentamethyl ether (3 : 5 : 7 : 3′ : 4′-pentamethoxyflavone) in presence of platinum-black affords 11% of *dl*-*epi*catechin pentamethyl ether (A., 1925, i, 1165). *Luteolin tetramethyl ether* (5 : 7 : 3′ : 4′-*tetramethoxyflavone*), m. p. 192°, obtained by simultaneous hydrolysis and methylation of luteolin tetra-acetate, is hydrogenated under similar conditions, yielding 24% of deoxy*epi*catechin tetramethyl ether (*ibid.*, 419), identified as the *monobromo*-derivative, m. p. 155—156°.

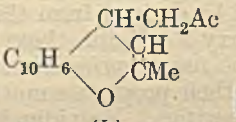
H. E. F. Notton.

Tannins and similar substances. XXIII. Syntheses of catechin derivatives. K. Freudenberg and M. Harder (Annalen, 1927, **451**, 213—222).—2 : 4 : 6-Trimethoxybenzaldehyde condenses with hippuric acid in presence of acetic anhydride and sodium acetate, forming 2-*phenyl*-4-*trimethoxybenzylideneoxazolone*, m. p. 172°. On hydrolysis with sodium hydroxide and oxidation of the resulting pyruvic acid with hydrogen peroxide, 2 : 4 : 6-*trimethoxyphenylacetic acid*, m. p. 183°, is obtained. The corresponding *acid chloride* condenses with veratrole in presence of aluminium chloride to give 3 : 4-*dimethoxyphenyl* 2 : 4 : 6-*trimethoxybenzyl ketone*, m. p. 144—145°. This is converted by magnesium methyl iodide into α-2 : 4 : 6-*trimethoxyphenyl*-β-3 : 4-*dimethoxyphenyl*-Δ^α^-*propylene*, which exists in two stereoisomeric forms, m. p. 89—90° and 101°, respectively, both of which are reduced by sodium and alcohol to α-2 : 4 : 6-*trimethoxyphenyl*-β-3 : 4-*dimethoxyphenylpropane*, identical with the pentamethoxy-derivative, m. p. 104—105° (A., 1925, i, 692), obtained from the reduction product of anhydrocatechin tetramethyl ether. The formation of the latter compound from catechin must therefore have been accompanied by a migration of the 3 : 4-dimethoxyphenyl group from the 2- to the 3-position.

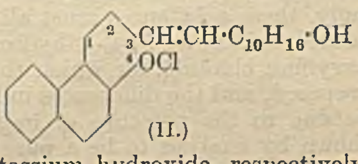
Attempts to isolate intermediate products of hydrogenation of cyanidin chloride (cf. *ibid.*, 1165) were unsuccessful. When, however, tetramethyl-luteolinidin chloride (*ibid.*, 825) is treated with 1 mol. of hydrogen in 96% alcoholic solution in presence of platinum-black and a little hydrochloric acid, α-3 : 4-dimethoxybenzoyl-β-2′-hydroxy-4′ : 6′-dimethoxyphenylethane is obtained. In absolute alcohol, ring-fission does not occur, the final and only isolable product being deoxy*epi*catechin tetramethyl ether (cf. preceding abstract). 2 : 4 : 6-Trimethoxybenzaldehyde is reduced by hydrogen and platinum-black to methylphloroglucinol trimethyl ether, b. p. 100—105°/1 mm., m. p. 27—28° (cf. Herzig, A., 1901, i, 205). When a nickel catalyst is used, a good yield of 2 : 4 : 6-*trimethoxybenzyl alcohol*, m. p. 63°, is obtained.

H. E. F. Notton.

Styrylpyrylium salts. VIII. 2-Styryl derivatives of β-naphthapyrylium chloride. R. Dickinson and I. M. Heilbron (J.C.S., 1927, 14—20; cf. *ibid.*, 1922, **121**, 1198; 1923, **123**, 2521).—Condensation of 2-naphthol-1-aldehyde with acetone in presence of alkali gives a poor yield of 1-*acetonyl*-3-*methyl*-1 : 4-β-*naphthapyran* (I), m. p. 152—153°. Condensation in presence of hydrogen chloride gives 3-(β-2′-*hydroxy*-1′-*naphthylvinyl*)-β-*naphthapyrylium chloride* (II). Addition of water to the warm alcoholic solution of this compound precipitates *di*-β-*naphtha*spiro*pyran* (cf. Löwenbein and Katz, A., 1926, 956; Dilthey and Wizinger, *ibid.*, 1163). Explanations are suggested for the colour-development in hot solutions of the spiran in nitrobenzene and



(I.)



(II.)

aqueous-alcoholic potassium hydroxide, respectively. The 2-styryl-β-naphthapyrylium salts are obtained in good yield by condensation of 2-naphthol-1-aldehyde with styryl methyl ketones in alcoholic solution in presence of dry hydrogen chloride. They show close resemblance to the 2-styrylbenzopyrylium salts. On treatment with aqueous sodium hydroxide, they give colourless solutions, slowly becoming intensely red. It is suggested that this may be due to fission of the pyrylium ring. The following are described: 3-*styryl*-β-*naphthapyrylium chloride* (+H·CO₂H);

3-p-*hydroxystyryl*-β-*naphthapyrylium chloride*, $(+2H_2O)$; 3-3′-*methoxy*-4′-*hydroxystyryl*-β-*naphthapyrylium chloride* $(+2H_2O)$; 3-p-*methoxystyryl*-β-*naphthapyrylium chloride* $(+H{\cdot}CO_2H,H_2O)$; 3-3′ : 4′-*dimethoxystyryl*-β-*naphthapyrylium chloride* $(+H{\cdot}CO_2H,H_2O)$; 3-3′ : 4′-*methylenedioxystyryl*-β-*naphthapyrylium chloride* $(+H{\cdot}CO_2H,H_2O)$; 3-p-*dimethylaminostyryl*-β-*naphthapyrylium perchlorate*.

M. Clark.

Synthesis of anthocyanins. II. Synthesis of 3- and 7-glucosidoxyflavylium salts. A. Robertson and R. Robinson (J.C.S., 1927, 242—247; cf. A., 1926, 956).—ω-O-*Tetra-acetylglucosidoxyacetophenone*, m. p. 104—105°, prepared from benzoylcarbinol and *O*-tetra-acetyl-α-glucosidyl bromide in presence of silver carbonate, condenses with β-resorcylaldehyde in ethereal solution in presence of hydrogen chloride, giving a product which yields, on deacetylation with methyl-alcoholic ammonia, 3-β-*glucosidoxy*-7-*hydroxyflavylium chloride*. This compound shows ψ-base formation on addition of sodium acetate. Hydrolysis of the chloride yields dextrose and 3 : 7-dihydroxyflavylium chloride. The latter is also obtained by direct condensation of β-resorcylaldehyde and benzoylcarbinol or its acetate. β-Resorcylaldehyde reacts with *O*-tetra-acetylglucosidyl bromide in acetone solution in presence of aqueous potassium hydroxide, giving 4-O-*tetra-acetylglucosidoxy*-2-*hydroxybenzaldehyde*, m. p. 134—135°, which condenses with ω-methoxyacetoveratrone, in presence of hydrogen chloride, giving, after deacetylation, 7-*glucosidoxy*-3 : 3′ : 4′-*trimethoxyflavylium chloride* (*picrate*, decomp. 240—252°). Hydrolysis yields fisetinidin chloride trimethyl ether.

M. Clark.

Vegetable colouring matters. I. Constitution of some anthocyanidins. P. Karrer and R. Widmer [in part with H. Hürlimann and O. Nievergelt] (Helv. Chim. Acta, 1927, **10**, 5—33).—Hydrolysis of anthocyanins with 10—15% sodium or barium hydroxide proceeds readily on boiling, and the acid product of fission, with methoxyl groups intact, may be isolated in the usual way. When œnin, myrtillin, althæin, ampelopsin, and malvin, or the corresponding anthocyanidins (cf. Willstätter, A., 1915, i, 282, 289), are treated in this way, pure syringic acid (4-hydroxy-3 : 5-dimethoxybenzoic acid) is obtained in each case in 10—35% yield. Accordingly, these substances must all be derived from the anthocyanidin, 5 : 7 : 4′-trihydroxy-3′ : 5′-dimethoxyflavylium chloride, for which the name *syringidin* is proposed, and the differences in their properties must be due to the presence of impurities. Malvidin is shown by analysis to be a pure compound, identical with syringidin. Œnin, which is conveniently purified by repeated recrystallisation of the picrate from boiling water, contains less than the theoretical amount of methoxyl, and is therefore not a pure compound. Œnidin chloride may be separated by fractional crystallisation from 7% sulphuric acid into more and less soluble fractions, of which the latter has a higher methoxyl content than the original material and a solubility of the same order as that of malvidin chloride. The dark red blooms of *Cyclamen persicum*, Mill., contain a monoglucoside, *cyclamin*, isolated as the *picrate*, $C_{29}H_{27}O_{19}N_3$, which yields œnidin on hydrolysis with acids and is probably identical with œnin. Pæonidin is hydrolysed by 16% sodium hydroxide, giving crystalline vanillic acid. This confirms the formula of Nolan, Pratt, and Robinson (A., 1926, 1043). Since cyanilidin (Kataoka, *ibid.*, 1150) also yields vanillic acid on hydrolysis, it must be identical and not isomeric with pæonidin. Myrtillin, regarded by Willstätter (*ibid.*, 1917, i, 47) as a galactoside of delphinidin monomethyl ether, is resolved by means of its picrate into two fractions. The more soluble one is methoxyl-free, and is hydrolysed by acids to delphinidin and a mixture of dextrose and galactose. The less soluble fraction increases in methoxyl content on repeated recrystallisation, and corresponding changes take place in its crystalline form and ferric chloride reaction. After 31 crystallisations, the product contains dextrose, but no galactose, and has a methoxyl content of 7·7% [1(OMe)=6·3%]. Although apparently homogeneous, it is undoubtedly a mixture of the glucosides of syringidin and delphinidin. Whether a delphinidin monomethyl ether is also present is not certain. The great difficulty encountered in separating this mixture accounts for its being previously regarded as a pure compound. On acid hydrolysis, it affords myrtillidin, which is identical in every respect with an artificial mixture of syringidin and delphinidin. Althæin is hydrolysed to dextrose and althæidin, which, although it corresponds in composition with a delphinidin monomethyl ether, is actually, like myrtillidin, a mixture or loose molecular compound of delphinidin and its dimethyl ether. When ampelopsin is purified through the picrate, its methoxyl content becomes much higher than that of the product described by Willstätter, and it is indistinguishable from œnin. The various reactions which these substances show with alcoholic ferric chloride may now be correlated with their syringidin content; thus malvin, a pure syringidin derivative, gives no reaction, œnin, cyclamin, and ampelopsin (80—90% pure) give a reddish-violet colour, whilst the different fractions of myrtillin (50% or less pure) give colours ranging from wine-red to pure blue as the methoxyl content decreases.

H. E. F. Notton.

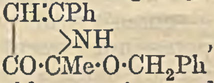
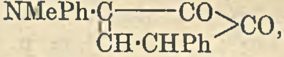
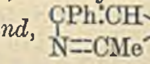
Vegetable colouring matters. II. P. Karrer and R. Widmer (Helv. Chim. Acta, 1927, **10**, 67—86).—*Monardæin*, the colouring matter of the flowers of the golden balm, *Monarda didyma*, is extracted by 2% methyl-alcoholic hydrogen chloride and purified by reprecipitating its *picrate* from hot water. *Monardæin chloride* is a red, amorphous powder which gives a scarlet aqueous solution. The picrate, *sulphate*, and *picrolonate* are also amorphous. It is hydrolysed by cold 10% sodium hydroxide to 1 mol. of *p*-hydroxycinnamic acid and 1 mol. of *monardin*. The latter is identical in composition, appearance, m. p. (280°), and reactions with pelargonin, but its specific rotation is smaller: $[\alpha]_D -244°$, $[\alpha]_{614} -133°$. It is hydrolysed by acids to 1 mol. of pelargonidin and 2 mols. of dextrose. Thus although monardæin chloride contains 4—6% of methoxyl, it must be a *p*-hydroxycinnamoylpelargonidin diglucoside. Pure pelargonidin may be rapidly and conveniently obtained from these flowers.

About 0·1% of a pure anthocyanin (*gentianin*) may be extracted from the dried flowers of the blue gentian, *Gentiana acaulis*, by digestion with 2% methyl-alcoholic hydrogen chloride, fractional precipitation of the crude dye with lead acetate, and reprecipitation of the amorphous *picrate* from hot water. *Gentianin chloride*, a bluish-red powder containing 10% of water, is hydrolysed by acids to 1 mol. of *p*-hydroxycinnamic acid, 1 mol. of delphinidin, and 1 mol. of dextrose, and is therefore a *p*-hydroxycinnamoyldelphinidin monoglucoside.

Dried pomegranate flowers (*Punica granatum*) contain about 0·1% of an anthocyanin, *punicin*, which may be isolated in the usual way and purified by means of its crystalline *ferrichloride*. *Punicin chloride* has m. p. 293°, $[\alpha]_D$ −232° or −246°, but in all other respects it is identical with monardin and pelargonin chlorides. It is hydrolysed by acids to dextrose and pelargonidin.

Sambucin, the anthocyanin of the elderberry (*Sambucus nigra*), is extracted from the fresh skins in the usual way and purified by recrystallising its picrate. *Sambucin chloride*, a red powder, which gives a brownish-red aqueous solution, consists principally of cyanidin rhamnoglucoside, $C_{27}H_{31}O_{15}Cl$, but analyses and determination of its partition coefficient between amyl alcohol and water indicate that it also contains a small amount of a monoglucoside of cyanidin. Sambucin is thus analogous to keracyanin and prunicyanin (Willstätter and Zollinger, A., 1917, i, 45).

Vicin, the anthocyanin of the dark-red vetch, is extracted from the dried flower in the usual way and purified through the crystalline *picrate*. *Vicin chloride*, which corresponds with the formula $C_{21}H_{21}O_{12}Cl,2H_2O$, forms apparently homogeneous brownish-red needles, and is hydrolysed by acids to a mixture of delphinidin with dextrose and rhamnose. The relative quantities of these indicate that vicin is a mixture of delphinidin monoglucoside and monorhamnoside in roughly equal amounts. The flowers of the scarlet vetch appear to contain a different anthocyanin. H. E. F. NOTTON.

New transformations of oximes and phenylhydrazones. O. DIELS, O. BUDDENBERG, and S. WANG (Annalen, 1927, 451, 223—241).—The perchlorates of α-phenyl-Δ^{α}-pentene-γδ-dione-δ-oxime and its methyl ether are decomposed into their components by water in the normal way. The *perchlorate*, m. p. 95°, of the corresponding *benzyl ether*, m. p. 80°, is, however, converted by a kind of Beckmann rearrangement into the isomeric 3-*keto*-5-*phenyl*-2-*methylpyrroline*-2-*benzyl ether*,  $\begin{array}{l}\text{CH:CPh}\\ |\qquad >\text{NH}\\ \text{CO·CMe·O·CH}_2\text{Ph}\end{array}$, m. p. 76°. This substance is highly reactive and readily absorbs atmospheric oxygen. With carboxyethylcarbimide, it gives a *compound*, $C_{22}H_{22}O_5N_2$, m. p. 95°. Alkali decomposes it into acetophenone and ammonia, whilst aniline, piperidine, and ammonia liberate benzyl alcohol, forming 2-*anilino*-, m. p. 192—194°, 2-*piperidino*-, m. p. 179°, and 2-*amino*-3-*keto*-5-*phenyl*-2-*methylpyrroline*, m. p. 201°, respectively. The last-named, for which the alternative formula NH₂·CPh:CH·CO·CMe:NH is suggested, is converted by nitrous acid into αβγδ-*tetraketo*-α-*phenylpentane*-β-*monoxime*, yellow, m. p. 56° (decomp.). This is readily and quantitatively decomposed, on warming in inert solvents, into benzoyl cyanide, carbon monoxide, and acetic acid. When a methyl-alcoholic solution of α-phenyl-Δ^{α}-pentene-γδ-dione-δ-phenylmethylhydrazone (A., 1911, i, 464) is boiled for a short time in absence of air, the isomeric 2-*phenylmethylamino*-3-*keto*-5-*phenyl*-2-*methylpyrroline* (I), m. p. 117—118°, is obtained. On shaking with oxygen, it gives a *dioxide*, decomp. 126—127°, which may be prepared in the same way from the original phenylmethylhydrazone in presence of formic or perchloric acid. When the dioxide is exposed to the air, or when (I) is treated with alkaline hydrogen peroxide, 2-*phenylmethylamino*-4-*hydroxy*-3-*keto*-5-*phenyl*-2-*methylpyrroline*, intense yellow, m. p. 151° [*semicarbazone*, m. p. 180°; *phenylhydrazone*, m. p. 99—111° (decomp.)], is formed. This gives a *quinoxaline* derivative, $C_{24}H_{22}N_4$, m. p. 158—159°, with *o*-phenylenediamine. When the pyrroline is heated with formic acid, nitrogen is eliminated from the ring, which then closes in a different way, yielding 3-*phenylmethylamino*-1:2-*diketo*-5-*phenyl*-Δ^3-cyclo*pentene*,  $\begin{array}{l}\text{NMePh·C——CO}\\ \quad\ \ \text{CH·CHPh}\end{array}>\text{CO}$, m. p. 200—201° (*quinoxaline* derivative, $C_{24}H_{19}N_3$, m. p. 182°). 2-*Phenylmethylamino*-3-*keto*-5-p-*anisyl*-2-*methylpyrroline dioxide*, decomp. 122°, is also described. When (I) is heated with formic acid in absence of air, methylaniline is eliminated, leaving the *compound*,  $\begin{array}{l}\text{CPh:CH}\\ \text{N==CMe}\end{array}>\text{CO}$, bright yellow, m. p. 220—221° (decomp.). H. E. F. NOTTON.

Catalytic hydrogenation of pyridine. W. S. SADIKOV and A. K. MIKHAILOV (J. Russ. Phys. Chem. Soc., 1926, 58, 527—540).—Pyridine was hydrogenated in an open tube, and by Ipatiev's method under pressure in the presence of catalysts prepared by Zelinsky's method. In an open tube at 150°, with 40% platinised asbestos, the hydrogenation was very slow (300 hrs.) The product was fractionated and the refractive indices and densities were determined. No amylamine was isolated, but 60% of tetrahydropyridine, together with condensation products of higher b. p. With 20% platinised asbestos at 200°, hydrogenation by Ipatiev's method was very slow: after 6 hrs. 6·6%, after 24 hrs., 7·8%; at 250° after 16 hrs., about 20%. Palladised asbestos (20%), under the same conditions, gave a 70% yield after 19 hrs., whilst 20% iridised asbestos gave complete absorption of hydrogen after 12 hrs. With 20% osmised asbestos, absorption is complete after 6 hrs. at 240°, and a 30% yield of condensation products of higher b. p. is obtained; 5% and 1% osmium catalysts also give complete absorption. The theories of contact catalysis of Willstätter, Langmuir, and Bodenstein are discussed, and a mechanism is suggested. The efficiency of the catalysts is in the order of their oxidisability: a colloidal suspension of the metal in pyridine may be formed which adsorbs oxygen and causes the hydrogen molecule to dissociate into atoms, which then add on to the unsaturated compound. The possible influence of traces of water is also mentioned. M. ZVEGINTZOV.

Syntheses of tetrahydro*iso*quinoline and *as*-homotetrahydro*iso*quinoline bases according to the glycine–aluminium chloride method. II. J. von Braun and K. Wirz (Ber., 1927, 60, [*B*], 102—110; cf. A., 1924, i, 873).—The primary effect of the successive action of phosphorus pentachloride and aluminium chloride on glycine derivatives, $C_6H_5\cdot[CH_2]_n\cdot NR\cdot CH_2\cdot CO_2H$ (where $n=2$ or 3), is to cause loss of carbon monoxide; ring closure to tetrahydro*iso*quinoline or *as*-homotetrahydro*iso*quinoline derivatives occurs subsequently and appears to be independent of the nature of the substituent, R.

Methyl-β-phenylethylamine is converted by ethyl bromoacetate in ethereal solution into *ethyl methyl-β-phenylethylaminoacetate*, $Ph\cdot[CH_2]_2\cdot NMe\cdot CH_2\cdot CO_2Et$, b. p. 151—155°/12 mm. (non-crystalline *hydrochloride* and *picrate*; *methiodide*, m. p. 160°), from which *methyl-β-phenylethylaminoacetic acid*, m. p. 163° (*hydrochloride*, m. p. 155°), is prepared. The acid is converted by phosphorus pentachloride in presence of acetyl chloride into *methyl-β-phenylethylaminoacetyl chloride hydrochloride*, which, with aluminium chloride in benzene, affords 2-*methyltetrahydro*isoquinoline, b. p. 213° (*hydrochloride*, m. p. 163°; *picrate*, m. p. 146°; *methiodide*, m. p. 189°).

p-Xylyl bromide is converted by potassium cyanide in aqueous acetone in 95% yield into the corresponding nitrile, which is catalytically hydrogenated to β-*p*-tolylethylamine. Alternatively, β-*p*-tolylethyl alcohol, from *p*-bromotoluene, magnesium, and ethylenechlorohydrin, is converted successively into β-p-*tolylethyl bromide*, b. p. 115°/14 mm., β-p-*tolylethylphthalimide*, m. p. 113°, and β-*p*-tolylethylamine. With ethyl bromoacetate, the base yields *ethyl* β-p-*tolylethylaminoacetate*, b. p. 176—177°/21 mm., transformed successively into β-p-*tolylethylaminoacetic acid hydrochloride*, m. p. 216°, and *benzenesulphonyl*-β-p-*tolylethylaminoacetic acid*, m. p. 89°. The latter substance with phosphorus pentachloride and aluminium chloride in nitrobenzene affords 2-*benzenesulphonyl*-7-*methyltetrahydro*isoquinoline, m. p. 154°, hydrolysed to 7-*methyltetrahydro*iso*quinoline*, b. p. 125°/18 mm., d_4^{24} 1·0176 (*hydrochloride*, m. p. 216°; *picrate*, m. p. 202°; *methiodide*, m. p. 133°; *nitroso*-compound, m. p. 87°; non-crystalline *benzoyl* derivative).

β-*p*-Tolylethyl bromide is converted by potassium cyanide into β-p-*tolylpropionitrile*, b. p. 137°/15 mm., which is reduced by Ladenburg's method to γ-p-*tolyl*-n-*propylamine*, b. p. 126°/23 mm. (*hydrochloride*, m. p. 225°; *picrate*, m. p. 154°; *benzoyl* derivative, m. p. 85°; *phenylthiocarbamide* compound, m. p. 82°). With ethyl bromoacetate, the amine affords *ethyl* γ-p-*tolylpropylaminoacetate*, b. p. 191°/22 mm., which yields γ-p-*tolylpropylaminoacetic acid hydrochloride*, m. p. 211°, and *benzenesulphonyl*-γ-p-*tolylpropylaminoacetic acid*, m. p. 116°. 2-*Benzenesulphonyl*-8-*methyl*-as-*homotetrahydro*iso*quinoline*, m. p. 126°, is hydrolysed by hydrochloric acid at 130° to the free *base*, b. p. 137—139°/19 mm., m. p. 27°, d_4^{23} 1·0048 (*hydrochloride*, m. p. 223°; *benzoyl* derivative, m. p. 101°; *nitroso*-compound, m. p. 91°).

p-Bromocumene is converted by magnesium and ethylenechlorohydrin into β-p-iso*propylphenylethyl alcohol*, b. p. 147°/20 mm., and thence successively into β-p-iso*propylphenylethyl bromide*, b. p. 134—136°/20 mm., β-p-iso*propylphenylpropionitrile*, b. p. 150°/17 mm., and γ-p-iso*propylphenyl*-n-*propylamine*, b. p. 143°/20 mm. (*hydrochloride*, m. p. 196°; *picrate*, m. p. 122°; *benzoyl* derivative, m. p. 71°). The amine is converted successively into *ethyl* γ-p-iso*propylphenyl*-n-*propylaminoacetate*, b. p. 205—210°/20 mm., γ-p-iso*propylphenyl*-n-*propylaminoacetic acid hydrochloride*, m. p. 210°, *benzenesulphonyl*-γ-p-iso*propylphenyl*-n-*propylaminoacetic acid*, m. p. 101°, 2-*benzenesulphonyl*-8-iso*propyl*-as-*homotetrahydro*iso*quinoline*, m. p. 92°, and 8-iso*propyl*-as-*homotetrahydro*iso*quinoline*, b. p. 146°/13 mm., m. p. 31° (*hydrochloride*, m. p. 248°; *picrate*, m. p. 236°; *methiodide*, m. p. 214°; *benzoyl* derivative, m. p. 83°; *nitroso*-compound, m. p. 70°).

Piperonal is very smoothly hydrogenated in decahydronaphthalene in the presence of nickel to piperonyl alcohol, b. p. 157°/16 mm., m. p. 54°, which is converted through the corresponding chloride and cyanide into homopiperonylamine. The ester formed from the amine and ethyl bromoacetate is very readily hydrolysed to β-*methylenedioxyphenylethylaminoacetic acid hydrochloride*, m. p. 241°. *Benzenesulphonyl*-β-*methylenedioxyphenylethylaminoacetic acid*, m. p. 131°, does not suffer smooth ring closure when treated with phosphorus pentachloride and aluminium chloride.

H. Wren.

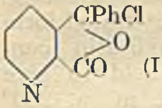
Preparation and properties of pyrrole-1-carboxylic acid, its amide, pyrrolide, and glycine derivative. W. Tschelinzev and B. Maxorov (Ber., 1927, 60, [*B*], 194—199).—*Pyrrole*-1-*carboxylic acid*, m. p. 95° (decomp.), is obtained by cautious hydrolysis of ethyl pyrrole-1-carboxylate, b. p. 180°, or from the aqueous liquors derived from the action of ethyl chloroformate on sodium pyrrole. It decomposes slowly at the ordinary temperature, rapidly when heated, into carbon dioxide and pyrrole. The *ammonium* salt is described, but the sodium, potassium, barium, calcium, and silver compounds are too unstable to permit isolation. The acid is converted by phosphorus pentachloride in presence of chloroform into the corresponding chloride, and thence into the amide, m. p. 166°, pyrrolide, $C_4H_4N\cdot CO\cdot NC_4H_4$, m. p. 61°, and *ethyl* 1-*pyrroylaminoacetate*, m. p. 77—78° (whence 1-*pyrroylglycine*, m. p. 156°). H. Wren.

Oxidation of pyridine and the pyridine nucleus with permanganate. M. Delépine (Compt. rend., 1927, 184, 206—208).—When a solution of pyridine in a mixture of potassium permanganate solution and a quantity of sulphuric acid equivalent to the potassium present is warmed to 70°, the pyridine is rapidly oxidised to carbon dioxide and ammonia. A portion of the latter is oxidised to nitric acid, since the quantity of permanganate required for the complete oxidation of the pyridine is in excess of that given by the equation $2C_5H_5N+11O_2=10CO_2+2NH_3+2H_2O$. α-Picoline similarly yields a considerable quantity of acetic acid (and some formic acid), whilst acetic and butyric acids are isolated from the products obtained by the oxidation of 2 : 5-dimethyl-4-propylpyridine. Quinoline and *iso*quinoline are similarly oxidised with the production of ammonia. J. W. Baker.

Tautomerism of 2-aminopyridine. II, III, IV. A. E. Tschitschibabin (J. Russ. Phys. Chem. Soc., 1926, 57, 399—425).—See A., 1924, i, 987; 1925, i, 158, 1328, respectively.

E. Rothstein.

Chloride and ester of 3-benzoylpyridine-2-carboxylic acid. A. Kirpal and H. Kunze (Ber., 1927, 60, [*B*], 138—140).—3-Benzoylpyridine-2-carboxylic acid is converted by thionyl chloride into a difficultly separable mixture of products; if, however, the reagent is saturated with hydrogen chloride, the *hydrochloride* of 3-*benzoylpyridine*-2-*carboxyl ψ-chloride*, m. p. 103°, separates, from which the *ψ-chloride* (I), m. p. 93°, is derived. Cautious treatment with methyl alcohol transforms the latter compound into the *methyl ψ-ester*, m. p. 89°, characterised by its ready hydrolysis by acids and rapid isomerisation to the normal ester by alkali.


(I.)

H. Wren.

Nitration of 2-, 3-, and 4-phenylpyridines. R. Forsyth and F. L. Pyman (J.C.S., 1926, 2912—2924; cf. Forsyth, Nimkar, and Pyman, A., 1926, 611).—By the action of acetyl chloride and acetic acid on sodium *p*-nitrobenzene*iso*diazotate dissolved in pyridine (Kühling, A., 1895, i, 290; 1896, i, 236) there is obtained a mixture of the three *p*-nitrophenylpyridines, separated by fractional crystallisation of the bases, hydrochlorides, and nitrates. 2-*p*-Nitrophenylpyridine, m. p. 130·5—131·5° (*hydrochloride*, m. p. 185—186°), is reduced by tin and hydrochloric acid to 2-p-*aminophenylpyridine*, m. p. 97—98° [*dihydrochloride* does not melt at 310°; *picrate*, m. p. 218—219° (decomp.)], which is converted by reduction of the diazo-compound into 2-p-*hydrazinophenylpyridine*, m. p. 117°. 2-Phenylpyridine [*nitrate*, m. p. 115—117°; picrate, m. p. 176—177°; chloroplatinate, m. p. 209° (decomp.)], obtained in poor yield, with much 2-p-*phenetylpyridine*, m. p. 74—75° (*picrate*, m. p. 168—170°), by the action of amyl nitrite and alcohol on 2-*p*-aminophenylpyridine dihydrochloride, and in good yield by oxidation of the hydrazine with cupric acetate, is volatile in steam. 3-p-*Nitrophenylpyridine*, m. p. 148—149° (*nitrate*, m. p. 198°), the corresponding *amine*, m. p. 102—104° (+H_2O) or 118—120° (anhyd.) [*dihydrochloride*, m. p. about 310° (decomp.); *picrate*, m. p. 185—188° (yellow form) or 219—220° (orange form)], and *hydrazine*, m. p. 156—157°, and 3-phenylpyridine (an oil, volatile in steam; picrate, m. p. 162—164°; *nitrate*, m. p. 78—80°), are described, and also 4-p-*nitrophenylpyridine*, m. p. 123—124° (*hydrochloride*, m. p. 255°); the corresponding *amine*, m. p. 232—234° [*dihydrochloride*, m. p. 312° (decomp.)], and *hydrazine*, m. p. 205—207° [*dihydrochloride*, m. p. 272° (decomp.)], and 4-phenylpyridine, m. p. 74°, b. p. 282—284°/762 mm. (*dinitrate*, m. p. 114—115°; *mononitrate*, m. p. 140°). 4-Phenylpyridine is also synthesised by the Hantzsch method from benzaldehyde, ethyl acetoacetate, and ammonia.

Nitration of the three phenylpyridines by addition of their nitrates to sulphuric acid gives mixtures of *o*-, *m*-, and *p*-nitrophenylpyridines, the yields being from 2-phenylpyridine, 6% *o*-, 34·9% *m*-, 42·3% *p*-; from 3-phenylpyridine, 64·3% *p*-; from 4-phenylpyridine, 12·7% *o*-, 28·5% *m*-, 38·0% *p*-. The following phenylpyridines are new: 2-m-*nitro*-, m. p. 73—74° (*nitrate*, m. p. 193°; *methosulphate*); 2-o-*nitro*-, m. p. 60—61°; 4-m-*nitro*-, m. p. 109—110° [*nitrate*, m. p. 222° (decomp.): *methosulphate*]; 4-o-*nitro*-, m. p. 51—52° (+H_2O) (*nitrate*, m. p. 178—179). All the above m. p. are corrected.

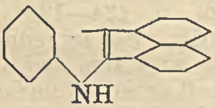
C. Hollins.

Indole group. I. H. Maurer and E. Moser (Z. physiol. Chem., 1926, **161**, 131—142).—The synthesis of β-3-indolinylpropionic acid (indole-3-propionic acid) from ethyl indole-2-carboxylate is described, and a synthesis of tryptophan is announced. Ethyl indole-2-carboxylate, m. p. 124—125° (free acid, m. p. 203°), prepared in 65% yield by reduction of ethyl *o*-nitrophenylpyruvate with zinc and acetic acid in presence of a little cobalt or nickel nitrate, is converted into the 3-aldehydo-ester (Fischer and Pistor, A., 1924, i, 86), which by condensation with ethyl malonate in presence of piperidine yields 3-*ethyl* 3-ββ-*dicarbethoxyvinylindole*-2-*carboxylate*, m. p. 141—142°. This is reduced by the Paal–Skita method to *ethyl* 3-ββ-*dicarbethoxyethylindole*-2-*carboxylate*, m. p. 77—78°, which is also prepared directly from ethyl indole-2-carboxylate and ethyl methoxymethylmalonate in alcoholic hydrochloric acid. The tricarboxylic *acid*, m. p. 198—199°, obtained by hydrolysis with aqueous-alcoholic alkali, is converted by heating at 200° into 2-carboxyindole-3-propionic acid (Kalb, Schweizer, and Schimpf, *ibid.*, 1926, 1151), m. p. 194° (ethyl ester, m. p. 94—85°), or at 215° into indole-3-propionic acid, m. p. 134°. Partial hydrolysis of the tricarboxylic ester gives 3-ββ-*dicarbethoxyethylindole*-2-*carboxylic acid*, m. p. 168—169°, which is decarboxylated at 190° to *ethyl* 3-*ethylindole*-ωω-*dicarboxylate*, m. p. 142° (free *acid*, m. p. 188—189°).

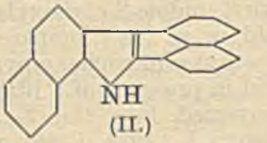
C. Hollins.

Indole condensation of phenylhydrazones. A. Korczyński, W. Brydowna, and L. Kierzek (Gazzetta, 1926, 56, 903—914).—It has been shown (A., 1925, i, 973, 1097) that the condensation of phenylhydrazones to indoles is catalysed by small quantities of salts such as cupric or nickelous chloride. It is now found that the metallic ions are not catalysts: acetonephenylhydrazone heated in an alcoholic solution of cupric chloride did not condense, nor did acetophenonephenylhydrazone in benzene or chloroform with copper acetylacetone. Comparing methods of condensation, heating with a small quantity of nickel chloride is found to be more effective than the use of excess of zinc chloride, and even to succeed when hydrogen chloride in alcohol has no action. Indoles have been prepared from the phenylhydrazones of the following substances: Butaldehyde: hydrogen chloride in alcohol has no action, but nickel chloride gives 3-ethylindole, b. p. 146—151°/12 mm. (cf. Pictet and Duparc, A., 1888, 370). *n*-Octaldehyde: excess of zinc chloride gives a much smaller yield than a little nickel chloride of 3-n-*hexylindole*, a yellow liquid, b. p. 212—224°/14 mm. *n*-Nonaldehyde: nickel chloride yields 3-n-*heptylindole*, a red liquid, b. p. 179—182°/3 mm. [It is concluded from the character of these two substances that the solid "3-pentylindole" previously described (*loc. cit.*), is a polymeride]. Acetoveratrone: the *phenylhydrazone*, b. p. 120—130°/12 mm. (*hydro-*

chloride described), gives on distillation, alone or with nickel chloride, 2-*veratrylindole*, b. p. 210—215°/15 mm.; this substance gives a brown pine-shaving reaction. *p*-Phenoxyacetophenone: alcoholic hydrogen chloride has no effect, but nickel chloride gives 2-p-*phenoxyphenylindole*, yellow, m. p. 169°. Acenaphthenone: alcoholic hydrogen chloride gives 2 : 3-peri*naphthyleneindole* (I), orange, m. p. 200°, no pine-shaving reaction. Acenaphthenone α-naphthylhydrazone gives with hydrogen chloride or nickel chloride 2 : 3-peri*naphthylene*-α-*naphthindole* (II), yellowish-brown, m. p. 256° (black *picrate*, m. p. 260°).



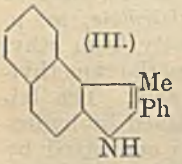
(I.)



(II.)

Phenyl propyl ketone: nickel chloride gives 2-*phenyl*-3-*ethylindole*, yellow, m. p. 65° (*picryl* derivative hydrolysed by alcohol); this is anomalous in giving a reddish-violet pine-shaving reaction. *Dibenzyl ketone* α-*naphthylhydrazone*, m. p. 105°, treated with alcoholic hydrogen chloride gives 3-*phenyl*-2-*benzyl*-α-*naphthindole*, pale violet, m. p. 155—156°, no pine-shaving reaction. *Propiophenone* β-*naphthylhydrazone* gives 2-*phenyl*-1-*methyl*-β-*naphthindole* (III) with nickel chloride, yellow, m. p. 115°.

(III.)



Attempts to prepare substituted indoles from phenylhydrazones substituted with negative groups in the nucleus of the phenylhydrazine have again failed.

When a phenylhydrazone condenses in two directions to give 2- and 2 : 3-substituted derivatives, the former can be determined by coupling with *p*-nitrobenzenediazonium chloride. This gives with 2-methyl- and 2-phenyl-indoles, respectively, 3-p-*nitrobenzeneazo*-2-*methylindole*, red, darkens at 210°, m. p. 219—220°, and 2-*phenyl*-3-p-*nitrobenzeneazoindole*, bluish-black, m. p. 280°, and when methyl ethyl ketone phenylhydrazone is heated with nickel chloride, the 2-ethylindole which forms 20% of the product is thus isolated as 3-p-*nitrobenzeneazo*-2-*ethylindole*, m. p. 60°.

E. W. Wignall.

Decomposition of β-3-indolylpropionic azide. R. H. F. Manske and R. Robinson (J.C.S., 1927, 240—242).—The *methyl* ester, m. p. 79—80°, of β-3-indolylpropionic acid (A., 1926, 1151) reacts with hydrazine hydrate to give β-3-*indolylpropionhydrazide*, m. p. 129—130°, converted by the action of nitrous acid into the corresponding azide. The latter is decomposed in boiling benzene solution, in presence of hydrogen chloride, giving 3-*keto*-3 : 4 : 5 : 6-*tetrahydro*-4-*carboline*, m. p. 173—174°. The constitution is established by distillation with zinc dust in a stream of hydrogen, when indole, accompanied by a small amount of norharman, is obtained.

M. Clark.

Relative stability of quinoline and indolinone rings. J. A. Aeschlimann (J.C.S., 1926, 2902—2912).—Gränacher and Mahal's "oxindole-3-acetic acid" (A., 1923, i, 713) is shown to be 2-ketotetrahydroquinolone-4-carboxylic acid; the quinoline ring is formed in preference to the indolinone ring.

2-Quinolone-4-carboxylic acid, m. p. 343° (methyl ester, m. p. 241°; ethyl ester, m. p. 205°), prepared (*a*) from isatin and malonic acid in presence of sodium acetate and acetic acid (Borsche and Jacobs, A., 1914, i, 322), (*b*) from acetylisatin and sodium hydroxide (Camps, *ibid.*, 1900, i, 115, 310), (*c*) from acetylisatin or acetylisatic acid and sodium acetate crystals, is reduced by sodium amalgam, by zinc and acetic acid, by hydriodic acid and phosphorus, or by aluminium amalgam, to 2-ketotetrahydroquinoline-4-carboxylic acid, m. p. 220° (methyl ester, m. p. 164°; ethyl ester, m. p. 146°), also obtained in the monohydrated form (*o*-aminophenylsuccinic acid). 1-Methylisatin condenses with malonic acid in acetic acid to give 1-methyl-2-quinolone-4-carboxylic acid, m. p. 250° (*methyl* ester, m. p. 120°; ethyl ester, m. p. 134—135°), together with *o*-methylamino-β-carboxycinnamic acid, m. p. 163°. Reduction of the former yields 2-*keto*-1-*methyltetrahydroquinoline*-4-*carboxylic acid*, m. p. 171° (*methyl* ester, m. p. 80°), also obtained by methylation of ketotetrahydroquinolinecarboxylic acid. 1-*Phenylacetylisatin*, m. p. 188°, prepared from sodioisatin and phenylacetyl chloride, is converted by hot sodium hydroxide solution into 3-phenyl-2-quinolone-4-carboxylic acid, m. p. 295° (Gysae, A., 1894, i, 27; Hübner, *ibid.*, 1908, i, 288; Borsche and Jacobs, *loc. cit.*). 3-Thiol-2-quinolone-4-carboxylic acid (Gränacher and Mahal's "oxindole-3-thiolacetic acid") condenses with *o*-phenylenediamine to give a *quinoxaline* derivative (+1MeOH or EtOH, not removable without decomp.). 2-Chlorocinchoninic acid, m. p. 196—200° (decomp.), and its ethyl ester, m. p. 63°, are obtained by the action of phosphorus pentachloride on 2-quinolone-4-carboxylic acid and ethyl ester, respectively. 6-Iodo-2-quinolone-4-carboxylic acid, unmelted at 300° (*methyl* ester, m. p. 261°; *ethyl* ester, m. p. 223°), is prepared by iodination and also from 5-iodoisatin and from 5-*iodo*-1-*acetylisatin*, m. p. 195°. Iodination of 2-ketotetrahydroquinoline-4-carboxylic acid at the ordinary temperature yields the 6(?)-*iodo*-derivative, m. p. 208° [*ethyl* ester, m. p. 169°; 5-*iodo*-2-*aminophenylsuccinic acid*, m. p. 180° (rapidly heated)]; the 6(?)-*bromo*-compound has m. p. 197°. 6-*Iodo*-3-*phenyl*-2-*quinolone*-4-*carboxylic acid*, obtained from 5-iodoisatin and phenylacetic acid, is reduced by sodium amalgam to 2-keto-3-phenyltetrahydroquinoline-4-carboxylic acid, m. p. 202° (Gysae's "dihydroisaphenic acid").

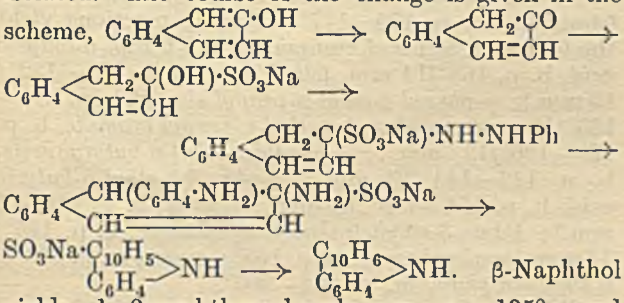
C. Hollins.

Synthesis of some substituted 3-methylquinolines. S. G. Willimott and I. A. Simpson (J.C.S., 1926, 2807—2811).—*o*-Nitroaldehydes are condensed with propaldehyde at the ordinary temperature in presence of pyridine to form an aldol which is reduced directly to the quinoline by zinc dust and acetic acid, or is converted by acetic anhydride into a cinnamaldehyde and thence by reduction with stannous chloride into the quinoline. *o*-Nitrobenzaldehyde gives in 64% yield 3-methylquinoline [chloroplatinate, m. p. 249°; *ethiodide*, m. p. 220° (decomp.); *dichromate*, m. p. 134°; *silver nitrate* double salt, m. p. 180°]. 6-Nitropiperonal gives an 18% yield of 6 : 7-*methylenedioxy*-3-*methylquinoline*, m. p. 74° (+$2H_2O$) or 105—106° (anhyd.) (*chloroplatinate*; *chloroaurate*; *picrate*, m. p. 259°; *methiodide*, m. p.

240°; *ethiodide*, m. p. 195°). From 6-nitroveratraldehyde are obtained β-*hydroxy*-β-6-*nitro*-3 : 4-*dimethoxyphenyl*isobutaldehyde, 6-*nitro*-3 : 4-*dimethoxy*-α-*methylcinnamaldehyde*, m. p. 165—166°, and 6 : 7-*dimethoxy*-3-*methylquinoline*, m. p. 81—83° [*hydrochloride*, m. p. 220—223° (decomp.); *methiodide*, m. p. 245° (decomp.)]; and from 6-nitro-3-methoxybenzaldehyde, 6-*nitro*-3-*methoxy*-α-*methylcinnamaldehyde*, m. p. 115—116°, and 6-*methoxy*-3-*methylquinoline* [*hydrochloride*, m. p. 213—215°; *methiodide*, m. p. 280—283° (decomp.); *chloroplatinate*]. C. HOLLINS.

Condensation of 2-methylquinoline with *m*-nitrobenzaldehyde. T. W. J. TAYLOR and C. P. WOODHOUSE (J.C.S., 1926, 2971).—The sole product of the interaction of 2-methylquinoline and *m*-nitrobenzaldehyde at 100°, with or without zinc chloride, is 2-*m*-nitrostyrylquinoline, m. p. 156° [picrate, m. p. 261° (decomp.); dibromide, m. p. 170—171°]. No 2-β-hydroxy-β-*m*-nitrophenylethylquinoline is formed (cf. Wartanian, A., 1890, 329). C. HOLLINS.

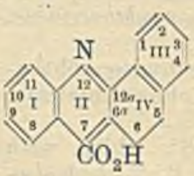
Tautomerism of phenols. IX. Formation of naphthacarbazoles from naphthols. W. FUCHS and F. NISZEL (Ber., 1927, 60, [*B*], 209—217; cf. this vol., 53).—The interaction of naphthols, phenylhydrazine, and sulphurous acid has been followed analytically by determination of excess of phenylhydrazine, ammonia, and aniline. Quantitative production of hydrazo-compounds involves the complete disappearance of phenylhydrazine, whereas subsequent formation of carbazoles requires the production of 1 mol. of ammonia for each mol. of phenylhydrazine used. Oxidation of the hydrazine produces equivalent amounts of ammonia and aniline. Smooth utilisation of phenylhydrazine with exclusive production of ammonia is observed with derivatives of β-naphthol, whereby naphthacarbazoles are formed and the intermediate *oo'*-diamines can be isolated. The course of the change is given in the scheme,



$$C_6H_4\lt\begin{matrix}CH{:}C\cdot OH\\ CH{:}CH\end{matrix} \longrightarrow C_6H_4\lt\begin{matrix}CH_2\cdot CO\\ CH{=}CH\end{matrix} \longrightarrow C_6H_4\lt\begin{matrix}CH_2\cdot C(OH)\cdot SO_3Na\\ CH{=}CH\end{matrix} \longrightarrow C_6H_4\lt\begin{matrix}CH_2\cdot C(SO_3Na)\cdot NH\cdot NHPh\\ CH{=}CH\end{matrix} \longrightarrow C_6H_4\lt\begin{matrix}CH(C_6H_4\cdot NH_2)\cdot C(NH_2)\cdot SO_3Na\\ CH{=\!=\!=}CH\end{matrix} \longrightarrow \begin{matrix}SO_3Na\cdot C_{10}H_5\\ C_6H_4\end{matrix}\gt NH \longrightarrow \begin{matrix}C_{10}H_6\\ C_6H_4\end{matrix}\gt NH.$$

β-Naphthol yields 1 : 2-naphthacarbazole, m. p. 135°, and 1-o'-*aminophenyl*-2-*naphthylamine*, m. p. 154°, which passes into the carbazole derivative when heated with sulphurous acid. 2 : 7-Dihydroxynaphthalene affords 7-*hydroxy*-1 : 2-*naphthacarbazole*, m. p. 178° (*benzoyl* derivative, m. p. 190°), and 7-*hydroxy*-1-o-*aminophenyl*-2-*naphthylamine* (*hydrochloride*); under modified conditions, 1 : 2 : 7 : 8-*naphthadicarbazole*, m. p. 338°, is produced. The formation of an additive *compound*, $C_{21}H_{21}O_4N_3S$, m. p. 193° (decomp.), from 2 : 7-dihydroxynaphthalene, sulphurous acid, and phenylhydrazine, is described. 2 : 7-Dihydroxynaphthalene methyl ether affords 7-*methoxy*-1 : 2-*naphthacarbazole*, m. p. 191° (also obtained from the hydroxy-compound and methyl sulphate), and 7-*methoxy*-1-o-*aminophenyl*-2-*naphthylamine*. 2 : 3-Dihydroxynaphthalene is converted by protracted treatment with phenylhydrazine hydrogen sulphite into a resin from which 3-*hydroxy*-1 : 2-*naphthacarbazole* and 3-*hydroxy*-1-o-*aminophenyl*-2-*naphthylamine*, m. p. 109—110° (*hydrochloride*), can be extracted with alkali hydroxide; the main product of the action appears to be 3-benzeneazo-1 : 2-naphthacarbazole. H. WREN.

Tetrophan. J. VON BRAUN (Annalen, 1926, **451**, 1—54; cf. A., 1923, i, 143, 947).—The physiological properties of a number of derivatives of tetrophan (annexed formula) have been examined with a view to determine the relationship between the structures and physiological actions of tetrophan and atophan (2-phenylquinoline-4-carboxylic acid). The presence of the carboxyl group appears essential, its elimination, substitution by other groups, or movement to one of the side rings causing the tetrophanic action to be lost. Removal of one of the rings I or III destroys the action, whilst the action is weakened by fusion of either another benzene ring in the 2 : 3-position or a saturated hydrocarbon ring in the 2 : 3- or 9 : 10-positions. Substitution in rings I, III, and IV does not affect the qualitative nature of the action, but the nature and position of the substituent have a quantitative effect. Rings II and III must be joined by a ring, IV, the length or degree of saturation of the carbon bridge having no qualitative although considerable quantitative effect on the action.



[With A. ROHMER.]—When 5 : 6-dihydro-α-naphthacridine is treated with nitric acid in acetic acid solution, it yields a *nitrate*, m. p. 158°, which is converted by sulphuric acid into a mixture of 8 : 10(?)-*dinitro*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 237°, and 8-*nitro*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 142° (*hydrochloride*, m. p. 220°; *nitrate*, m. p. 163°; *picrate*, m. p. 226°), which is oxidised by chromic acid in acetic acid solution to 8-*nitro*-5 : 6-*diketo*-α-*naphthacridine*, m. p. 250—270° (decomp.), and is readily hydrogenated to 8-*amino*-5 : 6-*dihydro*-α-*naphthacridine*, yellow needles, m. p. 94—95° [*dihydrochloride*, m. p. 280°; *dipicrate*, m. p. 202°; *methiodide* of *dimethyl* derivative, m. p. 176°; *acetyl* derivative, m. p. 197° (*hydrochloride*, m. p. 281°)]. The amino-compound is reduced by tin and hydrochloric acid to 8-*amino*-5 : 6 : 6*a* : 7 : 12 : 12*a*-*hexahydro*-α-*naphthacridine*, m. p. 103° (*diacetyl* derivative, m. p. 208°), and by Sandmeyer's reaction yields 8-*cyano*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 167°, which with alkalis yields 5 : 6-*dihydro*-α-*naphthacridine*-8-*carboxylic acid*, m. p. 237°.

[With H. JUNGMANN.]—Phosphorus pentachloride reacts with sodium 5 : 6-dihydro-α-naphthacridine-7-carboxylate, and treatment of the product with aqueous ammonia yields 5 : 6-*dihydro*-α-*naphthacridine*-7-*carboxylamide*, m. p. 220—222°, which by the Hofmann reaction in methyl-alcoholic solution gives the *methylurethane* derivative, m. p. 232—234°; this with hydrochloric acid yields 7-*amino*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 94—98° (*hydrochloride* described).

The silver salt of tetrophan reacts with acetobromoglucose in toluene solution, yielding the *acetylglucoside*, $C_{26}H_{31}O_{11}N$, m. p. 156°, $[\alpha]_D^{22}$ +21·5° in pyridine, which with methyl-alcoholic ammonia solution gives *tetrophanglucoside*, m. p. 78—80°. The physiological action of this substance is equal to that of tetrophan, probably due to the ready hydrolysis of the glucoside.

ω-Phthalimido-*o*-aminoacetophenone condenses with 1-ketotetrahydronaphthalene, yielding 7-*phthalimidomethyl*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 300°, which with hydrochloric acid gives 7-*aminomethyl*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 113° (*dihydrochloride*, m. p. 188—190°; *acetyl* derivative, m. p. 183°). Nitrous acid converts the amino-compound into 7-*hydroxymethyl*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 140° (*hydrochloride*, m. p. 190°).

[With F. Zobel.]—*ar*-β-Aminotetrahydronaphthalene reacts with hydroxylamine and chloral hydrate, yielding the iso*nitroso*-compound, $C_{10}H_{11}\cdot NH\cdot CO\cdot CH:NOH$, m. p. 166°, which with sulphuric acid gives a mixture of 4 : 5 : 6 : 7-*tetrahydro*-ang-β-*naphthisatin*, m. p. 189—190° (*phenylhydrazone*, m. p. 221°; *bromo*-derivative, m. p. 223°; *quinoxaline* derivative described), and 5 : 6 : 7 : 8-*tetrahydro*-lin-β-*naphthisatin*, m. p. 195° (*phenylhydrazone*, m. p. 255°; *bromo*-derivative, m. p. 236°; *quinoxaline* derivative described). The *lin*-β-compound yields the following substances: with hydrogen peroxide, 2-*amino*-5 : 6 : 7 : 8-*tetrahydronaphthalene*-3-*carboxylic acid*, m. p. 183°, which by elimination of the amino-group gives 5 : 6 : 7 : 8-*tetrahydro*-β-*naphthoic acid*, m. p. 153°; with *cyclo*hexanone, 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydrobenzacridine*-5-*carboxylic acid*, which on distillation yields 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydrobenzacridine*, m. p. 146° (*picrate*, m. p. 208°; *methiodide*, m. p. 231°), and this, when distilled over lead oxide, gives *benzacridine*, m. p. 223° [*chloroplatinate*, m. p. 242° (decomp.)]; with 1-ketotetrahydronaphthalene, 9 : 10-*tetramethylenetetrophan*, m. p. 308°. *ar*-Tetrahydro-α-naphthylamine reacts with hydroxylamine and chloral hydrate, yielding an iso*nitroso*-compound, m. p. 179°, which with sulphuric acid gives 6 : 7 : 8 : 9-*tetrahydro*-α-*naphthisatin*, m. p. 228° (*phenylimide*, m. p. 245°; *oxime*, m. p. above 300°; 6 : 7 : 8 : 9-*tetrahydro*-α-*naphthoxindole*, m. p. 161°). The naphthisatin condenses with acetophenone, yielding tetramethyleneatophan (cf. A., 1923, i, 144) (*methyl* ester, m. p. 66°).

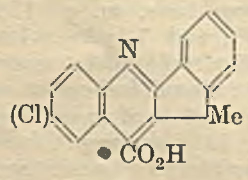
[With (Frl.) L. Brauns.]—Methylene di-isatin, during the preparation of which *methylene disalicylformic acid* and *di-isatylbenzophenone*, $CO\left(C_6H_3<\substack{NH\\CO}>CO\right)_2$, both melting above 360°, were isolated, condenses with 1-ketotetrahydronaphthalene, yielding *ditetrophanylmethane*, $CH_2(C_{18}H_{13}O_2N)_2$, m. p. 305—308° (decomp.). As this substance contains two tetrophan complexes, it should be very active, but the insolubility of its salts made it difficult to test its physiological action.

[With O. Bayer.]—1-*Ketotetrahydroanthracene*, m. p. 95—96° [*oxime*, m. p. 170°; *semicarbazone*, m. p. 250° (decomp.); *phenylhydrazone*, m. p. 116°; *picrate*, m. p. 118°], condenses with isatin, yielding 2 : 3-*benztetrophan*, m. p. 300° (decomp.), which gives 2 : 3-*benz*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 160°.

[With H. Jungmann.]—7-*Nitro*-1-*ketotetrahydronaphthalene*, m. p. 72°, yields the following series of compounds: 7-*amino*-1-*ketotetrahydronaphthalene*, m. p. 136° (*hydrochloride*, m. p. 181°; *picrate*, m. p. 165°; *acetyl* derivative, m. p. 166°; o-*hydroxybenzylidene* derivative, m. p. 139°); 7-*dimethylamino*-1-*ketotetrahydronaphthalene* (*picrate*, m. p. 153°; *methiodide*, m. p. 202—203°); 7-*hydroxyethylamino*-1-*ketotetrahydronaphthalene* (*picrate*, m. p. 126°); 7-*hydroxy*-1-*ketotetrahydronaphthalene*, m. p. 159° (*acetyl* derivative, m. p. 82°); 7-*chloro*-1-*ketotetrahydronaphthalene*, m. p. 94° (*semicarbazone*, m. p. 226°). These ketones when condensed with isatin yield the following substances: 2-*chlorotetrophan*, m. p. 207—208° (decomp.); 2-*chloro*-5 : 6-*dihydro*-α-*naphthacridine*, m. p. 124°; 2-*aminotetrophan*, m. p. 297° (*dihydrochloride*, yellow needles; *acetyl* derivative, m. p. 315°); 2-*dimethylaminotetrophan*, m. p. 278°; 2-*hydroxyethylaminotetrophan*, m. p. 295°; 2-*hydroxytetrophan*, m. p. above 300° (*acetyl* derivative, m. p. 102°); 2-*methoxytetrophan*, m. p. 123°.

[With A. Stuckenschmidt.]—Acetophenone and ethyl α-bromopropionate react with zinc in benzene solution, yielding *ethyl* αβ-*dimethylcinnamate*, b. p. 133°/13 mm. (αβ-*dimethylcinnamic acid*, m. p. 101°), which is hydrogenated to *ethyl* β-*phenyl*-α-*methyl*-n-*butyrate*, b. p. 133°/13 mm. Reduction of this ester with alcohol and sodium yields γ-*phenyl*-β-*methyl*-n-*butyl alcohol*, b. p. 132—133°/13 mm., which with hydrobromic acid gives γ-*phenyl*-β-*methyl*-n-*butyl bromide*, b. p. 132—133°/13 mm. Potassium cyanide converts the bromide into γ-*phenyl*-β-*methyl*-n-*valeronitrile*, b. p. 148—149°/15 mm., which yields γ-*phenyl*-β-*methyl*-n-*valeric acid*, b. p. 175°/13 mm., on hydrolysis. By the Friedel–Crafts reaction, the *acid chloride*, b. p. 134°/13 mm., yields 1-*keto*-3 : 4-*dimethyltetrahydronaphthalene*, b. p. 142—143°/13 mm., n_α^{15} 1·5524, d_{15}^{15} 1·0513 (*semicarbazone*, m. p. 177°), which condenses with isatin to give 5 : 6-*dimethyltetrophan*, m. p. 175—177°. Similar reactions yield the following series of compounds: α-*benzyl*-n-*butyric acid*, b. p. 168°/14 mm. (*ethyl* ester, b. p. 131—132°/13 mm.); γ-*phenyl*-β-*ethyl*-n-*propyl alcohol*, b. p. 134—135°/13 mm.; γ-*phenyl*-β-*ethyl*-n-*propyl bromide*, b. p. 125—126°/13 mm.; γ-*phenyl*-β-*ethyl*-n-*butyronitrile*, b. p. 142—143°/13 mm.; γ-*phenyl*-β-*ethyl*-n-*butyric acid*, b. p. 174—175°/13 mm. (*chloride*, b. p. 146°/13 mm.); 1-*keto*-3-*ethyltetrahydronaphthalene*, b. p. 145°/13 mm. (*semicarbazone*, m. p. 165°; *oxime*, m. p. 188°); 6-*ethyltetrophan*, m. p. 204—205°.

[With J. Reutter.]—Condensation of isatin with the appropriate ketones yields 4 : 5-*ethylenetetrophan*, m. p. 300° (decomp.), and 4 : 5-*trimethylenetetrophan*, m. p. 262—264° (decomp.).



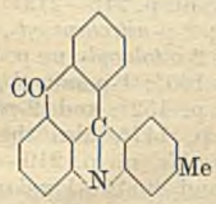
α-Methylhydrindone yields, with isatin, iso*tetrophan* (annexed formula), m. p. 310° (decomp.), and with 5-chloroisatin, *chloro*iso*tetrophan*, m. p. 292° (decomp.). The preparation of 2-*phenyl*-3-γ-*phenylpropylcinchoninic acid*, m. p. 244—246° (decomp.), is described.

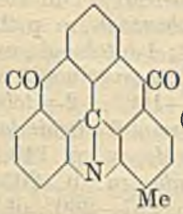
R. W. West.

Triphenylmethane compounds with linked benzene nuclei. III. Derivatives of diketo-5-

phenylacridine. R. Weiss and W. Knapp (Monatsh., 1926, 47, 485—491).—By the condensation of 1-chloroanthraquinone with *m*-toluidine, *m*-5-xylidine, *p*-xylidine, and *m*-aminobenzoic acid are obtained, respectively, 1-*anthraquinonyl*-m-*toluidine*, m. p. 154°; 1-*anthraquinonyl*-m-5-*xylidine*, m. p. 210°; 1-*anthraquinonyl*-p-*xylidine*, m. p. 210°; and 1-*anthraquinonyl*-m-*aminobenzoic acid*, m. p. 282—285°. On heating the first three with 75% sulphuric acid at 160°, dehydration occurs, yielding, respectively, 2-*methylketomethylene*-5-*phenylacridine* (I) (3-*methylcœramidonine*), m. p. 206°, the corresponding 2 : 4-*dimethyl*-, m. p. 180°, and 1 : 4-*dimethyl*-compounds, m. p. 160°, whilst the substituted benzoic acid is unattacked.

(I.)





(II.)

1 : 4-Dimethylcœramidonine, on heating with yellow mercuric oxide at 180°, yields 1-*methyldiketomethylene*-5-*phenylacridine* (II), amorphous. The 1 : 3-dimethylcœramidonine, similarly treated, yields the substance $(C_{22}H_{10}O_2N)_2O$, 1 mol. of water being eliminated from 2 mols. after oxidation. The monomethyl compound is unattacked. J. W. Baker.

isoDialuric acid. H. Biltz and H. Paetzold [with P. Nachtwey] (Annalen, 1927, 452, 67—89; cf. A., 1923, i, 1233).—*iso*Dialuric acid can be regarded as

$$\begin{array}{l}\mathrm{NH{\cdot}CO{-}C(OH)_2}\\ \;|\qquad\qquad\;|\\ \mathrm{CO{\cdot}NH{\cdot}CH{\cdot}OH}\end{array}, H_2O\,(I) \text{ or } \begin{array}{l}\mathrm{NH{\cdot}CO{-}CO}\\ \;|\qquad\qquad\;|\\ \mathrm{CO{\cdot}NH{\cdot}CH{\cdot}OH}\end{array}, 2H_2O\,(II).$$

By treatment of *iso*dialuric acid (monohydrate, m. p. 133°, decomp., resolidifying at 180° and decomposing further at 250°; anhydrous, decomposes about 170°) with methyl alcohol and hydrochloric acid, a methyl ether, 5 : 6-*dihydroxy*-5-*methoxy*-5 : 6-*dihydrouracil*, $C_4H_5O_4N_2{\cdot}OMe,H_2O$, decomp. slowly at 180°, vigorously at 215°, and with ethyl alcohol an ethyl ether, the -5-*ethoxy*-analogue, decomp. 210°, anhydrous decomp. 160°, resolidifying to the same product as is given by an *iso*dialuric acid melt, have been obtained. The ethyl ether is hydrolysed by water, and with hydroxylamine hydrochloride gives slowly *iso*dialuric acid oxime, indicating that ether-formation occurs on one of the 5-hydroxyl groups of the structure (I); it reacts with diazomethane to give a syrup. *iso*Barbituric acid treated in methyl alcohol with chlorine gives a dimethyl ether of *iso*dialuric acid, 6-(or 5-)*hydroxy*-5 : 5-(or 5 : 6-)*dimethoxy*-5 : 6-*dihydrouracil* (III), decomp. 215° (corr.). This is more probably the 5 : 5-dimethoxy-derivative, since *iso*dialuric acid oxime is easily obtained from it, and since it is stable to water. Uric acid and *iso*barbituric acid can be obtained from (III), which is converted by diazomethane into a syrupy substance, the 1 : 3-*dimethyl* derivative. In ethyl alcohol, the corresponding diethyl ether, 6-(or 5-)*hydroxy*-5 : 5-(or 5 : 6-) *diethoxy*-5 : 6-*dihydrouracil* (IV), decomp. about 210°, is obtained, from which uric acid, *iso*barbituric acid, and, by diazomethane, the 1 : 3-*dimethyl* derivative, m. p. 115° (corr.), which with carbamide gives 1 : 3-dimethyluric acid, are derived. The third hydroxyl group cannot by any means be methylated.

From 5-methoxy-1 : 3-dimethyluracil, now prepared by the action of methyl sulphate on *iso*barbituric acid (new m. p. 198°, corr.), are obtained 6-*chloro*- (V) and 6-*bromo*-5 : 5-*dimethoxy*-1 : 3-*dimethyl*-5 : 6-*dihydrouracil* (VI), m. p. 86° (corr.) and 125° (corr.), respectively; attempts to replace halogen in these by hydroxyl have failed, silver oxide giving the original methoxydimethyluracil. The latter when treated with concentrated nitric acid gives 5-*hydroxy*-5-*methoxy*-1 : 3-*dimethyl*-5 : 6-*dihydrouracyl* 6-*nitrite*, decomp. 145° (corr.), which is converted by carbamide into 1 : 3-dimethyluric acid, and thus belongs to the *iso*dialuric acid series.

When treated with sodium and methyl alcohol, (V) and (VI) give 5 : 5 : 6-*trihydroxy*-1 : 3-*dimethyl*-5 : 6-*dihydrouracil*, m. p. 132° (corr.), reduced by hydriodic acid to 1 : 3-*dimethyl*iso*barbituric acid*, and converted by carbamide into 1 : 3-dimethyluric acid.

*iso*Barbituric acid fails to react with phenylhydrazine, semicarbazide, or hydroxylamine (cf. Behrend and Roosen, A., 1888, 581; Annalen, 1889, 251, 240). *iso*Dialuric acid gives the following derivatives: an oxime anhydride, m. p. 295° (corr.) after turning brown at 175° (cf. Behrend and Roosen, *loc. cit.*; the substance is shown not to be keto*iso*barbituric acid oxime monohydrate, which might be expected); *phenylhydrazone*, sinters at 240°, decomp. 260° (corr.), and p-*nitrophenylhydrazone*, decomp. 278°, both also obtainable from (III); *semicarbazone*, which darkens from 180°, but does not melt or decompose below 290°; from (V), 1 : 3-*dimethyl*iso*dialuric acid phenylhydrazone*, decomp. 148° (corr.).

Acetyl chloride reacts with (III) or with *iso*dialuric acid to give 6-*chloro*-5-*acetoxyuracil* (VII), decomp. 260° (corr.), hydrolysed by alkali to *iso*barbituric acid, by acid to 6-*chloro*-5-*hydroxyuracil* (VIII), which reddens from 270° and decomposes at 300°. Bromine converts (VII) and (VIII) into alloxan; (VII) is reduced by zinc and acetic acid to *iso*barbituric acid, and converted by chlorine and methyl alcohol into 6-*chloro*-5-*hydroxy*-5 : 6-*dimethoxy*-5 : 6-*dihydrouracil*, which turns yellow from 140°, decomposes from 160° to 260°, and is hydrolysed by water to alloxan.

*iso*Barbituric acid, when treated with acetic acid, acetic anhydride, and chlorine, gives *diacetyl*iso*dialuric acid*, decomposed at 118° or by water, converted by carbamide into uric acid; with acetic anhydride alone, *diacetyl*iso*barbituric acid*, m. p. 161° (corr.), which is hydrolysed by water to the monoacetyl derivative. The latter is oxidised by chlorine to *iso*dialuric acid, or in presence of methyl alcohol to the 5 : 5-dimethyl ether. The diacetyl compound is unaffected by chlorine in acetic acid.

From these results, it is concluded that *iso*dialuric acid has the formula (I), and, since 5 : 6-methylenedioxy- and 5 : 6-dimethoxy-uracil do not condense with carbamide, that in the Behrend synthesis of uric acid, the 5- and 6-hydroxyl groups of *iso*dialuric acid are first eliminated with hydrogen atoms of carbamide to give a compound which then loses water to give the double linking of uric acid.

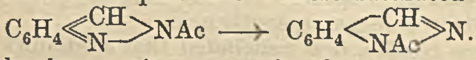
E. W. Wignall.

Catalytic hydrogenation of azines. K. A. Taipale (J. Russ. Phys. Chem. Soc., 1926, 57, 487—548).—A fuller description of work already published (cf. A., 1923, i, 547). E. Rothstein.

Anilopyrine and antipyrine. P. K. Dutt (Proc. Leeds Phil. Lit. Soc., 1926, 1, 113—115).—Theoretical. The relative merits of the Michaelis and the Stolz formula for anilopyrine are discussed. The behaviour of anilopyrine alkohydroxides indicates a further resemblance between anilopyrine and antipyrine, since the quaternary hydroxides, in the absence of water, decompose spontaneously, giving anilopyrine methohydroxide, antipyrine, and methylaniline. This result proves that, in the successive alkylation of 5-anilino-1-phenylpyrazoles, the first alkyl group attaches itself to the nitrogen in position 2 and the second one to the amino-nitrogen. The nature of the groups attached to the nitrogen atom appears greatly to affect the relative yields of the products of decomposition. M. S. Burr.

Opening of the glyoxaline ring. B. Oddo and Q. Mingoia (Gazzetta, 1926, 56, 958—960).—The long-accepted observation of Bamberger and Berlé (A., 1893, i, 437) that Schotten–Baumann benzoylation opens the ring of glyoxaline to give formic acid and dibenzamidoethylene is incorrect. The actual product from either glyoxaline or magnesyl-glyoxaline is a benzoylglyoxaline; any excess of benzoyl chloride appears as benzoic acid, and very little formic acid is detected. Traces of a *by-product*, m. p. 246—247°, are formed. E. W. Wignall.

Wandering of acyl groups in indazole derivatives. K. von Auwers and W. Demuth (Annalen, 1927, 451, 282—307).—A large number of new acylindazoles have been prepared in order to determine the factors which condition the mobility of the acyl groups in these compounds. The new facts are in agreement with previous conclusions (cf. A., 1920, i, 638; 1924, i, 878, 1347; 1925, i, 1460; 1926, 306, 529). The mobility of the acyl radical in 2-acylindazoles is affected by the following factors: (*a*) the nature of the acyl radical; the mobility of any given group does not, however, run parallel with its ease of removal by hydrolysis, or with the strength of the corresponding acid; (*b*) the position of other substituents, their nature being comparatively unimportant; for instance, 2-acyl derivatives of 3-substituted indazoles can rarely be prepared, whilst those with a 5- or 7-substituent are unusually stable; the stability of the last-named may be due to the steric effect of the 7-substituent; (*c*) the relative basicity of the 1- and 2-nitrogen atoms, and (*d*) the tendency of the indazole nucleus to pass into a more saturated form, thus:

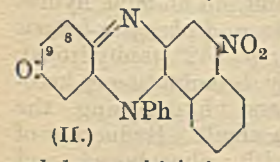


$C_6H_4{\ll}\begin{smallmatrix}CH\\N-\end{smallmatrix}{>}NAc \longrightarrow C_6H_4{<}\begin{smallmatrix}-CH\\NAc\end{smallmatrix}{\gg}N$.

Indazoles having a nitro-group in the benzene nucleus are unexpectedly difficult to halogenate; in absence of a carrier, only the 3-position is attacked. 4-*Chloroindazole*, m. p. 156° (1-*acetyl*-, m. p. 66·5—67·5°; 2-*acetyl*-, m. p. 93—94°; 1-o-*nitrobenzoyl*-, m. p. 174°; 2-o-*nitrobenzoyl*-, m. p. 192—194°; 1-p-*nitrobenzoyl*-, m. p. 181—182°, and 2-p-*nitrobenzoyl*-, m. p. 154°, derivatives); 3-*chloro*-4-*nitroindazole*, m. p. 215°; 3-*bromo*-4-*nitroindazole*, m. p. 220—221°; 3-*bromo*-5-*nitroindazole*, m. p. 223—224°; 3-*chloro*-5-*nitroindazole*, m. p. 209—215°; 3-*chloro*-6-*nitroindazole*, m. p. 200°; 3-*bromo*-6-*nitroindazole*, m. p. 228—230° (1-*acetyl* derivative, m. p. 168°), and 3-*iodo*-6-*nitroindazole*, m. p. 259—261°, are described. The stability of the 2-acyl-6-nitroindazoles is, in general, closely similar to, but slightly less than, that of the corresponding indazole derivatives. Halogenated acetic acids and *m*-substituted benzoic acids again failed to give 2-acyl derivatives. The following are mentioned: 1-*chloroacetyl*-, m. p. 149°; 1-*dichloroacetyl*-, m. p. 137—138°; 1-*trichloroacetyl*-, m. p. 101—102°; 1-o-*nitrobenzoyl*-, m. p. 206—207°; 2-o-*nitrobenzoyl*-, m. p. 185—186°; 1-m-*nitrobenzoyl*-, m. p. 212—213°; 1-p-*nitrobenzoyl*-, m. p. 236—237°; 2-p-*nitrobenzoyl*-, m. p. 220°; 1-o-*toluoyl*-, m. p. 188°; 2-o-*toluoyl*-, m. p. 140—142°; 1-m-*toluoyl*-, m. p. 159—160°; 1-p-*toluoyl*-, m. p. 165—166°; 2-p-*toluoyl*-, m. p. 152°, and 2-*phenylcarbamyl*-6-*nitroindazole*, m. p. 147°, also the *acid chloride*, m. p. 140—141°; *amide*, m. p. 219—220°; *anilide*, m. p. 205—207°, and 6-*nitro*-1-*indazylide*, m. p. 257—260°, of 6-nitroindazole-1-carboxylic acid. 3-*Bromo*-7-*nitroindazole* has m. p. 177—178°. 7-*Nitro*-1-*acetylindazole*, m. p. 147°, has now been obtained by treating the 7-nitroacetylindazole of m. p. 135—136° (*ibid.*, 1920, i, 642) with bromine; the latter is therefore an unexpectedly stable 2-acetyl derivative. The 1-acetyl and also the 1-*benzoyl* derivative, m. p. 132—133°, unlike most 1-acylindazoles, are hydrolysed by hydrogen chloride in indifferent solvents. 2-*Benzoyl*-, m. p. 185°; 1-o-*nitrobenzoyl*-, m. p. 173—175°; 2-o-*nitrobenzoyl*-, m. p. 111—113°; 1-p-*nitrobenzoyl*-, m. p. 155—157°, and 2-p-*nitrobenzoyl*-7-*nitroindazole*, m. p. 205°, are described. Methylation of 6-nitroindazole with methyl sulphate in alkaline solution yields a mixture of 6-nitro-1- and 6-nitro-2-methylindazole, not the -2-derivative only, as previously stated. *Methyl* 6-*nitroindazole*-1-*carboxylate*, m. p. 169°, is converted by boiling absolute alcohol into the corresponding *ethyl* ester, m. p. 147—148°, from which N-*ethyl*-6-*nitroindazole*, m. p. 61—62°, is prepared by heating at 210°. An isomeric N-*ethyl*-6-*nitroindazole*, m. p. 91—93°, is formed when the ethyl ester is heated with ethyl iodide in a sealed tube. 6-Aminoindazole, conveniently prepared by reducing 6-nitroindazole with sodium sulphide in alkaline solution, gave the following derivatives: 6-*benzylideneaminoindazole*, m. p. 79—80°; 6-o-*hydroxybenzylideneaminoindazole*, m. p. 200—201° (1-*acetyl* derivative, m. p. 144—146°); 6-p-*anisylideneaminoindazole*, m. p. 155—156°; 6-p-*hydroxybenzeneazoindazole*, red, m. p. 253° (1-*acetyl* derivative, m. p. 228—230°); 6-*amino*-1-*methylindazole*, m. p. 172—173°; 6-*hydroxy*-1-*methylindazole*, m. p. 215—216°, and 6-*hydroxy*-2-*methylindazole*, m. p. 167—169°. H. E. F. Notton.

Synthesis of phenazine and some derivatives. F. Kehrmann and C. Mermod (Helv. Chim. Acta, 1927, 10, 62—66).—The synthesis of the simpler phenazines from *o*-diamines and *o*-quinones is possible only in the absence of water. *o*-Benzoquinone and *o*-phenylenediamine react in dry ether in presence of anhydrous sodium sulphate to give 35% of phenazine. 2-Methylphenazine (50%) is obtained by the same method from *o*-phenylenediamine and 4-methyl-*o*-benzoquinone and 88% of naphthaphenazine from *o*-phenylenediamine and 1 : 2-naphthaquinone. When 4-nitro-*m*-phenylenediamine is boiled with glacial acetic acid and acetic anhydride, *4-nitro-3-amino-acetanilide*, m. p. 178°, is formed. It is reduced by iron powder and water to 3 : *4-diaminoacetanilide*. 4-Acetamido-*o*-benzoquinone (A., 1925, i, 560) and *o*-phenylenediamine yield, in absence of water, 68% of 2-acetamidophenazine (Fischer and Hepp, *ibid.*, 1889, 499). 2-Hydroxyphenazine could not be prepared by diazotising and boiling a solution of 2-aminophenazine, but it is formed when this substance is heated at 180° with 15% hydrochloric acid. 1 : 2 : 4-Triaminobenzene and 1 : 2-naphthaquinone condense in presence of acetic acid to 3-aminonaphthaphenazine (Nietzki and Otto, *ibid.*, 1888, 843). 3-*Hydroxy-naphthaphenazine*, decomp. 290°, is prepared by heating this with 25% hydrochloric acid in a sealed tube. H. E. F. Notton.

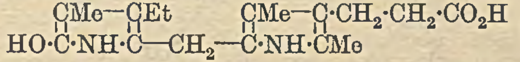
New azine colouring matters from naphthalene. F. Kehrmann and B. Perrot (Helv. Chim. Acta, 1927, **10**, 53—61).—Phenyl-2 : 4-diamino-α-naphthylamine (Ullmann and Bruck, A., 1909, i, 21) condenses with benzil to give 6-*amino*-1 : 2 : 3-*tri-phenyl*-7 : 8-*benzoquinoxalinium chloride* [colour of alcoholic solution (*a*) Ponceau-red, colour with concentrated sulphuric acid (*b*) reddish-violet], but not with other α-diketones. The corresponding *perchlorate* and *chloroplatinate*, and the *chloride* [(*a*) lemon-yellow, (*b*) reddish-violet] and *perchlorate* of its *acetyl* derivative are described. Phenyl-2 : 4-dinitro-α-naphthylamine is reduced by alcoholic ammonium sulphide to *phenyl*-4-*nitro*-2-*amino*-α-*naphthylamine* (I), m. p. 160—161°. This condenses with 4-acetamido-1 : 2-naphthaquinone, and on addition of nitric acid, 2-*nitro*-7-*acetamido*-5-*phenyl*-3 : 4-8 : 9-*dibenzo*-5-*phenazonium nitrate* [(*a*) reddish-violet with red fluorescence, (*b*) dark blue] (*chloride*) is obtained. The latter is hydrolysed by hot hydrochloric acid to the corresponding 7-*amino*-derivative [(*a*) violet-red, (*b*) bluish-green], and reduced by stannous chloride to 2-*amino*-7-*acetamido*-5-*phenyl*-3 : 4-8 : 9-*dibenzo*-5-*phenazonium chloride* [(*a*) greenish-blue, (*b*) dark blue] (*chloroplatinate*), which gives on acetylation the corresponding *diacetamido*-derivative [(*a*) reddish-violet, (*b*) dark blue], and, on hydrolysis, the 2 : 7-*diamino*-derivative [(*a*) greenish-blue, (*b*) bluish-green]. When 2-hydroxy-1 : 4-naphthaquinone and (I) are heated with hydrochloric acid in alcoholic solution, the 8 : 9-*benzo*-derivative of the *nitro-naphthindone* (II) [(*a*) dark red, (*b*) bluish-green], which is reduced by stannous chloride to a violet *amino*-derivative, remains dissolved, whilst 2-(4-*nitro*-1-*anilino*-2-*naphthylamino*)-1 : 4-*naphthaquinone* [(*a*) brownish-orange] and 4-(4-*nitro*-1-*anilino*-2-*naphthyl-imino*)-2-*hydroxy*-1 : 4-*naphthaquinone* [(*a*) yellow, (*b*) bluish-violet] crystallise out. The solution of the second substance in concentrated sulphuric acid is red, immediately changing to blue owing to the formation of 8-*nitro*-2-*hydroxy*-5-*phenyl*-3 : 4-6 : 7-*dibenzophenazonium sulphate*, which is precipitated when the solution is diluted. The third product is recovered unchanged from its sulphuric acid solution. 2 : 5-Dihydroxy-*p*-benzoquinone and (I) afford the 8-*hydroxy*-derivative of (II) [(*a*) yellowish-red, (*b*) reddish-violet], which gives an *acetyl* derivative [(*a*) red, (*b*) red]; (I) also condenses with phenanthraquinone, but not with benzil. H. E. F. Notton.



(II.)

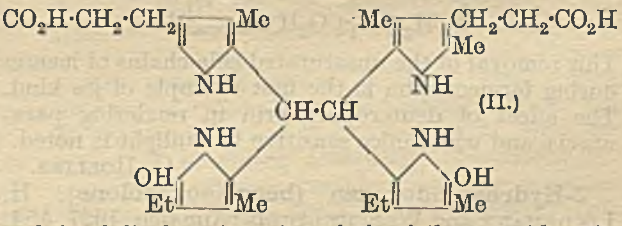
Action of hydrazine hydrate on uridine. P. A. Levene and L. W. Bass (J. Biol. Chem., 1926, **71**, 167—172).—The action of hydrazine hydrate on uridine yields pyrazolone (isolated as dixanthyl derivative), but no free carbamide; in view of the results of Fosse and others (A., 1924, i, 428), this affords additional evidence in favour of the authors' previous conclusion (*ibid.*, 1926, 1260) that, in uridine, the ribose is attached to the 3-position of the pyrimidine nucleus. Carbamide glucoside yields a *xanthyl* derivative, m. p. 216—219° (decomp.); after heating the glucoside with hydrazine for 1 hr. at 65°, no unchanged glucoside and no free carbamide were detected. C. R. Harington.

Bile pigment. X. (Porphyrin syntheses V.) Conversion of bile pigment and bilirubic acid into mesoporphyrin. Hæmopyrrole from mesobilirubinogen. H. Fischer and F. Lindner (Z. physiol. Chem., 1926, **161**, 1—16).—When bilirubic acid (I) is heated at 145° for 1·5 hrs. with hydrobromic–acetic acid, the hydroxyl is replaced by bromine and condensation to mesoporphyrin occurs; bilirubin itself requires 6 hrs. at 180° for the same change; mesobilirubinogen, 1·5 hrs. at 165°. In each case there is also formed a porphyrin or porphyrins with the same spectra, but giving a more soluble sodium salt; the corresponding methyl ester melts indefinitely at about 160° (mesobilirubinogen experiment).



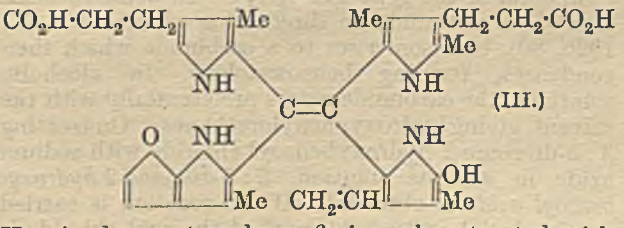
$$\begin{array}{l} \quad\;\; \mathrm{CMe{-}CEt} \qquad\quad \mathrm{CMe{-}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H} \\ \mathrm{HO{\cdot}C{\cdot}NH{\cdot}C{-}CH_2{-}C{\cdot}NH{\cdot}CMe} \end{array} \qquad \text{(I.)}$$

The Küster formula for hæmin involving neighbouring ethyl groups is rendered untenable by this synthesis. For mesobilirubinogen is suggested the structure (II),



(II.)

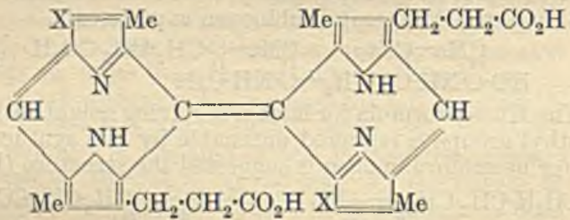
and for bilirubin, in spite of the failure to identify opsopyrrolecarboxylic acid (see A., 1926, 1256) in the bilirubic acid mother-liquors, the structure (III).



(III.)

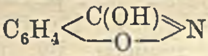
Hæmin does not undergo fission when treated with hydrobromic–acetic acid at 145° or 180°, but mesoporphyrin (methyl ester, m. p. 208—209°) is formed quantitatively at 180°. C. Hollins.

Natural porphyrins. XXI. Deuterohæmin and deuteroporphyrin. H. Fischer and F. Lindner (Z. physiol. Chem., 1926, **161**, 17—36).—Fresh ox-blood is fermented with yeast or spontaneously at 37°, alkalinity being maintained by successive additions of sodium carbonate and the progress of reaction followed by measurements of the hæmochromogen spectrum in pyridine. The diluted liquid is acidified and the precipitate is separated by decantation, pressed, washed with methyl alcohol, pressed again, and extracted with methyl alcohol containing 1% of sulphuric acid. After concentration of the extract, crude *deuterohæmin* crystallises on addition of concentrated hydrochloric acid, and is purified as the *methyl* ester, $C_{32}H_{30}O_4N_4ClFe$, m. p. 233°. The crude hæmin is converted by sodium amalgam, by hydrobromic– or hydriodic–acetic acid, or by hydrazine and acetic acid, into *deuteroporphyrin* (crystallographic data by Steinmetz) (*methyl* ester, $C_{30}H_{32\text{ or }34}O_4N_4$, m. p. 218°; *copper* salt, m. p. 335°; *iron* salt; *copper* salt of the methyl ester, m. p. 230°; *iron* salt of the methyl ester, m. p. 250°). When heated in a vacuum for 3 hrs. at 200°, deuteroporphyrin is practically unchanged, whilst hæmatoporphyrin under the same conditions gives protohæmin. Deuteroporphyrin is converted by bromine in acetic acid into a *bromo*-compound, which with aqueous acetone loses only half its bromine and gives *dibromodeuteroporphyrin*, $C_{30}H_{26}O_4N_4Br_2$ (*methyl* ester, m. p. 261°). The oxidation of dibromodeuteroporphyrin with chromic acid to bromocitraconimide and hæmatic acid, and of deuteroporphyrin to citraconimide and hæmatic acid leads to the annexed structure (X=Br or H) for these two compounds.

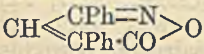


This removal of the unsaturated side-chains of hæmin during fermentation is the first example of its kind. The effect of deuteroporphyrin in rendering paramæciæ and white mice sensitive to sunlight is noted.

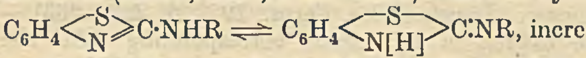
C. Hollins.

2-Hydroxyindoxazen (benz*iso*oxazolone). H. Lindemann and W. Schultheis (Annalen, 1927, **451**, 241—255).—When *o*-hydroxybenzoyl azide is heated in solvents, nitrogen is evolved, an intermediate compound of the type $OH·C_6H_4·CO·N⋮$ being formed. This does not undergo direct ring closure (cf. A., 1926, 80), but isomerises to a carbimide which then condenses, forming benzoxazolone. In alcoholic solutions, the carbimide reacts preferentially with the solvent, giving hydroxyphenylurethanes. On treating 3 : 5-dibromo-2-hydroxybenzoyl chloride with sodium azide in acetone solution, 3 : 5-*dibromo-2-hydroxybenzoyl azide* is obtained. If the reaction is carried out in glacial acetic acid, part of the acid chloride is converted into the quinonoid substance, (*o*) $O⋮C_6H_4⋮CO$ (cf. *loc. cit.*), which then combines with the solvent, yielding 3 : 5-dibromo-2-acetoxybenzoic acid. The azide melts at 114°, with loss of nitrogen, being converted into 4 : 6-dibromobenzoxazolone. 3 : 5-Dibromo-2-acetoxybenzoic acid affords successively the *acid chloride*, m. p. 68—69°, b. p. 184°/20 mm., and 3 : 5-*dibromo-2-acetoxybenzoyl azide*, m. p. 70—73°. When boiled in glacial acetic acid, the latter is converted into 3 : 5-dibromo-2-hydroxyacetanilide, m. p. 178° (cf. Holz, *ibid.*, 1885, 1211). In boiling benzene, it loses nitrogen, forming 3 : 5-*dibromo-2-acetoxyphenylcarbimide*, m. p. 76°, which further condenses to 4 : 6-dibromo-2-acetylbenzoxazolone when heated at 140°. Both azide and carbimide react with methyl alcohol, giving *methyl* 3 : 5-*dibromo-2-acetoxyphenylcarbamate*, m. p. 178° (decomp.). The corresponding *ethyl* ester, m. p. 163°, is hydrolysed by alcoholic potassium hydroxide to *ethyl* 3 : 5-*dibromo-2-hydroxyphenylcarbamate*, m. p. 122°. *o*-Acetoxybenzoyl chloride, m. p. 49—50°, prepared by an improved method, yields successively o-*acetoxybenzoyl azide*, m. p. 64—65° (decomp.); o-*acetoxyphenylcarbimide*, b. p. 112°/12 mm.; *methyl* o-*acetoxyphenylcarbamate*, m. p. 100—101°, and the corresponding *ethyl* ester, m. p. 75—76°. The *acetate*, $OH·C_6H_4·C(OH)⋮N·OAc$, m. p. 141—142°, of salicylhydroxamic acid (*ibid.*, 1889, 870) loses the elements of acetic acid when heated above its m. p. or treated with alkali, but instead of the expected 2-hydroxybenz*iso*oxazole (cf. *ibid.*, 1926, 1047), benzoxazolone was again obtained. When, however, the isomeric o-*acetoxybenzhydroxamic acid*, m. p. 102—103°, is boiled with ammonia solution, 2-*hydroxybenziso-oxazole*,  $C_6H_4{<}\overset{C(OH)}{\underset{O}{\quad}}{>}N$, m. p. 139° (*acetyl* derivative, m. p. 149°; *methyl ether*, m. p. 127·5°), is produced. This dissolves unchanged in dilute alkali; with more concentrated solutions, salicylic acid is obtained. The compound, m. p. 133—134°, of this formula described by Ransom and Nelson (*ibid.*, 1914, i, 269) was probably benzoxazolone.

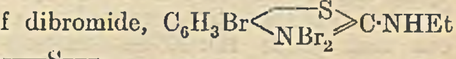
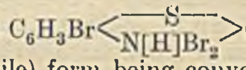
H. E. F. Notton.

[So-called] *iso*oxazoline oxides. E. P. Kohler and R. C. Goodwin (J. Amer. Chem. Soc., 1927, **49**, 219—227; cf. A., 1926, 1140).—The action of methyl-alcoholic potassium acetate on α-bromo-γ-nitro-β-phenylpropiophenone (A., 1924, i, 571) has been re-examined in view of more recent results obtained in an analogous reaction (*ibid.*, 1926, 1140). The product, first reported as 2-hydroxy-3-methoxy-5-benzoyl-4-phenyl*iso*oxazolidine, has now been identified as *methyl* β-*hydroxy-γ-oximino-αγ-diphenyl*-n-*butyrate* (I), and it becomes the sole product of the above reaction if this is carried out in presence of acetic acid. Controlled hydrolysis with dilute aqueous potassium hydroxide affords β-*hydroxy-γ-oximino-αγ-diphenyl*-n-*butyric acid*, m. p. 168° (decomp.), which, with methyl-alcoholic hydrochloric acid, affords *methyl* β-*hydroxy-γ-keto-αγ-diphenyl*-n-*butyrate*, m. p. 78°; this yields the above oximino-ester when treated with hydroxylamine, and, on alkaline hydrolysis, affords β-*hydroxy-γ-keto-αγ-diphenyl*-n-*butyric acid*, m. p. 115° ($0·5H_2O$), m. p. 142° (anhydrous). The latter was synthesised by brominating γ-keto-αγ-diphenyl-*n*-butyric acid and hydrolysing the *product*, m. p. 207—208°, with alkali. Reduction of the hydroxyketonic acid with phosphorus and hydriodic acid affords the ketodiphenylbutyric acid, whilst hydroxylamine yields the above oximino-acid. The N-*acetyl* (m. p. 126°), ON-*diacetyl* (m. p. 98°), O-*acetyl* (m. p. 142°), N-*benzoyl* (m. p. 114°), and ON-*dibenzoyl* derivatives (m. p. 113°) of (I) are described. Treatment of the diacetate with aqueous potassium hydroxide affords *γ-keto-αγ-diphenylcrotonic acid*, m. p. 124°, identified by treatment with ozone, and by synthesis effected by brominating methyl γ-keto-*αγ*-diphenyl-*n*-butyrate and hydrolysis with alkali of the resulting stereoisomeric *bromo*-derivatives, m. p. 78° and 108°, respectively. A by-product in the preparation of (I) has now been identified as 6-*keto*-3 : 5-*diphenyl*-1 : 2-*oxazine*,  $\mathrm{CH}<\begin{smallmatrix}\mathrm{CPh{=}N}\\ \mathrm{CPh\cdot CO}\end{smallmatrix}>\mathrm{O}$, m. p. 153°. It is obtained by the action of hydroxylamine on the above crotonic acid or on methyl β-bromo-γ-keto-*αγ*-diphenyl-*n*-butyrate. When heated with acetyl chloride, or, in strong alkaline solution, with silver nitrate, it is converted into 3 : 5-*diphenylisooxazole*. F. G. Willson.

Oxazinesulphonic acids. J. S. Turski, J. Bojanowski, K. Moniuszko, and J. Vogelgarn (Rocz. Chem., 1926, 6, 747—755).—An acid dye, staining wool indigo-blue, 6-naphthylphenoxazinesulphonic acid, is prepared by the action of Schaeffer's salt on nitrosodimethylaniline hydrochloride, whilst a pure blue dye with similar properties is obtained by condensation of the latter substance with β-naphthol-8-sulphonic acid, and with sodium *p*-phenylsulphonate a grey dye, fast for mordanted cotton, but not for wool, is obtained. R. Truszkowski.

Aminobenzthiazoles. V. Stability of the 1-alkylaminobenzthiazole bromides. R. F. Hunter (J.C.S., 1926, 2951—2957).—In the system  $\mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{S}\\ \mathrm{N}\end{smallmatrix}\geqslant\mathrm{C{\cdot}NHR} \rightleftharpoons \mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{S}\\ \mathrm{N[H]}\end{smallmatrix}>\mathrm{C{:}NR}$, increase in atomic volume of R should, according to Ingold's modified strain theory (*ibid*., 1921, **119**, 305), enhance the aminothiazole phase, with consequent increased stability of the bromides. A stability curve for homologous series could not be obtained for the simple 1-alkylaminobenzthiazoles, but the prediction is verified for the 5-bromo-derivatives (see following abstract).

1-Methylaminobenzthiazole dibromide, decomp. 144—146°, prepared from bromine and *s*-phenylmethylthiocarbamide, is almost unchanged after 46 hrs.' exposure to air at 17°. The 1-ethylamino-dibromide, m. p. 76—78° (decomp.), loses one third of its labile bromine in 44 hrs. 1-n-*Propylaminobenzthiazole tetrabromide*, m. p. 54—56°, loses nearly half its bromine in 44 hrs., and in 5 days a thin layer is converted completely into *dibromide*, m. p. 80—82° (decomp.). s-*Phenyl*-n-*butylthiocarbamide*, m. p. 65°, is converted by bromine into 1-n-*butylaminobenzthiazole dibromide*, m. p. 86° (decomp.), practically unaltered by 44 hrs.' exposure; 1-n-*butylaminobenzthiazole* melts at 87°. 1-iso*Butylaminobenzthiazole dibromide hydrobromide*, m. p. 66—68° (decomp.), loses nearly half its labile bromine in 48 hrs.; 1-iso*butylaminobenzthiazole* has m. p. 103—104°. The following 1-alkylaminobenzthiazoles are also described : n-*amyl*, m. p. 68—69° [*dibromide hydrobromide*, m. p. 90° (decomp.)]; iso*amyl*, m. p. 69—71° (*dibromide hydrobromide*); n-*hexyl*, m. p. 57° [*dibromide*, m. p. 100—102° (decomp.)]; n-*heptyl*, m. p. 55° (*dibromide hydrobromide*, m. p. 79—81°); and the following new *s*-phenylalkylthiocarbamides : n-*amyl*, m. p. 69—71°; n-*hexyl*, m. p. 103—104°; n-*heptyl*, m. p. 70—71°. C. Hollins.

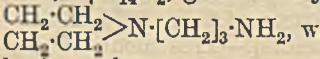
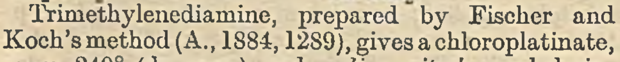
Aminobenzthiazoles. VI. Stability of the 5-bromo-1-alkylaminobenzthiazole bromides. R. F. Hunter and C. Soyka (J.C.S., 1926, 2958—2964; cf. preceding abstract and this vol., 236).—*s*-Di-*p*-bromophenylthiocarbamide, m. p. 184—185°, is converted by means of acetic anhydride into *p*-bromophenylthiocarbimide, which is condensed with alkylamines to give the following *s*-*p*-bromophenylalkylthiocarbamides : *methyl*, m. p. 148°; *ethyl*, m. p. 129°; n-*propyl*, m. p. 120°; n-*butyl*, m. p. 111°; iso*butyl*, m. p. 119°; n-*amyl*, m. p. 115°; iso*amyl*, m. p. 120°; n-*hexyl*, m. p. 106°; n-*heptyl*, m. p. 100°. Treatment of the ethyl, *n*-propyl, *n*- and *iso*-butyl compounds with bromine in hot chloroform yields 5-*bromo*-1-*alkylaminobenzthiazole dibromides*, melting at 140° (decomp.), 146° (decomp.), 149° (decomp.), and 127° (decomp.), respectively, which are reduced by hydriodic acid to the corresponding 5-*bromo*-1-*alkylaminobenzthiazoles*, m. p. 256—258°, 130°, 118°, and 137°, respectively. The dibromides show increasing stability as the alkyl group increases in atomic volume, the proportion of the labile bromine removed by dilute hydriodic acid under comparable conditions being respectively 98·9, 42·4, 37·3, and 19·0%. In the case of the ethyl compound, both forms of dibromide,  $\mathrm{C_6H_3Br}<\begin{smallmatrix}\mathrm{S}\\ \mathrm{NBr_2}\end{smallmatrix}\geqslant\mathrm{C{\cdot}NHEt}$ and  $\mathrm{C_6H_3Br}<\begin{smallmatrix}\mathrm{S}\\ \mathrm{N[H]Br_2}\end{smallmatrix}>\mathrm{C{:}NEt}$, are isolated, the latter (labile) form being converted into the former under special conditions. The following 5-bromo-1-alkylaminobenzthiazoles are also described : *methyl*, m. p. 225° [*hexabromide*, m. p. 122—124° (decomp.)]; n-*amyl*, m. p. 105° [*tetrabromide*, m. p. 86° (decomp.)]; iso*amyl*, m. p. 171° [impure; *dibromide*, m. p. 95° (decomp.)]; n-*hexyl*, m. p. 156° (*dibromide*); n-*heptyl*, m. p. 86° [impure; *dibromide*, m. p. 118—120° (decomp.)]. C. Hollins.

Aminobenzthiazoles. VII. The 2-alkylamino-β-naphthathiazole system. G. M. Dyson, R. F. Hunter, and C. Soyka (J.C.S., 1926, 2964—2969; cf. preceding abstracts).—Treatment of *s*-α-naphthylalkylthiocarbamides with bromine in hot chloroform yields a series of 2-alkylamino-β-naphthathiazole bromides, reducible by hydriodic or sulphurous acid to the bases. A tetrabromide is probably the normal product, but this may add on up to ten more bromine atoms, and a stability curve cannot be obtained. The following *s*-α-naphthylalkylthiocarbamides are new : n-*propyl*, m. p. 67°; n-*butyl*, m. p. 98°; iso*butyl*, m. p. 106°; n-*amyl*, m. p. 103°; iso*amyl*, m. p. 92°; n-*hexyl*, m. p. 89°; n-*heptyl*, m. p. 62°. The 2-alkylamino-β-naphthathiazoles described are : *methyl*, m. p. 193° [*hexabromide*, m. p. 163° (decomp.)]; *ethyl*, m. p. 218° [*tetrabromide*, m. p. 203° (decomp.)]; n-*propyl*, m. p. 242° (*hexabromide* sinters at 153°); n-*butyl*, m. p. 177° [*tetrabromide*, m. p. 134° (decomp.)]; iso*butyl*, m. p. 242°

[*hexabromide hydrobromide*, m. p. 103° (decomp.)]; n-*amyl*, m. p. 107° [*tetrabromide hydrobromide*, m. p. 123° (decomp.)]; iso*amyl*, m. p. 117° (*hexabromide hydrobromide* sinters at 135°); n-*hexyl*, m. p. 111° [*tetrabromide hydrobromide*, m. p. 127° (decomp.)]; n-*heptyl*, m. p. 97° (decomp.; *tetradecabromide*, $C_{18}H_{22}N_2Br_{14}S$, chars at 220°). C. HOLLINS.

[Phosphonitrilic chlorides and their transformations.] R. SCHENCK (Ber., 1927, **60**, [*B*], 160—161; cf. Schenck and Römer, A., 1924, ii, 752).—Revision of the determination of the mol. wts. of the anilide, piperidide, and phenylhydrazide derived from triphosphonitrilic chloride shows them to be termolecular. The quadrimolecular structure of tetraphosphonitrilic chloride persists in the anilide derived therefrom. H. WREN.

Derivatives of 10-chloro-5 : 10-dihydrophenarsazine. IV. Carboxy-derivatives. H. BURTON and C. S. GIBSON (J.C.S., 1927, 247—250).—Anthranilic acid condenses with *o*-bromophenylarsinic acid in boiling nitrobenzene in presence of anhydrous potassium carbonate and a trace of copper powder, forming 2-*carboxydiphenylamine*-6′-*arsinic acid*, m. p. 243° (decomp.). Reduction with sulphur dioxide in alcoholic hydrochloric acid solution containing a trace of iodine gives 2-*carboxydiphenylamine*-6′-*arsenic dichloride*, which immediately undergoes partial elimination of hydrogen chloride. Complete conversion into 10-*chloro*-5 : 10-*dihydrophenarsazine*-4-*carboxylic acid*, m. p. 243° (decomp.), is effected by boiling in acetic acid or sodium hydroxide solution. Reduction of the carboxylic acid with hypophosphorous acid yields 10 : 10′-*bis*-4-*carboxy*-5 : 10-*dihydrophenarsazine*, m. p. 253° (decomp.). *m*-Aminobenzoic acid yields, by a similar series of reactions, 3-*carboxydiphenylamine*-6′-*arsinic acid*, m. p. 238—239°, and 10-*chloro*-5 : 10-*dihydrophenarsazine*-3-*carboxylic acid*, m. p. above 300°. M. CLARK.

Spermine. V. F. WREDE, H. FANSELOW, and E. STRACK (Z. physiol. Chem., 1926, **161**, 66—73; cf. A., 1926, 751; Dudley and others, *ibid.*, 1925, i, 294; 1926, 308).—The base " $C_4H_{12}N_2$ " obtained by oxidation of spermine (*loc. cit.*) is shown to be actually trimethylenediamine, $C_3H_{10}N_2$. The second base, $C_7H_{14}N_2$, gives a dihydro-derivative,  $\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!>\!N\cdot[CH_2]_3\cdot NH_2$, which is synthesised. This leads to the structure $NH_2\cdot[CH_2]_3\cdot NH{-}\vdots{-}[CH_2]_4\cdot NH\cdot[CH_2]_3\cdot NH_2$ for spermine, $C_{10}H_{26}N_4$. The oxidation with copper and oxygen probably produces hydrolysis at the position marked, with oxidation of the amino-alcohol so produced to aminoaldehyde, which then condenses to  $\begin{matrix}CH{=}CH\\|\quad\quad\\CH_2\cdot CH_2\end{matrix}\!>\!N\cdot[CH_2]_3\cdot NH_2$ or $\begin{matrix}CH\cdot CH_2\\\|\quad\quad\\CH\cdot CH_2\end{matrix}\!>\!N\cdot[CH_2]_3\cdot NH_2$.

Trimethylenediamine, prepared by Fischer and Koch's method (A., 1884, 1289), gives a chloroplatinate, m. p. 240° (decomp.), and a *di*-m-*nitrobenzoyl* derivative, m. p. 212—213°, identical with those from the base, $C_3H_{10}N_2$, from spermine.

N-γ-Bromopropylphthalimide, condensed with pyrrolidine and subsequently hydrolysed with hydrochloric acid, yields *N*-γ-aminopropylpyrrolidine (chloroaurate, m. p. 206°; picrate, m. p. 216°), identical with the dihydro-compound of the base, $C_7H_{14}N_2$, from spermine. C. HOLLINS.

Rapid determination of opium in stomach contents. E. R. DOVEY (Analyst, 1927, **52**, 26—27).—The coloration produced by adding hydrochloric acid, mercuric chloride solution, and ferric chloride solution to the filtered liquid is compared with that of a similarly treated standard solution of the kind of opium most likely to have been taken.

D. G. HEWER.

ψ-Morphine. Separation and determination of morphine, ψ-morphine, and related substances. A. K. BALLS (J. Biol. Chem., 1927, **71**, 537—542, 543—558).—ψ-Morphine was prepared by oxidation of morphine with hydrogen peroxide in presence of potassium cuprous cyanide, and was purified through the hydrochloride. It differs from morphine chiefly in its more acidic character and in the greater insolubility of its acidic salts. If a mixture of morphine with ψ-morphine and other higher oxidation products in alkaline solution be treated with silicotungstic acid, and the reaction be adjusted to p_H 7·8, the ψ-morphine is completely precipitated; on further acidification of the filtrate, the morphine is precipitated together with the other oxidation products. Alternatively, the filtrate may be adjusted to p_H 9·0 and the morphine alone then removed by extraction with amyl alcohol. On the above basis, a method has been elaborated by which morphine and ψ-morphine in concentrations of the order of 0·01% may be determined in muscle-tissue with an error of about 30%. C. R. HARINGTON.

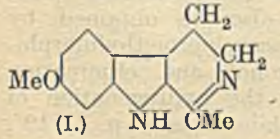
Dependence of the degree of hydrolysis of cocaine on hydrogen-ion concentration. E. SADOLIN (Dansk Tidss. Farm., 1927, **1**, 223—233).—The degree of hydrolysis corresponding with the first stage of the hydrolysis of cocaine ($\cdot CO_2Me \longrightarrow \cdot CO_2H$) has been investigated by boiling 2% solutions of cocaine hydrochloride for 1 hr. under reflux, the p_H values of the solutions being previously adjusted to a known figure by employing Sörensen's buffer solutions. The extent of hydrolysis was found by determining the methyl alcohol formed, using Pregl's micro-modification of Zeisel's apparatus, the values obtained being corrected for the dilution and the effect due to the presence of cocaine hydrochloride. A 2% solution of cocaine hydrochloride is practically completely hydrolysed by boiling for 1 hr. when the p_H value exceeds 7·5, whilst for p_H values between 1 and 5 the hydrolysis shows a minimum of about 10%. The extent to which the second stage of hydrolysis of cocaine (benzoylecgonine ⟶ ecgonine) takes place was investigated by boiling 2% cocaine hydrochloride solutions for 1 hr. as above and determining the benzoic acid formed; this was done either by acidifying the liquid and boiling it almost to dryness, the benzoic acid which passed over being titrated with 0·04*N*-sodium hydroxide, or, more exactly, by extracting the acidified solution twice with ether, evaporating this off, and titrating the residual benzoic acid as before. The values obtained show that the hydrolysis is minimal for p_H values between 2 and 7, where it amounts to approximately 3% for 1 hr.'s boiling of the solution; with p_H values greater than 13, hydrolysis is complete. It is recommended to utilise this reaction for the determination of cocaine, the material being boiled for 1 hr. under reflux with sodium hydroxide solution of at least $0{\cdot}1N$; the solution is then acidified, extracted twice with ether, and the benzoic acid in the ether extract determined as above.

H. F. Harwood.

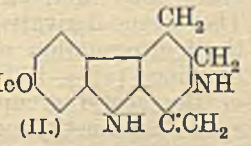
Double salt crystals of cocaine with rare metals. E. Pace (Arch. farm. sperim., 1926, 42, 35—41).—Crystalline double salts are described of cocaine with the following: *rubidium chloride*, m. p. 158° (decomp.); *beryllium chloride*, $Cn,BeCl_2$ (writing Cn for 1 mol. of cocaine, $C_{17}H_{21}O_4N$); *thallic chloride*, $Cn_2,TlCl_3$, m. p. 112°; *titanic acid*, Cn_2,H_4TiO_4, m. p. 106°; *zirconium sulphate*, $Cn_2,Zr(SO_4)_2$, m. p. 132°; *thorium chloride*, $Cn_2,ThCl_4$, m. p. 200°; *orthovanadic acid*, Cn,H_3VO_4, m. p. 139°; *tungstic acid*, Cn_2,H_2WO_5, m. p. 109°; *uranyl nitrate*, $Cn,UO_2(NO_3)_2$, m. p. 226°; *palladous chloride*, $Cn,PdCl_2$, m. p. 185°; *chloroplatinic acid*, Cn_2,H_2PtCl_6, m. p. 205°; *cerous nitrate*, $Cn,Ce(NO_3)_3$, m. p. 98°; *neodymium nitrate*, m. p. 82°; *yttrium nitrate*, $Cn,Yt(NO_3)_3$, m. p. 115°; *erbium sulphate*, m. p. 121°. Cocaine forms with selenium chloride a colourless *compound*, m. p. 42°, which changes on exposure to air into a red *compound*, Cn_2,Se_2Cl_2, m. p. 151°; this is suggested as a test for cocaine.

E. W. Wignall.

Harmine and harmaline. IX. Synthesis of harmaline. R. H. F. Manske, W. H. Perkin, jun., and R. Robinson (J.C.S., 1927, 1—14).—The formulæ (I) and (II) are the only representations of the harmaline molecule consistent with its synthesis. The reactions of the base are satisfactorily interpreted on the hypothesis that these are tautomerides, the crystalline base being probably (I).



(I.)



(II.)

Ethyl α-acetyl-β-phenylpropionate condenses with benzenediazonium chloride in alkaline–alcoholic solution, and the product, after hydrolysis and treatment with alcoholic hydrogen chloride, yields the *ethyl* ester, m. p. 137—138°, of 3-*phenylindole*-2-*carboxylic acid*, m. p. 186°. Sodium α-acetyl-β-phenylpropionate and benzenediazonium chloride react in alkaline solution to give α-*phenylbutane*-βγ-*dione*-β-*phenylhydrazone*, m. p. 108°. (Analogous reactions give the β-m-*nitrophenylhydrazone*, m. p. 146°, and the β-2 : 5-*dimethoxyphenylhydrazone*, m. p. 107°.) The β-phenylhydrazone is converted by boiling concentrated hydrochloric acid into 2-*acetyl*-3-*phenylindole*, m. p. 151°, which yields 3-phenylindole on fusion with sodium hydroxide. Hydrolysis of ethyl δ-phthalimido-α-acetylvalerate with cold aqueous-alcoholic sodium hydroxide gives sodium δ-*o*-carboxybenzamido-α-acetylvalerate, which couples in alkaline solution with benzenediazonium chloride, yielding, after acidification, ζ-o-*carboxybenzamidohexane*-βγ-*dione*-γ-*phenylhydrazone*, m. p. 156—157°. Treatment with acetic anhydride gives ζ-*phthalimidohexane*-βγ-*dione* γ-*phenylhydrazone*, m. p. 172°, converted by boiling alcoholic hydrochloric acid into 2-*acetyl*-3-β-*phthalimidoethylindole*, m. p. 214°. The action of hydrazine hydrate in hot alcoholic solution, followed by treatment of the product with hydrochloric acid (cf. A., 1926, 1132), yields phthalylhydrazide and the hydrochloride of *harmalan* (demethoxyharmaline). The free base ($+10H_2O$) has m. p. 182—183° and, on oxidation with chromic acid, yields harman. A similar series of reactions with sodium δ-*o*-carboxybenzamido-α-acetylvalerate and *m*-methoxybenzenediazonium chloride yields ζ-o-*carboxybenzamidohexane*-βγ-*dione*-γ-m-*methoxyphenylhydrazone*, m. p. 208° (decomp.); ζ-*phthalimidohexane*-βγ-*dione*-γ-m-*methoxyphenylhydrazone*, m. p. 167—168°; 6-*methoxy*-2-*acetyl*-3-β-*phthalimidoethylindole*, m. p. 218°, and harmaline, yielding, on oxidation with chromic acid, harmine. In the indole cyclisation, effected in this case with *n*-butyl-alcoholic hydrogen chloride, closure takes place in the *p*-position to the methoxy-group (cf. J.C.S., 1921, **119**, 1614).

ζ-*o*-Carboxybenzamidohexane-βγ-dione-γ-phenylhydrazone is converted by the action of hydrogen chloride in hot acetic acid solution into the *hydrochloride*, m. p. 286° (decomp.), of 5-*keto*-6-*methyl*-2 : 3 : 4 : 5-*tetrahydropyridine*-5-*phenylhydrazone* ($+0{\cdot}5C_6H_6$), m. p. 134—135°. The following are also described: ζ-o-*carboxybenzamidohexane*-βγ-*dione*-γ-m-*chlorophenylhydrazone*, m. p. 210° (decomp.), and 5-*keto*-6-*methyl*-2:3:4:5-*tetrahydropyridine*-5-m-*chlorophenylhydrazone*, m. p. 161° (*hydrochloride*); 5-*keto*-6-*phenyl*-2 : 3 : 4 : 5-*tetrahydropyridine*-5-*phenylhydrazone*, m. p. 146—147° (*hydrochloride*).

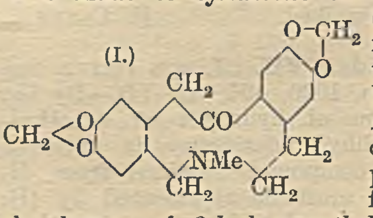
Preparation of γ-phthalimidobutyronitrile by direct replacement of bromine by the cyano-group in γ-bromopropylphthalimide can be effected by the use of anhydrous methyl-alcoholic sodium cyanide. The experimental details described must be closely followed.

M. Clark.

Chloroarsinosoquinine. II. F. X. Erben and E. Philippi (Ber., 1927, 60, [*B*], 122—124; cf. Erben and others, A., 1926, 188).—Chloroarsinosoquinine, m. p. 207—209° after darkening at 199—200° and softening at 204°, is most conveniently prepared by heating dehydroquinine with arsenic trichloride at 130—135° in the absence of a solvent. Neither the base nor its salts could be caused to crystallise.

H. Wren.

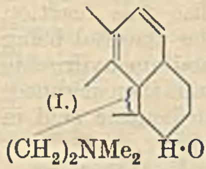
Synthesis of protopine and allied alkaloids. I. T. S. Stevens (J.C.S., 1927, 178—187).—Attempts were made to synthesise the protopine isomeride (I) without previous formation of a structure of the tetrahydroberberine type (cf. A., 1926, 964). Condensation of homopiperonylic acid with formaldehyde yields the *lactone* of 6-*hydroxymethylhomopiperonylic acid* (II), m. p. 137°, the constitution of which is established by oxidation with permanganate to 4 : 5-methylenedioxyhomophthalic acid. The corresponding 6-*hydroxymethylhomopiperonylamide*,

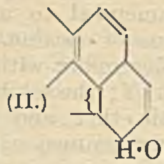


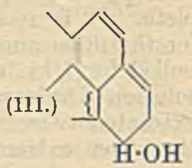
m. p. 164—167°, reacts with phosphorus trichloride, giving 6-*chloromethylhomopiperonylonitrile* (III), m. p. 83—85°, which condenses with *N*-methyl-β-piperonylethylamine to give N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile*, m. p. 74—76° [*nitrate*, m. p. about 150° (decomp.)]. Attempted conversion into (I) by an intramolecular Hoesch reaction gives N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylamide*, m. p. 140° [*picrate*, m. p. 210° (decomp.)]. Bromination of *N*-methyl-β-piperonylethylamine yields N-*methyl*-6-*bromo*-β-*piperonylethylamine* (IV) (*hydriodide*, m. p. 175°; *hydrochloride*, m. p. 162—164°; *benzoyl* derivative, m. p. 98—100°); this substance is alternatively obtained [together with a *compound*, m. p. 260° (*picrate*, m. p. 151—153°), probably trimethyl-6-bromo-β-piperonylethylammonium iodide] by successive treatment with methyl iodide and alcohol of the *piperonylidene* derivative, m. p. 108—112°, of 6-*bromo*-β-*piperonylethylamine* [*hydrochloride* (+H_2O), m. p. 208—210°; *hydriodide*, m. p. 221°; *benzoyl* derivative, m. p. 138—140°]. The last-named compound is obtained by the action of sodium hypochlorite on 6-bromo-β-piperonylpropionamide (*ibid.*, 952). The nitrile (III) reacts with (IV), giving N-*methyl*-N-6′-*bromo*-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (*hydrochloride*, m. p. 205°; *nitrate*, decomp. 160°). Attempts to obtain (I) by an internal Grignard reaction involving the bromine atom and the nitrile group were unsuccessful. Successive treatment of the lactone (II) with phosphorus trichloride and methyl alcohol gives the *methyl* ester, m. p. 41—43°, of 6-*methoxymethylhomopiperonylic acid*, m. p. 93—95° (*silver* salt), which loses the methoxy-group, with regeneration of the lactone, on treatment with hot dilute hydrochloric acid. (Homopiperonyl methyl ether passes similarly into 2 : 3 : 6 : 7-bismethylenedioxy-9 : 10-dihydroanthracene.) Treatment of (II) with hydrogen bromide gives 6-*bromomethylhomopiperonylic acid*, m. p. 146—149°, reconverted into the lactone by primary or secondary bases or attempted condensation with β-piperonylethylamine or its *N*-methyl derivative. The *methyl* ester, m. p. 68—70°, obtained by the action of diazomethane, condenses with *N*-methyl-β-piperonylethylamine, giving, after hydrolysis, N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylic acid*, m. p. 136—140° [*oxalate* (+$C_2H_2O_4$), m. p. 178° (decomp.)]. Ring-closure to the compound (I) by conversion into the acid chloride and treatment with aluminium chloride could not be effected.

An improved method for the preparation of homopiperonylic acid is described. M. CLARK.

Morphine alkaloids. VII. J. VON BRAUN and R. S. CAHN (Annalen, 1926, 451, 55—74).—By the action of two atoms of hydrogen on α-methylmorphimethine, a dihydro-derivative is obtained identical with the compound obtained from dihydrocodeine, which must be represented by (I). The action of two atoms of hydrogen on β-methylmorphimethine yields an isomeric dihydro-derivative, in which the double linking in the 9 : 10-position must have been reduced. The conclusion is reached that the facts are best explained by the 7 : 8-position of the double linking in codeine. Thus formula (II) represents α- and (III) β-methylmorphimethine.


(I.)


(II.)


(III.)

Since when the hydroxyl group is replaced by chlorine in the tetrahydronormethylmorphimethines obtained from α-, β-, or γ-derivatives there is no tendency for the chlorine atom to combine with the hydrogen atom of the ·NHMe group with evolution of hydrogen chloride and ring closure, it is considered that the side-chain including the nitrogen atom is probably not attached to position 5. This suggests that the Wieland and Kotake (A., 1925, i, 1090) formula for codeine may be more nearly correct than that of Robinson.

Hydrogenation of α-methylmorphimethine in alcoholic solution using nickel as catalyst gives (III) dihydro-α-methylmorphimethine (I) (methiodide, m. p. 223—225°), but when either α- or β-methylmorphimethine is reduced using sodium and alcohol, (II) dihydro-β-methylmorphimethine (methiodide of acetyl derivative, $[\alpha]_D^{20}$ +75°) is obtained.

When cyanogen bromide reacts with acetyltetrahydromethylmorphimethine, it yields the *methobromide* of the base, m. p. 225—226°, and *cyanoacetyltetrahydronormethylmorphimethine*, m. p. 100—101°, $[\alpha]_D^{20}$ −58° in chloroform. The cyanoacetyl derivative dissolves in a solution of sodium methoxide and the non-acetylated *cyano*-derivative separates as plates, m. p. 140°, $[\alpha]_D^{20}$ −51·4° in chloroform. This substance is slowly hydrolysed by dilute hydrochloric acid to tetrahydronormorphimethine, an oil which yields oily derivatives and poorly-defined salts. The cyano-derivative may also be obtained by the hydrogenation of cyanoacetylnormethylmorphimethine, $[\alpha]_D^{16}$ −106° in alcohol, and elimination of the acetyl group, or by the hydrogenation of cyano-α-normethylmorphimethine, m. p. 119°, $[\alpha]_D^{19}$ −196°.

Acetyl-β-methylmorphimethine (*methobromide*, indefinite m. p.) reacts with cyanogen bromide, yielding *cyanoacetyl*-β-*methylmorphimethine* as an oil, which, on keeping with sodium methoxide solution, is hydrolysed to the *carbamide* derivative, β-$C_{17}H_{16}O_2(OH)\cdot NMe\cdot CO\cdot NH_2$, m. p. 130—131°, $[\alpha]_D^{15}$ +364° in chloroform. This carbamide is readily hydrogenated to yield the *tetrahydro*-derivative as an oil, which is hydrolysed to tetrahydronormorphimethine. When treated in chloroform solution with phosphorus pentachloride, the tetrahydro-base yields the *chloro*-base, $C_{17}H_{20}O_2Cl\cdot NHMe$, an oil stable towards sodium carbonate solution, as the *hydrochloride*, m. p. 267° (decomp.) [*chloroplatinate*, m. p. 223° (decomp.)].

Similarly, the following substances are derived from acetyltetrahydro-γ-methylmorphimethine (*methobromide* +$3H_2O$, m. p. 100—102°): *cyanoacetyltetrahydro-γ-normethylmorphimethine*, m. p 102°, $[\alpha]_D^{18}$ −104·5° in chloroform; *cyanotetrahydro-γ-normethylmorphimethine*, m. p. 117°, $[\alpha]_D^{17}$ −90·7° in chloroform; *tetrahydro-γ-normethylmorphimethine*, a vitreous substance yielding no well-defined salts, which with phosphorus pentachloride yields a mixture of the chloro-derivative with a chlorine-free substance, probably the unchanged base. The chlorine in the mixture is stable towards sodium carbonate solution.

R. W. West.

Organic derivatives of silicon. XXXII. Carbon–silicon binding. F. S. Kipping (J.C.S., 1927, 104—107).—There is no authentic evidence for the formation of an ethylenic linking between carbon and silicon. The reactions leading to olefine formation are inapplicable, and it is exceedingly doubtful whether this linking is a possible one. Schlenk and Renning (A., 1913, i, 34) claim to have prepared the compound $SiPh_2{:}CH_2$ by distillation of crude diphenylmethylsilicol. This silicol is, however, only very slowly decomposed at its b. p., giving *diphenylmethylsilicyl oxide*, m. p. 51—52°. No evidence for the formation of an unsaturated compound could be obtained. *Diphenyldimethylsilicane*, obtained by the action of an excess of magnesium methyl iodide on dichlorodiphenylsilicane, has b. p. 176—178°/45 mm. M. Clark.

Preparation of *m*-nitro-*p*-hydroxyphenylarsinic acid. I. Ostromisslensky.—See B., 1927, 93.

Production of arsinic acids of aromatic [heterocyclic] compounds [dihydrobenzoxazolones]. L. Cassella & Co.—See B., 1927, 125.

Dicyanates and dibenzoates of triphenylbismuthine and triphenylstibine. F. Challenger and V. K. Wilson (J.C.S., 1927, 209—213).—*Triphenylbismuthine dicyanate*, m. p. 128·5—129°, is stable at the ordinary temperature, whereas triphenylbismuthine dithiocyanate and diselenocyanate immediately revert to derivatives of tervalent bismuth, yielding phenyl thiocyanate and selenocyanate. Comparative experiments indicate that the dithiocyanate is slightly more stable than the di-iodide, hence iodine is, apparently, more positive than thiocyanogen. This is in agreement with Birckenbach and Kellermann's electrochemical series (A., 1925, ii, 568; 1926, 965). *Triphenylstibine dicyanate* has m. p. 111—112°. Triphenylbismuthine and triphenylstibine react with benzoyl peroxide, giving *triphenylbismuthine dibenzoate*, m. p. 172—173·5°, and *triphenylstibine dibenzoate*, m. p. 171·5°, whilst triphenylphosphine gives benzoic anhydride and triphenylphosphine oxide. M. Clark.

Arylseleninic acids. W. H. Porritt (J.C.S., 1927, 27—29).—Arylseleninic acids are obtained by oxidation of the corresponding arylselenoglycollic acids with hydrogen peroxide (cf. A., 1925, i, 1196). If the temperature is allowed to rise during the first stage of this reaction, diaryl diselenides are also formed. The following are described: o-*tolylselenoglycollic acid*, m. p. 70—71°; m-*xylyl*-4-*selenoglycollic acid*, m. p. 90·5°; o-*xylyl*-4-*selenoglycollic acid*, m. p. 88°; toluene-*o*-seleninic acid, m. p. 126—127°, and toluene-*p*-seleninic acid, m. p. 171° (cf. Doughty and Elder, *ibid.*, 1913, i, 962); *toluene*-m-*seleninic acid*, m. p. 119—120°; *bromobenzene*-p-*seleninic acid*, m. p. 187°; m-*xylene*-4-*seleninic acid*, decomp. 146—147°; o-*xylene*-4-*seleninic acid*, decomp. 125°. *Di*-o-*tolyl selenide*, m. p. 64°, is obtained as a by-product in the preparation of the selenomercaptan from magnesium *o*-tolyl bromide and selenium. M. Clark.

Preparation of organo-selenium compounds by means of the Friedel–Crafts reaction. R. E. Lyons and W. E. Bradt (Ber., 1927, **60**, [*B*], 60—63).—The action of anhydrous aluminium chloride on selenium dioxide and benzene yields diphenylselenium dichloride, m. p. 183—183·5° (cf. Lyons and Bush, A., 1908, i, 417), diphenyl selenide, diphenyl diselenide, and dichlorodiphenyl selenide, m. p. 96·5—97°. The *compound*, $Ph_2SeCl_2,2CH_3{\cdot}CO{\cdot}CH_3$, m. p. 127·8—127·9°, is incidentally described.

H. Wren.

Cyclic organo-metallic compounds. III. Nitro- and amino-derivatives of phenoxtellurine. H. D. K. Drew and R. W. Thomason (J.C.S., 1927, 116—125).—Phenoxtellurine (see this vol., 164) on treatment with nitric acid is first oxidised to the 10 : 10-dinitrate and afterwards undergoes nitration of the nucleus. The colourless nitro-dinitrates or basic nitrates thus produced are readily reduced by alkali hydrogen sulphite to the nitro-derivatives. Nitration with concentrated nitric acid thus yields 2-*nitrophenoxtellurine*, m. p. 129°, and a lesser yield of 4-*nitrophenoxtellurine*, m. p. 104°, accompanied by a small quantity of the 2 : 8-dinitro-derivative. Nitration with fuming nitric acid gives 2 : 8-*dinitrophenoxtellurine*, m. p. 228°, and a lesser yield of 4 : 8-*dinitrophenoxtellurine*, m. p. 197—198°. The $>Te(NO_3)_2$ grouping is therefore either *meta*-directive or its influence is negligible compared with that of the ether oxygen atom.

Additive *compounds* of indefinite m. p., containing one and two mol. proportions of the 2 : 8-dinitro-derivative, respectively, with one of the 2-nitro-derivatives are described. A similar but more stable additive *compound*, m. p. 59°, containing 1 mol. of phenoxtellurine and 1 mol. of 2(?)-chloro-8(?)-methylphenoxtellurine is obtained as a by-product in the preparation of phenoxtellurine from tellurium tetrachloride and solid diphenyl ether, its formation being ascribed to the presence of phenyl *p*-tolyl ether as an impurity in the last-named substance. These additive compounds are capable of recrystallisation from certain organic solvents, whilst other solvents effect their complete or partial separation into the constituent substances. Union of the bivalent tellurium atoms of the associated molecules does not occur, since the corresponding complex 10 : 10-dichlorides and dinitrates, containing only quadrivalent tellurium, may also, in some cases, be recrystallised unchanged.

Reduction of the corresponding nitro-derivatives gives: 2-*aminophenoxtellurine*, m. p. 157° (*hydrochloride*); 2 : 8-*diaminophenoxtellurine*, m. p. 198° (*hydrochloride*); 4 : 8-*diaminophenoxtellurine*, m. p. 156° (*hydrochloride*).

The constitutions of the nitro- and amino-derivatives were established by conversion of their 10 : 10-dichlorides, dinitrates, or similar salts into the corresponding diphenyl ethers by means of aqueous potassium hydroxide, which detaches the tellurium atom, replacing it by two atoms of hydrogen.

M. Clark.

Phenylgermanium derivatives. C. A. Kraus and L. S. Foster (J. Amer. Chem. Soc., 1927, 49, 457—467).—Germanium tetraphenyl is obtained in 93% yield by a method analogous to that applied by Chambers and Scherer (A., 1926, 629) to the preparation of tin tetraphenyl. It has m. p. 235·7°, and is white when pure (cf. Morgan and Drew, *ibid.*, 1925, i, 1197). When boiled with bromine in carbon tetrachloride, it affords triphenylgermanium bromide, m. p. 138·7°, which yields triphenylgermanium oxide on hydrolysis with water or alkalis, and is converted by liquid ammonia into *triphenylgermanylamine*, $(GePh_3)_3N$. Hexaphenyldigermane (cf. Morgan and Drew, *loc. cit.*) is converted into sodium triphenylgermanide by sodium in liquid ammonia, and yields triphenylgermanium bromide when treated with bromine in carbon tetrachloride. *Triphenylgermanium fluoride*, m. p. 76·6°, obtained by evaporating the above oxide with hydrofluoric acid, is the most stable of the triphenylgermanium halides. *Triphenylgermanium iodide*, m. p. 157°, obtained by agitating a chloroform solution of the oxide with aqueous hydriodic acid, is unstable in air and in light petroleum solution. *Sodium triphenylgermanide*, obtained as above, crystallises with $3NH_3$, and is strongly ionised in liquid ammonia solution, in which it is readily oxidised to *sodium triphenylgermanolate*, $NaO{\cdot}GePh_3$, m. p. not below 250° (from liquid ammonia) or m. p. about 100° (from light petroleum). Treatment of the latter with water affords *triphenylgermanol*, m. p. 134·2°, above which it loses water with formation of the oxide. Ammonium bromide in liquid ammonia converts sodium triphenylgermanide into *triphenylgermane*, $GeHPh_3$. This exists in two forms, (α) m. p. 47°, and (β) m. p. 27° (monotropic relationship), and is stable at 250°. It gradually oxidises in air, and reacts with halogens or with strong halogen acids to form triphenylgermanium halides. It is reduced by sodium in liquid ammonia, with formation of sodium triphenylgermanide and disodium diphenylgermanide. Treatment of sodium triphenylgermanide in liquid ammonia with trimethylstannyl bromide affords *trimethylstannyltriphenylgermane*, $Me_3Sn{\cdot}GePh_3$, m. p. 88°. This reacts quantitatively with bromine to form the corresponding substituted tin and germanium bromides, but does not appear to dissociate in boiling benzene.

F. G. Willson.

Mercuration in the aromatic series. VI. Mercurated derivatives of *o*-cresol. E. Mameli (Gazzetta, 1926, 56, 948—958; cf. A., 1922, i, 695, 1080—1083).—Mercuration of *o*-cresol is most satisfactory in aqueous acetic acid, and gives 50·3—62·3% of o-*cresol-4-mercuriacetate* (I), m. p. 153—155°, decomp. 186—190°, 13·4—20·7% of o-*cresol-6-mercuriacetate* (II), m. p. 123—125°, decomp. 191°, and 2·6—7·0% of o-*cresol-4 : 6-dimercuriacetate* (III), m. p. 192—195° (decomp.), which is obtained in larger quantities by raising the temperature, and in good yield when 2 mols. of mercuric acetate are employed. Benzenediazonium chloride reacts with (I) to give phenyldisazo-*o*-cresol (Nölting and Kohn, A., 1884, 902). Treatment of (I) with bromine gives 4-bromo-*o*-cresol; of (II), 6-bromo-*o*-cresol. All three compounds on nitration yield 4 : 6-dinitro-*o*-cresol. o-*Cresol-4-mercurichloride*, m. p. 200—202° (decomp.), -6-*mercurichloride*, m. p. 160—162° (decomp.), and -4 : 6-*dimercurichloride*, m. p. 210—212° (decomp.), and the corresponding *mercurinitrates*, m. p. 212—213°, 208—210°, and 222°, respectively (decomp.), and *mercurisulphates* have been obtained.

E. W. Wignall.

Nuclein metabolism. XV. Hydrolysis of thymus-nucleic acid with methyl-alcoholic hydrogen chloride. XVI. Action of human intestinal juices on thymus-nucleic acid. S. J. Thannhauser and G. Blanco (Z. physiol. Chem., 1921, 161, 116—125, 126—130; cf. Thannhauser and Ottenstein, A., 1921, i, 521).—XV. With the view of stabilising as a methylglucoside any carbohydrate present, dry thymus-nucleic acid is heated with hydrogen chloride in absolute methyl alcohol for 48 hrs. at 100°. Hydrochlorides of guanine and adenine separate out on cooling, and the diluted filtrate, after removal of phosphoric and hydrochloric acids as silver salts (together with a non-carbohydrate which gives the orcinol test), contains a mixture of pyrimidine nucleotides. Brucine salts of a cytosine–hexosediphosphoric acid, m. p. 220—222° (*brucine* salt), a cytosine–hexosephosphoric acid, m. p. 215—216°, a thymine–hexosediphosphoric acid, m. p. 195—196°, all previously prepared by hydrolysis with picric acid (*loc. cit.*) are obtained from the mixture (the higher m. p. are confirmed by purification of the earlier products). Cytosine, but no carbohydrate or methylglucoside, could be detected after removal of these nucleotides, and it is concluded that the purines of animal nucleic acid are not attacked in the molecule by means of a nucleotide linking.

XVI. Thymus-nucleic acid, fermented with human intestinal juices under a thick toluene layer at 37° for 3 days with hourly shaking, yields cytosine– and thymine–hexosediphosphoric acids (brucine salts, m. p. 120—121° and 250°, respectively) and adenine, charring at 206°.

C. Hollins.

Proteins. IV. Preparation of rice-glutelin. V. Point of optimum flocculation of rice glutelin. K. Kondo and T. Hayashi (Mem. Coll. Agric., Kyōtō Imp. Univ., 1926, 37—53, 55—69).—IV. The molecule of rice-glutelin having been found susceptible to change in 0·2% sodium hydroxide solution, the authors have modified the usual technique of isolating proteins; 0·5*N*- instead of 10% (2*N*-) sodium chloride is used to extract the globulin, albumins, etc., 0·05*N*-sodium hydroxide to dissolve the glutelin, and 0·05*N*-acetic acid to flocculate it. The nitrogen distribution figures for the anhydrous protein so prepared are tabulated.

V. Maximum flocculation and precipitation of rice-glutelin (cf. *supra*) occurs in dilute sodium acetate solution, the reaction of which is near absolute neutrality. The reaction of the solution, in which maximum flocculation of the protein takes place, changes after the addition of the protein. Examining the factors that may be responsible for this, the conclusion is reached that the protein cannot completely take the form $NH_2{\cdot}R{\cdot}CO_2H$

in the presence of salt in the solution, *i.e.*, the protein cannot behave as an isoelectric ion in presence of salt. Applying these considerations to the theory, it is further concluded that it is impossible to determine the isoelectric point of a protein difficult of solution, *e.g.*, casein or rice-glutelin, by the usual method. Determination by this customary method gives an apparent isoelectric point, which must be differentiated from the theoretical value. W. ROBSON.

Proteins. VI. Influence of salts on the point of optimum flocculation of rice-glutelin. K. KONDO, T. HAYASHI, and T. MATSUSHITA (Mem. Coll. Agric., Kyōtō Imp. Univ., 1926, 71—81).—Results of the study of the influence of sodium acetate, sodium chloride, potassium chloride, and lithium chloride on solutions of rice-glutelin, made according to the procedure described above, show that these salts carry the optimum point of flocculation to the acidic side, and that the apparent isoelectric reaction of a protein difficult of solution is variable according to the salt used and its concentration. W. ROBSON.

Proteins. VII. Refractive indices of protein solution. I. K. KONDO and T. HAYASHI (Mem. Coll. Agric., Kyōtō Imp. Univ., 1926, 83—94).—In contradistinction to the theory propounded by Robertson and by Wington, the authors conclude, from their results, that the refractive indices of solutions of sodium rice-glutelinate or sodium caseinate are not linearly related to their concentrations. The authors, moreover, maintain that the determination of the nitrogen-equivalent-refractivity of the protein indicates the degree of dissociation of the protein salt, and conclude that to an ampholyte such as protein belong different nitrogen-equivalent-refractivities, according as the protein behaves as a cation or an anion. W. ROBSON.

Rate of hydrolysis of solutions of proteins in acids as measured by the formation of amino-nitrogen. D. M. GREENBERG and M. F. BURK.—See this vol., 213.

Analysis of proteins. VIII. Determination of cystine in the modified Van Slyke method. R. H. A. PLIMMER and J. LOWNDES (Biochem. J., 1927, 21, 247—253).—97% of pure cystine is precipitated by phosphotungstic acid. On boiling with acids it loses 7% of its nitrogen and only 40% is then precipitated by phosphotungstic acid. The amounts of cystine sulphur in the egg-proteins and caseinogen have been determined. The presence of another sulphur compound is indicated. A crystalline precipitate consisting in part of arginine, possibly racemic, was formed in the monoamino-fractions of egg-proteins and caseinogen on keeping for more than 15 months. The sulphur of cystine can be determined in the presence of phosphotungstic acid by a modification of the Benedict method of sulphur determination. S. S. ZILVA.

Separation and determination of 2 : 5-diketopiperazines in presence of amino-acids and peptides. A. BLANCHETIÈRE (Bull. Soc. chim., 1927, [iv], 41, 101—110).—Siegfried's carbamate reaction (A., 1905, ii, 332; 1906, i, 144) can be utilised for the determination of diketopiperazines in presence of amino-acids and peptides, with an experimental error of up to 10%. The amino-acids are precipitated quantitatively and the peptides almost quantitatively, acetone in both cases giving better results than 70% alcohol as used by Schryver (*ibid.*, 1921, i, 182; 1925, i, 89). Acetone, however, causes difficulties in the Kjeldahl determination of the nitrogen remaining in solution (from which figure the proportion of diketopiperazines is calculated). Details of the determination are given. The maximum experimental error (10%) is obtained with diketopiperazines such as *cyclo*glutamylglutamic acid which are more readily hydrolysed by barium hydroxide. Proteins such as egg-albumin are not appreciably hydrolysed by barium hydroxide under these conditions. R. BRIGHTMAN.

Determination of arginine in pure proteins and tissues by a modification of Jansen's method. A. BONOT and T. CAHN (Compt. rend., 1927, 184, 246—247).—Arginine may be accurately determined by a modification of the method of Jansen (A., 1917, ii, 184), the arginine being decomposed by arginase in a medium of exactly p_H 9·9, the carbamide formed being precipitated by means of a 10% methyl-alcoholic solution of xanthydrol, and weighed as dixanthylcarbamide. Full details are given, the method giving results accurate within 2%. J. W. BAKER.

Sources of error in organic elementary analysis. III. Rubber, cork, and tap lubricants. J. LINDNER (Ber., 1927, 60, [*B*], 124—129; cf. this vol., 66, 166).—In three cases investigated, the errors introduced into the carbon values by the volatilisation of organic substances from the rubber were found to be very slight. Errors introduced by the ability of rubber to absorb foreign organic matter are more serious; even very volatile compounds are most tenaciously retained. Penetration of carbon dioxide from the atmosphere through the rubber causes perceptible error only with very long tubes. Cork absorbs moisture and carbon dioxide and is not more suitable than rubber for joining the combustion tube with the absorption apparatus. The common tap lubricants absorb carbon dioxide and may cause appreciable error if injudiciously applied. Heavy mineral oils emit appreciable amounts of carbon dioxide to the atmosphere. H. WREN.

Organic micro-combustion. G. KEMMERER and L. T. HALLETT (Ind. Eng. Chem., 1927, 19, 173—176).—Pregl's micro-combustion method is modified with regard to control and raising of the temperature of the furnace by substitution of an electric furnace built in sections. Further, the gas train is simplified by elimination of the air train to wash oxygen from the apparatus; the pyrex combustion tube is replaced by a silica tube. Micro-absorption tubes are used which are capable of being sealed by drops of mercury and on rotating through 90° allow the mercury to fall back into little pockets to leave free passage for air. Phosphoric oxide was the most satisfactory drying agent, whilst ascarite followed by 1 cm. layer of phosphoric oxide was used in the carbon dioxide tubes. Water residues may be successfully analysed in this apparatus. D. G. Hewer.

Pyridine test as quantitative method for determination of small amounts of chloroform. W. H. Cole (J. Biol. Chem., 1926, 71, 173—180).—The pink colour obtained by heating solutions containing chloroform with pyridine in presence of sodium hydroxide (cf. Ross, A., 1924, ii, 352) has been made the basis of a colorimetric method for the determination of chloroform in aqueous solution in concentrations of 0·1 to 0·0001% with an error of ±1%. Chloroform in animal tissues (in the absence of blood) may be determined by extraction of the material with acidulated distilled water, and direct application of the colorimetric method to the extract. If blood be present, the chloroform must first be separated by distillation, in which case the determination is not so accurate. C. R. Harington.

Determination of ethyl iodide. I. Starr, jun., and C. J. Gamble.—See below.

Precipitation of bases as silver compounds. A. Kresel (Z. physiol. Chem., 1926, 161, 147—148).—The inconveniences of the introduction of nitric acid when silver nitrate is used for the precipitation of bases, and of the large volume necessary when silver sulphate is substituted, are avoided by using freshly-precipitated silver oxide in presence of sulphuric acid. Aspartic acid is readily separated from phenylalanine, and nuclein bases from "hexone" bases. C. Hollins.

Biochemistry.

Aërobic and anaërobic metabolism of the common cockroach (*Periplaneta orientalis*). II. W. K. Slater (Biochem. J., 1927, 21, 198—203; cf. this vol., 66).—After a period of anaërobiosis the cockroach not only uses an excess of oxygen, but also retains a considerable volume of carbon dioxide. The oxygen debt and the carbon dioxide retention are related through the removal of lactic acid. S. S. Zilva.

Oxygen consumption of the kidney. K. Tamura, S. Watanabe, and H. Kaburaki (Proc. Imp. Acad. Tokyo, 1926, 2, 431—433).—In contrast to the conclusions of Barcroft and his associates and of Tashiro and Abe, the authors find that the oxygen consumption of the resting kidney of rabbits shows neither appreciable variations in different animals nor time variations in the same individual. J. M. Gulland.

Colorimetric determination of the oxidation of hæmocyanin. L. Hogben (Nature, 1927, 119, 122—123).—Polemical (cf. Stedman and Stedman, A., 1926, 1164). A. A. Eldridge.

Determination of minute amounts of ethyl iodide. Determination of blood flow by ethyl iodide. I. Starr, jun., and C. J. Gamble (J. Biol. Chem., 1927, 71, 509—535).—Small amounts of ethyl iodide vapour in air may be determined by keeping the sample for 16 hrs. in contact with excess of standard silver nitrate in concentrated nitric acid, followed by titration by means of Volhard's method. A similar procedure may also be applied to dilute solutions of ethyl iodide in water and in blood (in the latter case after preliminary distillation of the ethyl iodide). The average error of the method is 2·3%. The coefficient of distribution of ethyl iodide between air and water is 2·7; that between air and normal whole blood is 7·6; the latter figure is reduced in the case of plasma and of anæmic whole blood. The method of Henderson and Haggard (Amer. J. Physiol., 1925, 73, 193) for the determination of blood flow is criticised both on the ground of the inaccuracy of their method of determining ethyl iodide and also because the rate of destruction of ethyl iodide in the blood has been found to be much slower than was previously supposed. C. R. Harington.

Heat denaturation of proteins. IV. Free basic and acidic groups of fresh and denaturated hæmoglobin. P. S. Lewis (Biochem. J., 1927, 21, 46—53).—In the equivalent of hæmoglobin (mass=16,660) there are 24 or 25 free basic and 16 acidic groups. Heat denaturation is without effect on the free basic or acidic groups of the hæmoglobin molecule, and consequently no rupture of the polypeptide linking can take place in the process. S. S. Zilva.

Reaction between globin and hæmatin. R. Hill and H. F. Holden (J. Physiol., 1926, 61, Proc. xxii).—At p_H 5—9, globin reacts with hæmatin, forming methæmoglobin. The oxyhæmoglobin thence obtained is spectroscopically indistinguishable from the original oxyhæmoglobin. A. A. Eldridge.

Mechanism of blood clotting. I. N. Kugelmass (Third Colloid Symposium Monograph, 1925, 158—207).—Fibrin formed as an amphoteric protein has a hydrogen-ion concentration (C_H) lower than the initial C_H of the mixture of all components necessary and sufficient for clotting. The diminution in the C_H on coagulation is the greater the higher is the original C_H. In 24 hrs. at 38°, clotting takes place at p_H 5—8, being optimal at p_H 7. Diminution of electrical conductivity, partly due to loss of ionic calcium, occurs during clotting. The effects of calcium buffers are considered. The speed of coagulation is determined by serozyme, a highly dispersed, thermolabile catalyst. A "nephelelectrometer" is used to determine the degree of dispersion in colloidal systems. Coagulation is an autocatalytic process of two stages. A torsion viscosimeter and an inverse ultrafilter are described. Chemical Abstracts.

Cholesterol content of normal human plasma. I. J. A. Gardner and H. Gainsborough (Biochem. J., 1927, 21, 130—140).—The free and ester cholesterol contents of the plasma of 48 normal individuals have been determined. The individuals differed widely both in the total cholesterol and in the ratio of the so-called free cholesterol to cholesterol in the form of esters. These variations could not be ascribed to the direct absorption of varying quantities of cholesterol from the food. S. S. Zilva.

Cholesterol content of normal human plasma. II. Attraction of the proteins of plasma for sterols. J. A. Gardner and H. Gainsborough (Biochem. J., 1927, **21**, 141—147).—About 80% of the cholesterol and cholesteryl esters of the plasma were accounted for in the precipitation of its various protein fractions with ammonium sulphate. By repeated reprecipitation and redissolution of these fractions, however, the total plasma cholesterol retained in the proteins was reduced to 16·36%. The greater portion of this cholesterol was associated with the euglobulin. S. S. Zilva.

Source of error in the determination of carbamide in blood. E. Kahane (Bull. Soc. chim., 1927, [iv], **41**, 110—113).—The high percentage of protein present in blood plasma renders a correction necessary for the volume change occasioned by the size of the protein precipitate, when methods of determining carbamide, valid for urine, are applied to its determination in blood. The correction factor 1·936 in place of 2·0, as generally used, is proposed for calculating the carbamide concentration in the plasma from the concentration determined in the clear filtered liquid. Alternatively, the plasma may be diluted sufficiently to render this correction insignificant (cf. Nicloux and Welter, A., 1921, ii, 523; 1922, ii, 170). R. Brightman.

Micro-determination of chlorine in whole blood-serum or corpuscles. F. H. Smirk (Biochem. J., 1927, **21**, 31—35).—The organic matter of the blood is destroyed by ammonium persulphate and concentrated nitric acid, and the chlorine precipitated as silver chloride with excess of silver nitrate. The excess is titrated against alcoholic ammonium thiocyanate solution with concentrated ferric iron alum as indicator. The maximum error is usually 4 mg. of sodium chloride per 100 c.c. of blood. Larger errors in the third place of decimals occur in about one tenth of the samples. S. S. Zilva.

Micro-determination of iron in blood. F. H. Smirk (Biochem. J., 1927, **21**, 36—39).—The organic matter of the blood is destroyed with ammonium persulphate and nitric acid and the iron is determined colorimetrically as ferric thiocyanate against an artificial standard consisting of a mixture of cochineal, methyl-red, and hydrochloric acid. 0·2 C.c. of blood can be employed in this method. S. S. Zilva.

Kinetics of hæmolytic systems. II. Series of Ryvosh. III. Time-dilution curves and zones of action. E. Ponder (Biochem. J., 1927, **21**, 56—65, 119—126).—II. The series of Ryvosh (Pflüger's Arch., 1907, **116**, 229) has been reinvestigated quantitatively and the results are mainly confirmed.

III. A series of tables comparing experimental and calculated results for different hæmolytic systems is given. A method for determining the dimensions of the zone of action round the cells of a hæmolytic system is described. The radii of the zones are determined for the cells of different animals, and it is shown that the cells arranged in order of increasing size of zone of action fall into Ryvosh's series. The volume of the zone of action is proportional to the resistance of the cell to the lysin. S. S. Zilva.

Changes in the amino-acids in the proteins of the hen's egg during development. R. H. A. Plimmer and J. Lowndes (Biochem. J., 1927, **21**, 254—258).—Determination of the amino-acids in the hen's egg during development by the modified Van Slyke method (A., 1926, 313) has shown an increase of about 2% in the diamino-nitrogen of which the arginine increases about 1% of the total nitrogen of the egg proteins. The monoamino-acid nitrogen decreases by about 4% during development with a corresponding decrease in the amino-nitrogen. S. S. Zilva.

Stomach oil of the Fulmar petrel (*Fulmarus glacialis*). O. Rosenheim and T. A. Webster (Biochem. J., 1927, **21**, 111—118).—The stomach oil is not a glyceride, but a liquid wax of similar composition to sperm oil. It gives the arsenious chloride reaction approximately to the same degree as cod-liver oil, and its content of vitamin-*A* is of the same order as its colour value. The oil also contains vitamin-*D*. S. S. Zilva.

Echinochrome. R. K. Cannan (Biochem. J., 1927, **21**, 184—189).—Echinochrome from the eggs, perivisceral fluid, and test of *Arbacia punctulata* is not a dissociable compound in combination with molecular oxygen, but is the oxidant of a reversible oxidation–reduction system. It therefore probably functions as an "activator" rather than as a "carrier" of oxygen if it takes part in any respiratory mechanism. The electrode potentials of the system have been measured over a p_H range 2·2—9·76. The normal electrode potential is +0·1995. The rate of oxidation of reduced echinochrome by atmospheric oxygen is too great to be measured by the ordinary technique. S. S. Zilva.

Inorganic phosphate and a labile form of organic phosphate in the gastrocnemius of the frog. P. Eggleton and G. P. Eggleton (Biochem. J., 1927, **21**, 190—195).—The supposed inorganic phosphate of muscle is in certain conditions mainly organic phosphate, "phosphagen," in a very labile condition which becomes hydrolysed during the determination by the acidity of the reagents (Neumann's, Embden's, or Briggs' method). Determinations performed in slightly alkaline solution yield more correct results in such cases. In a resting frog's gastrocnemius 70 mg. of phosphorus per 100 g. of muscle out of the 100 mg. of "inorganic" phosphorus obtained by the Briggs or Embden method are of "phosphagen" origin. In rapidly induced fatigue, the true inorganic phosphate is doubled at the expense of the "phosphagen," but considerably more "phosphagen" disappears than could account for the rise in inorganic phosphate. When muscle goes into rigor, the "phosphagen" disappears entirely and the inorganic phosphate rises to about four times the resting value. S. S. Zilva.

Sensitising and stabilising action of the skin on colloidal solutions. A. Janek and B. Jirgensons

(Biochem. Z., 1927, **180**, 193—200).—The non-colloid portion of a solution obtained by rubbing two clean fingers together in distilled water and filtering sensitises colloidal solutions of ferric hydroxide, silver, and arsenic trisulphide, whereas the colloidal portion sensitises ferric hydroxide solution, but stabilises the silver sol and the arsenic trisulphide sol.

P. W. Clutterbuck.

Biochemistry of tooth growth. Y. Matsuda (J. Biol. Chem., 1927, **71**, 437—444).—During growth the ash content of the incisor teeth of rats increases, whilst the water content decreases, the content of organic matter showing no marked change. The alterations are continuous in character, except for a break which occurs at puberty. The calcium and phosphorus content of the ash does not alter with age, but the magnesium tends to increase. Minor differences are observed between the upper and lower incisors. C. R. Harington.

Biochemistry of the aqueous humour. S. Duke-Elder (Biochem. J., 1927, **21**, 66—77).—All the colloidal substances found in the normal aqueous humour are in much smaller concentration than in the serum; the proteins, however, are found in the same proportion as in the blood. The diffusible non-dissociated substances are partitioned between serum and the aqueous humour in approximately equal amounts, whilst in the case of dissociated diffusible substances, the latter fluid contains an excess of acidic radicals. The sugar content of the aqueous humour lies between that of arterial and venous plasma. Diffusible substances find their way freely into the aqueous humour when injected intravenously. Only traces of colloidal substances diffuse in this way. Aqueous humour seems, therefore, to be a dialysate of the capillary blood. Evidence is produced to show that this is also the case in abnormal aqueous humour. S. S. Zilva.

Constituents of hen bile. A. Windaus and A. van Schoor (Z. physiol. Chem., 1926, **161**, 142—146; cf. Windaus, Bohne, and Schwarzkopf, A., 1925, i, 405).—From the products of hydrolysis of 150 g. of hen bile with 10% potassium hydroxide at 135—140° there are isolated succinic acid (0·4 g.), aliphatic acids (60 g.), a *hydroxystearic acid* (6 g.), m. p. 81—82° (*sodium* salt; *methyl* ester, m. p. 52—53°), which is oxidised by chromic–acetic acid to a *ketostearic acid*, m. p. 83—84° (*sodium* and *potassium* salts; *methyl* ester, m. p. 48°), reducible by Clemmensen's method to stearic acid, m. p. 79—80°, and a bile acid identical with the chenodeoxycholic acid obtained from goose bile (*loc. cit.*) and human bile (Wieland and Reverey, *ibid.*, 181). Hydroxystearic acid is absent from goose bile. C. Hollins.

Electrometric titration of gastric juice as a method for the determination of its degree of buffering. K. A. Sčukarev (Biochem. Z., 1927, **180**, 117—126).—The mean p_H of pure gastric juice at the isoelectric point, of dog and of man, either fasting or after a test meal, is a little less than 6·2. The total hydrochloric acid may therefore be determined by titration of juice to p_H 6·2. The following quantities characterise the degree of buffering of the juice: (*a*) the ratio free hydrochloric acid : p_H calculated for the total hydrochloric acid, which if greater than 0·5 indicates poor buffering power and inversely; (*b*) the number of c.c. of 0·1*N*-sodium hydroxide used to increase the p_H from 6·2 to 8·5 (*i.e.*, from the isoelectric point to the point of colour change of phenolphthalein), which in well-buffered juice lies between 5 and 14, but in poorly-buffered solutions lies between 0·5 and 5; (*c*) the maximal increase in p_H on adding 1 c.c. of 0·1*N*-sodium hydroxide, which for well-buffered solutions is about 1, but for poorly-buffered juice may lie between 2 and 3. The buffering power of pure juice from the isolated stomach is remarkably constant.

P. W. Clutterbuck.

Electrometric determination of small amounts of hydrochloric acid in gastric juice. K. A. Sčukarev (Biochem. Z., 1927, **180**, 127—131).—Electrometric titration (see preceding abstract) is used to determine small amounts of the hydrochloric acid in cases of subacidity and small changes in its concentration. P. W. Clutterbuck.

Milk of the Monotreme. H. R. Marston (Austral. J. Exp. Biol., 1926, **3**, 217—220).—The absence of glycerides of the volatile fatty acids from the milk fat is the only peculiarity noted.

W. Robson.

Variations in chemical composition of normal human colostrum and early milk. M. F. Lowenfeld, S. T. Widdows, M. Bond, and E. I. Taylor (Biochem. J., 1927, **21**, 1—15).—The protein and ash content of the milk vary regularly according to the day of lactation, being very high in *primiparæ*, less so in *multiparæ* on the second and third days, and falling rapidly during the first week, to reach an approximately normal level. The sugar content varies also according to the day of lactation, but inversely as the protein and the ash. The sugar content of the milk appears to be higher at the beginning than at the end of a feed. The fat content of the milk varies only according to the physical conditions of the breast and the extraction of the milk. In *primiparæ* the general behaviour is reversed in the first days of lactation. The calcium content of the milk varies up to the fifteenth day with the individual. There is a suggestion of the possibility that the protein content rises slightly at the end of a single feed. S. S. Zilva.

Iron in nutrition. III. Effects of diet on iron content of milk. C. A. Elvehjem, R. C. Herrin, and E. B. Hart (J. Biol. Chem., 1927, **71**, 255—262).—Whilst the iron content of the milk of cows and goats showed considerable variations from one animal to another, it could not be increased by addition of ferric oxide, ferrous sulphate, or combinations of these with fresh cabbage (cf. A., 1925, i, 1354) to the diet. Young rabbits, when fed on the milk of animals treated in these ways, developed the same nutritional anæmia as has been observed to result from a diet of ordinary cow's milk.

C. R. Harington.

Phosphorus compounds of milk. III. Dephosphorised caseinogen. Action of alkali on caseinogen. C. Rimington (Biochem. J., 1927, **21**, 204—207).—The amide nitrogen of "dephosphorised" caseinogen, *i.e.*, the protein produced by treating caseinogen with 0·25*N*-sodium hydroxide for 24 hrs. at 37° (Rimington and Kay, A., 1926, 970), is distinctly lower than that of caseinogen. There is also some decrease in the arginine-nitrogen accompanied by an increase in the lysine + cystine fraction of the "dephosphorised" protein. The "dephosphorised" compound is only slowly attacked by proteolytic enzymes and is not coagulated by rennin.

S. S. Zilva.

Phosphorus nucleus of caseinogen. S. Posternak (Compt. rend., 1927, **184**, 306—307).—Hydrolysis of caseinogen with a very active trypsin yields α-, β-, and *γ-lactotyrins* of compositions $C_{64}H_{111}O_{43}N_{15}P_4$, $C_{67}H_{116}O_{44}N_{16}P_4$, and $C_{72}H_{124}O_{47}N_{18}P_4$, respectively. The α-compound, $[\alpha]_D^{19\cdot5}$ −67·84°, after long-continued hydrolysis with 25% hydrochloric acid, yields glutamic acid (3 mols.), aspartic acid (0·6 mol.), *iso*leucine (3 mols.), serine (3 mols.), and phosphoric acid (4 mols.), small quantities of dipeptides, larger quantities of tripeptides, and some tetrapeptides all containing serine, the decomposition being represented by the equation $C_{64}H_{111}O_{43}N_{15}P_4 + 18H_2O = 3C_5H_9O_4N + C_4H_7O_4N + 4C_6H_{13}O_2N + 7C_3H_7O_3N + 4H_3PO_4$. Hence the phosphorus-containing nucleus of caseinogen is probably formed of four serine-phosphoric acid residues.

J. W. Baker.

Determination of chlorine in milk. A. D. Husband and W. Godden (Biochem. J., 1927, **21**, 259—261).—It is essential for accuracy that the protein be removed before the addition of the silver nitrate in the determination of chlorine in milk volumetrically by precipitation of the chlorine as silver chloride.

S. S. Zilva.

Total carbohydrate content of normal urine. B. Glassmann (Z. physiol. Chem., 1927, **162**, 149—154).—The total carbohydrate in the fasting urines of twelve normal individuals of varying ages, determined by the colorimetric micro-method of the author (A., 1926, 192), varies from 0·48% to 0·94%, with an average of 0·66% (calculated as dextrose). This value is determined by the polysaccharides and urinary dextrin, and no part is contributed by nucleoproteins. The intake of food causes fluctuations, slight rises following breakfast and the midday meal. Age has no influence on the total carbohydrate content. Normal urine and whole blood contain about the same amount of total carbohydrate after hydrolysis (cf. *ibid.*, 1169).

A. Wormall.

Nature of urinary sugars. S. H. Eagle (J. Biol. Chem., 1927, **71**, 481—495).—By the use of sufficiently large amounts of yeast, dextrose in urine, up to 0·4%, can be completely fermented in 40 min. at 37—38°. After treatment of normal urine with Lloyd's reagent, no fermentable sugar was ever detected in the filtrate, although dextrose added to the filtrate was rapidly fermented; normal urine does not, therefore, contain any dextrose. It is thought that the positive results obtained by previous workers have been due to the bacterial decomposition, during the prolonged periods of fermentation employed, of some substances which are removed by the treatment with Lloyd's reagent. Ingestion of dextrose in amounts below that which causes an actual glycosuria, and ingestion of an ordinary meal, both cause an increase in the excretion of non-fermentable reducing substances. Alimentary glycosuria in a normal individual may continue after the blood-sugar has fallen below the original threshold value.

C. R. Harington.

Picrate obtained from normal urine by the method of Findlay and Sharpe. F. D. White (J. Biol. Chem., 1927, **71**, 419—427).—Application of the method of Findlay and Sharpe (Quart. J. Med., 1920, **13**, 433) to normal human urine led to the isolation of no dimethylguanidine picrate, as claimed by these workers. A picrate was indeed obtained which, on purification, proved to be potassium creatinine picrate. The method of Findlay and Sharpe is therefore not applicable to the determination of guanidines in urine.

C. R. Harington.

Lipin excretion. IV. Relation of bile to fæcal lipins. Cholesterol metabolism. W. M. Sperry (J. Biol. Chem., 1927, **71**, 351—378).—Following artificial exclusion of bile from the intestine, dogs, on a lipin-free diet, excrete 1·5—4·5 times as much lipin in the fæces as they do under normal conditions; the composition of the fæcal lipins is, however, very similar to that of the fæcal lipins of normal dogs under the same dietary conditions. This indicates that the source of the fæcal lipins (including cholesterol) is the same in each group of animals and is therefore not the bile; further support is thus afforded to the view that such cholesterol as passes into the intestine with the bile is normally completely reabsorbed, but not to the author's recently expressed opinion (A., 1926, 859) that a function of the normal fæcal lipin excretion is the removal from the body of waste sterols.

C. R. Harington.

Changes in inorganic constituents of the blood following adrenalectomy in cats and rabbits. E. J. Baumann and S. Kurland (J. Biol. Chem., 1927, **71**, 281—302).—Following adrenalectomy, there was observed in cats and rabbits a fall in the sodium and chloride content of the blood plasma; in the cat, the potassium, magnesium, and sometimes the calcium were increased in amount. No alkalosis was observed.

C. R. Harington.

Proteins having the Bence-Jones reaction. Reversibility of heat coagulation. R. Willheim (Biochem. Z., 1927, **180**, 231—246).—Bence-Jones proteins must be regarded as different individuals having in common a heat coagulability at 60° with subsequent dissolution at 100°. The redissolution occurs only in presence of other substances, chiefly electrolytes. If the heat-coagulated protein is repeatedly dissolved by boiling and precipitated by cooling, a portion—modification *B*—remains in solution, but can be reconverted into a heat-coagulable substance by passing in carbon dioxide or adding a weak acid. There appears, therefore, to be a reversibility of heat coagulation in presence of electrolytes. Modification *B* becomes increasingly ionised during heating and shows cathodic migration, whereas the original protein shows anodic migration. Similarly, the coagula of serum proteins, when heated with potassium thiocyanate, or with alkali salicylates, benzoates, or phthalates, can be dissolved, and after removal of the salts by dialysis the protein remains in solution in coagulable form.

P. W. Clutterbuck.

Effect of extirpation of the liver on the cholesterol metabolism of dogs. Appearance of a yellow pigment in the blood. E. Enderlen, S. J. Thannhauser, and M. Jenke (Arch. exp. Path. Pharm., 1927, **120**, 16—24).—In those animals that survived the operation for the longest periods there was a notable increase in the cholesterol esters of the whole blood. The increase was much less marked in the serum. The reddish-yellow colour of the serum of such animals is not due to bilirubin, but to a new pigment, *xanthorubin*. This may be extracted by chloroform or, from acid solution, by ether. In the spectrum of the ethereal solution, two weak bands are found at 552—535 and 512—483 μμ. The instability of the pigment renders its solubilities inconstant.

R. K. Cannan.

Preferential utilisation of carbohydrates in diabetes. W. R. Campbell and J. Markowitz (J. Clin. Investn. [Proc.], 1926, **2**, 608).—No preferential utilisation of lævulose, insulin, glycerol, or dihydroxyacetone occurred in depancreatised dogs.

Chemical Abstracts.

Theory of Lang's gold-sol reaction on the cerebrospinal fluid in syphilis and metalues of the central nervous system. E. Epstein and H. Rubinstein (Kolloid-Z., 1926, **40**, 307—318).—A discussion of the theory of Lang's reaction.

E. S. Hedges.

Glycolytic power of cell-free extracts from tumour and other tissues. N. Alders, H. Chiari, and D. Laszlo (Biochem. Z., 1927, **180**, 46—60).—A method is described for preparation of cell-free tissue filtrates which enables the testing after any time interval of the carbohydrate content without endangering sterility. In the great majority of cases, the sterile filtrates from mouse and tissue carcinoma showed glycolytic power, the amount being a very considerable part of the total glycolytic power of the tissue. The glycolytic agent of kidney and muscle-tissue of normal animals was detected in the filtrates, but the filtrate from liver pulp never showed activity.

P. W. Clutterbuck.

Glutathione contents of malignant tumours, especially the Rous chicken sarcoma. H. Yaoi and W. Nakahara (Proc. Imp. Acad. Tokyo, 1926, **2**, 449—456; cf. Hopkins, A., 1921, i, 635).—The nitroprusside test and determination by titration with 0·01*N*-iodine solution show that glutathione occurs in the Rous chicken sarcoma in negligible quantity, whilst it is present in abundance in other malignant tumours and normal tissues. These results are remarkable in view of the rapid growth of the Rous sarcoma, and its unique ability to withstand desiccation may be connected with the absence of glutathione.

J. M. Gulland.

Carbohydrate metabolism. II. Influence of alkali phosphates and some other electrolytes on carbohydrate metabolism. B. Kobori (Biochem. Z., 1927, **180**, 218—230).—The increased production of carbon dioxide which accompanies the normal metabolism of dextrose in rats is considerably reduced by administration with the carbohydrate, of alkali phosphates, calcium chloride, or sodium hydrogen carbonate. Similarly, phosphate inhibits the oxidation of calcium hexosediphosphate, dihydroxyacetone, sucrose, and rice starch. Lævulose, however, behaves differently, phosphate having little or no effect (cf. A., 1926, 539). P. W. Clutterbuck.

Differences in chemical and biological behaviour of surviving muscle of different kinds of fish. I. Sea-fish. G. Embden, H. J. Deuticke, E. Lehnartz, and H. Perger. **II. Fresh-water fish.** G. Martino (Z. physiol. Chem., 1927, **162**, 155—171, 172—187).—I. The isolation of lactacidogen as the osazone compound is more difficult, and the yield less, with muscle of the cod, which dies quickly after removal from the water, than with that of the sole, which survives longer in the air. Thus there appears to be a causative relationship between the rapid disappearance of lactacidogen from cod muscle and the death of the fish in the air. There is a noticeable decrease in the inorganic phosphoric acid content of fresh sole muscle kept at 17° in a sodium hydrogen carbonate solution containing sodium fluoride, and this disappearance, due to synthesis of lactacidogen, is increased by the addition of glycogen. These changes are almost insignificant with apparently fresh cod muscle, and the difference in the two fishes is attributed to quicker changes in the muscle colloids of the cod. A small but significant disappearance of lactic acid takes place under anaërobic conditions after addition of sodium fluoride.

II. The rates of disappearance of inorganic phosphoric acid from trout and carp muscle are compared, using fresh muscle and muscle which has been kept for 2 hrs. in 2% hydrogen carbonate solution at 40—45°. The trout, which dies quickly after removal from the water, loses the power to cause disappearance of inorganic phosphoric acid much more quickly than does the carp, which survives longer in the air, thus supporting the contention of the preceding paper. The differences in biological behaviour of the two fishes are not due to differences in glycogen content, for these are approximately equal. A marked anaërobic disappearance of lactic acid in the fresh muscle pulp was observed after the addition of sodium fluoride in varying concentrations. A. Wormall.

Significance of phosphorus in muscular contraction. P. Eggleton and M. G. Eggleton (Nature, 1927, **119**, 194—195).—Muscle tissue appears to contain an organic phosphorus compound, "phosphagen," readily yielding inorganic phosphate in determinations of the latter. Phosphagen, which is intimately connected with the chemical mechanism of contraction and may be "active" hexosemonophosphate, is stable in neutral or slightly alkaline solution. Whilst unstriated muscle contains about the same amount of genuine inorganic phosphate as does skeletal muscle, it appears not to contain phosphagen. Embden's observation of the disappearance of inorganic phosphate in a suspension of minced muscle in sodium fluoride solution is criticised.

A. A. Eldridge.

Influence of diet on fat reserves. P. Belin (Bull. Soc. Chim. biol., 1926, **8**, 1120—1150).—The fat deposited in living organisms when the only available source of such fat is carbohydrate has an iodine value which is characteristic for each species. This result holds for organisms ranging from bacteria to mammals, and so it appears that the fat-forming process differs from species to species. If the diet is rich in fats with a low iodine value, the iodine value of the fats deposited is only slightly lower than the characteristic iodine value found when the same species is fed almost exclusively on carbohydrates. If, however, the fats administered have a high iodine value, the fats deposited have much above the characteristic iodine value, but not exceeding and usually somewhat below that of the fats administered. With such feeding, the fats of the egg in the case of fowls and of the embryo in the case of mammals have an iodine value lower than that of the fats deposited in the parent. W. O. Kermack.

Fat metabolism. VIII. Behaviour of cetyl acetate in the animal body. R. Mancke (Z. physiol. Chem., 1927, **162**, 238—263).—In a case of human chyluria, the administration *per os* of a solution of 50 g. of cetyl alcohol in olive oil produced no increase in the unsaponifiable matter of the fat in the urine, and no cetyl alcohol could be detected. The Reichert–Meissl value of the milk fat of goats and sheep, to which considerable amounts of cetyl acetate were given daily for 12 days, showed no variation which could be attributed to the presence of the ester, and the unsaponifiable matter of the milk fat contained no cetyl alcohol. A goose fed on a fat-deficient diet and given 20—25 g. of cetyl alcohol per day stored no cetyl acetate in the fat depôts. After intravenous injection over 6 days of 16·5 c.c. of a 10% well-dispersed emulsion of cetyl acetate into a rabbit, or 51 c.c. of a 20% emulsion over 12 days into a dog, no unchanged cetyl acetate or either of its components could be detected in the organs or fat depôts. The conclusion is reached that the ester is saponified in the blood-stream or on passing into the tissues and that the cetyl alcohol is probably oxidised to palmitic acid. The same oxidation process takes place in the intestinal epithelium or the lymphatics during absorption. A. Wormall.

Comparative metabolism of aromatic acids. XI. Fate of diphenylacetic acid in the animal body. S. R. Miriam, J. T. Wolf, and C. P. Sherwin (J. Biol. Chem., 1927, **71**, 249—253).—After administration of diphenylacetic acid to man, the dog, and the rabbit, the greater part of the substance can be recovered unchanged from the urine; in all cases there was, however, obtained a small amount of *diphenylacetylglycuronic acid*, m. p. 180—185° (decomp.), $[\alpha]_D^{20}$ −34·75°. *Diphenylacetylglycine* has m. p. 157°. C. R. Harington.

Diet determinations. D. W. Richards, jun., and A. F. Coburn (Arch. Int. Med., 1927, **39**, 93—97).—A nomographic diagram is given for the determination of the individual constituents of a diet when the total calorie requirement is known and the amount of one food constituent is fixed. C. R. Harington.

Diet and assimilation of calcium. VIII. Calcium level and sunlight as affecting calcium equilibrium in milking cows. E. B. Hart, H. Steenbock, H. Scott, and G. C. Humphrey. **IX. Influence of cod-liver oil on calcium assimilation in lactating animals.** E. B. Hart, H. Steenbock, S. W. Kletzien, and H. Scott (J. Biol. Chem., 1927, **71**, 263—269, 271—280).—VIII. Milking cows, on a typical "summer diet," consisting largely of green grasses, remained in a negative calcium balance whether they were exposed to sunlight or not; the calcium balance could be made positive by addition of calcium carbonate to the diet. The results indicate that, whilst the supply of vitamin-*D* in such a diet is sufficient, the food should be supplemented with calcium salts.

IX. Administration of the unsaponifiable matter of cod-liver oil to lactating goats had no effect when the material was given in gelatin capsules; this result was apparently due to failure in absorption of vitamin-*D*, since the same material, administered in solution in maize oil (which was itself physiologically inert), improved the calcium assimilation considerably. The same effect could be obtained by feeding whole cod-liver oil provided that the animals were first accustomed to this material, so that loss of appetite did not result from its administration. C. R. Harington.

Physiological effects of diets unusually rich in protein or inorganic salts. T. B. Osborne, L. B. Mendel, E. A. Park, and M. C. Winternitz (J. Biol. Chem., 1927, **71**, 317—350).—Good growth in rats can be obtained on diets containing a large proportion of protein provided that sufficient fresh green food be given to maintain an adequate supply of vitamins. Neglect of the latter factor probably accounts for the failure of other workers to secure good growth under these conditions. The rats on the high protein diet had a higher concentration of non-protein nitrogen in the blood than the normal animals, but their urine showed no indications of nephritis; there was observed a marked hypertrophy of the kidneys, which manifested itself after a very short time, but was not associated with significant morbid anatomical changes (cf. Addis and others, this vol., 170). Addition of abnormally large amounts of various inorganic salts or of carbamide to an ordinary mixed diet failed to bring about a similar renal hypertrophy. Retrogression in the size of the kidneys was not observed on changing from a diet rich in protein to one poor in protein. C. R. Harington.

Nutritional protein value of beef liver, heart, and kidney. H. H. Mitchell and J. R. Beadles (J. Biol. Chem., 1927, **71**, 429—435).—As determined on rats, the biological values of the proteins of beef liver, heart, and kidney are closely similar to one another, being somewhat higher than the values for beef and pork muscle, but lower than that of milk protein. C. R. Harington.

Nutritive value of plastein. H. H. Beard (J. Biol. Chem., 1927, **71**, 477—480).—Good growth was obtained in white mice which received the whole of their nitrogen in the form of plastein, prepared by the method of Wasteneys and Borsook (A., 1925, i, 102). C. R. Harington.

Specific dynamic action of food. V. Influence of sodium phosphate on gaseous exchange after ingestion of meat. J. Abelin and B. Kobori (Biochem. Z., 1927, 180, 211—217).—The increase in gaseous exchange in rats on ingestion of meat is considerably decreased by adding sodium phosphate to the food, an action analogous to the effect on carbohydrate metabolism (cf. A., 1926, 539).

P. W. Clutterbuck.

Tryptophan feeding. I. C. S. Hicks (Austral. J. Exp. Biol., 1926, 3, 193—202).—A diet lacking in tryptophan causes a falling off in heat production commensurate only with starvation wasting. Respiratory exchange measurements furnish no evidence that this amino-acid is required for the elaboration of the thyroid hormone. Tryptophan added to a synthetic diet differs in its action from that present in a normal protein diet. An addition of 2% or more of tryptophan per 100 g. of protein produces toxic symptoms. W. Robson.

Feeding she-goats with glycine as a substitute for protein. J. Williger (Biochem. Z., 1927, 180, 156—192).—Glycine cannot replace protein in the diet. By feeding glycine, the percentage of dry matter of the fæces is increased and a considerable amount of nitrogen is retained probably as ammonia in the blood. Only in one case was a stimulation of the mammary gland found, the fat of the milk being increased for from 2 to 3 days.

P. W. Clutterbuck.

Quantitative law of minimal nitrogen usage. E. F. Terroine and H. Matter (Compt. rend., 1927, 184, 166—168).—Finding that the minimal nitrogen usage bears a constant relation to calories produced, the authors have enunciated the following law: the minimal nitrogen usage in the adult, per unit body-weight, is directly proportional to the minimal intensity of heat production. W. Robson.

Behaviour of 2 : 5-diketopiperazines in the animal body. E. Abderhalden and S. Buadze (Z. physiol. Chem., 1927, 162, 304—314).—Glycyl-*d*-alanyl anhydride and *dl*-leucylglycyl anhydride were administered *per os* to a dog. The former could not be detected unchanged in the urine, but glycyl-*d*-alanine was present, indicating the decomposition of this anhydride in the body. After feeding with *dl*-leucylglycyl anhydride, in keto- and enol-forms, four fifths of the amount given were recovered from the urine, and small amounts were detected in the fæces. The anhydride could be detected in the blood 1 hr. 20 min. after feeding, was at a maximum after 5 hrs., and disappeared in 8 hrs. The significance of these results in relation to the structure of proteins is discussed. A. Wormall.

Changes of metabolism under various conditions. I. Influence of adrenaline and pilocarpine on the excretion of nitrogenous substances. II. Influence of potassium and calcium on the excretion of nitrogenous substances. L. Pincussen. (Biochem. Z., 1927, 180, 132—135, 136—140).—I. [With A. Walter.]—Injection of adrenaline in rabbits causes an increase in the urea-nitrogen (expressed as a percentage of the total nitrogen), whilst injection of pilocarpine appears slightly to decrease it.

II. [With E. Coelho.]—In rabbits on a diet poor in calcium, injection of calcium causes an increase in urea-nitrogen excreted, but injection of potassium has little effect. P. W. Clutterbuck.

Blood changes in strychnine convulsions. J. von Mikó and T. Pala (Arch. exp. Path. Pharm., 1927, 119, 273—284).—In strychnine convulsions, the blood calcium rises 25—30% above the normal. The red corpuscles increase, but the oxygen saturation and carbon dioxide content of the blood fall.

R. K. Cannan.

ψ-Morphine. Separation and determination of morphine, ψ-morphine, and related substances. A. K. Balls.—See this vol., 264.

Local anæsthetics and antipyretics of the thiophen series. H. Steidle (Arch. exp. Path. Pharm., 1927, 120, 100—119).—Substitution of the benzoyl group in cocaine, eucaine, and stovaine by the radical of thiophen-2-carboxylic acid and the addition of the latter group to quinine and *p*-phenetidine reduced the toxicity of these substances without notably changing their pharmacological activity.

R. K. Cannan.

Alcohol poisoning. II. E. Keeser and I. Keeser (Arch. exp. Path. Pharm., 1927, 119, 285—290).—In contrast to chronic poisoning, there is no disturbance of protein metabolism in acute poisoning with alcohol. One hr. after administering 110 c.c. of alcohol there was a fall in the cholesterol, phosphatides, and fatty acids and bile pigment in the serum, followed in 10 hrs. by an excessive rise above normal. In acute poisoning there was an increased activity of the lipase, phosphatase, catalase, and oxydase of the serum. In chronic poisoning, the activity of these enzymes (with the exception of phosphatase) was decreased. R. K. Cannan.

Depression of oxidative metabolism and recovery from dilute potassium cyanide poisoning. Antagonistic and additive effects of anæsthetics and potassium cyanide. J. W. Buchanan (J. Exp. Zool., 1926, 44, 285—306; 307—325).—Four hrs.' exposure of *Planaria dorotocephala* to dilute potassium cyanide solution depressed the oxygen consumption to a constant minimum level; removal of the cyanide caused the oxygen consumption to rise above, and then to reach the normal value. The depressive action is probably largely physical. There is no evidence for the reconstitution of a residual substance containing oxygen or for the accumulation of oxidisable substances during depression. With dilute cyanide solutions, ethyl ether and ethyl alcohol are protective; the action of more concentrated cyanide solutions is accelerated by ethyl ether. Chemical Abstracts.

Toxicological detection of hydrocyanic acid. G. Sensi and M. Revello (Annali Chim. Appl., 1926, 16, 603—611).—Hydrocyanic acid is not detectable in the animal organism if administered in quantities just sufficient to cause death. When poisoning is effected by means of gaseous hydrogen cyanide, detection of the latter is impossible, since the quantity absorbed never exceeds the minimum fatal dose. If the body is examined shortly after death, the tests give positive results if at least three times the fatal dose is administered, but otherwise four times this dose is necessary to ensure response. In any case, the poison does not remain in the organism later than the twentieth day after death. T. H. POPE.

Spectroscopic detection of hydrocyanic acid in blood. G. SENSI (Annali Chim. Appl., 1926, **16**, 612—622; cf. preceding abstract).—Kobert's reaction (A., 1892, 361) and Schönbein's reaction for the spectroscopic detection of hydrocyanic acid in blood are positive only when the poison is detectable also by chemical tests. They serve, however, as control tests, Schönbein's reaction being more sensitive than that of Kobert. T. H. POPE.

Toxicology of lead and its compounds. P. W. DANCKWORTT and W. UDE (Arch. Pharm., 1926, **264**, 712—740).—The increasing risk of lead poisoning in cattle due to weed-killers and insecticides (cf. Danckwortt, Deuts. Tierärztl. Woch., 1926, **34**, 639), fumes from smelting-works, and lead-containing effluents has led to a survey of methods for the determination of small quantities of lead in biological material, and an improved method is described. The minced organs (400—500 g.) are treated with sufficient pure nitric acid to cover about half the mass. The mixture is kept for some time and is then heated on the water-bath until all organic matter except fat is destroyed. Troublesome frothing takes place if the mixture is heated immediately. The solution is evaporated to a syrup in a silica capsule (porcelain cannot be used, as it always gives up traces of lead), and this syrup is gently evaporated to dryness, dilute nitric acid being added from time to time to facilitate the process. After repeated evaporation to dryness, the ash, which must not have been overheated or lead may have been lost, is dissolved in dilute nitric acid. The lead is precipitated as sulphide and determined by the chromate method, or, if traces only are present, by the "triple-nitrite test" (cf. Fairhall, A., 1922, ii, 659; 1924, ii, 61). From nitric acid weaker than $N/3$, lead sulphide is quantitatively precipitated, and the precipitation of small quantities is facilitated by adding 10 mg. of copper to the solution. Quantities as small as 1 mg. of lead per 100 g. of oxygen can be determined (cf. Geilmann and Höltje, *ibid.*, 1926, 591).

Using the above methods, lead poisoning has been studied experimentally in dogs. Lead is disseminated in all the organs in varying amounts. The curative action of various substances, administered by intravenous injection, has also been investigated. Colloidal silica is useless. Sodium sulphate and potassium iodide are possibly useful, but relapses may occur. The best medicament, which is useful also as a prophylactic, is colloidal sulphur.

The properties and composition of the soil of certain areas in the Innerste valley and the composition of certain well-waters were investigated. Adsorption of lead by the soil is independent of the phosphoric acid content. W. A. SILVESTER.

Anticoagulant power of certain dyes and arsenic compounds. G. LEFROU (Compt. rend., 1927, **184**, 241—243).—Malachite-green in very small quantities has a powerful anticoagulating influence on blood. Fuchsine and crystal-violet are somewhat less effective, and only a slight effect is observed with methylene- and toluidine-blues. Under similar conditions, phenylarsenates have no action, but the compound "Bayer 205" is a strong anticoagulant. It is suggested that the presence of several amino-groups, either free or substituted, in the compound is necessary to render it anticoagulant.

J. W. BAKER.

Effects of salts on the penetration of brilliant-cresyl-blue into *Nitella*. M. IRWIN (J. Gen. Physiol., 1927, **10**, 425—436).—Cells of *Nitella* previously exposed to solutions of salts containing univalent cations are penetrated less readily by brilliant-cresyl-blue when subsequently immersed in a solution of this dye in a borate buffer mixture. Salts with bivalent and tervalent cations do not produce this effect, but rather neutralise the effect of the univalent cations. W. O. KERMACK.

The two components of malt diastase. E. OHLSSON (Compt. rend. Trav. Lab. Carlsberg, 1926, **16**, [7], 1—68).—In accordance with modern usage, the two enzymes present in malt (cf. A., 1923, i, 620) have been renamed dextrinogenamylase and saccharogenamylase. In a filtrate from green malt, p_H 4·20, dialysed against distilled water, the activity of saccharogenamylase is reduced to about half and that of dextrinogenamylase to 1—2% of its former value. The preparation of a solution of one enzyme free from admixture of the other is described. Results obtained with such solutions indicate that there is present in the malt some substance—protein in character—which has an inhibitory effect on dextrinogenamylase. The activity of this substance is destroyed by heat, is dependent on the p_H of the medium, and shows minimum activity at p_H 5—5·5. The optimum activity of saccharogenamylase occurs in the zone p_H 4—5·75, whilst that of dextrinogenamylase is at p_H 5·5—6·0. The relationship of the activities of these enzymes to the modern theories of starch hydrolysis is discussed. W. ROBSON.

Enzyme action. XXXIX. Lipase actions of extracts of the whole mouse at different ages. K. G. FALK and H. M. NOYES (J. Gen. Physiol., 1927, **10**, 359—368).—The relative ester-hydrolysing actions of an extract of a whole mouse tested on a series of simple esters varies according to the age of the mouse. The action of extracts of embryo mice is similar to that of embryo rats or rat tumour, and not to that of a mouse carcinoma, whilst the extracts of adult mice and rats are similar in lipase activity.

W. O. KERMACK.

Oxidation–reduction potential of the luciferin–oxyluciferin system. E. N. HARVEY (J. Gen. Physiol., 1927, **10**, 385—393).—The oxidation–reduction potential of the system luciferin–luciferase appears to lie between that of sodium anthraquinone-2 : 6-disulphonate ($E_0'=-0·22$ at p_H 7·7) and that of quinhydrone ($E_0=+0·24$ at p_H 7·7). The system luciferin–luciferase does not appear to be truly reversible, since it is always unaffected at an oxidation–reduction potential lying between the above two values, although any reducing agent stronger than the anthraquinonedisulphonate will reduce the oxidised form and any oxidising agent stronger than quinhydrone will oxidise the reduced form. Although luciferin is readily oxidised in absence of oxygen by many reagents and is also oxidised at a high temperature by oxygen in absence of luciferase, luminescence is always absent except when oxidation takes place by oxygen in presence of luciferase.

W. O. Kermack.

Acceleration of enzymic synthesis of proteins by lipoidal emulsions. H. R. Marston (Austral. J. Exp. Biol., 1926, 3, 233—236).—Colloidal emulsions of egg-fat greatly increase the reaction velocity of the re-synthesis of protein from its digestion products by trypsin. W. Robson.

Stages of the peptic hydrolysis of egg-albumin. J. McFarlane, V. E. Dunbar, H. Borsook, and H. Wasteneys (J. Gen. Physiol., 1927, **10**, 437—450).—The method of protein fractionation of Borsook and Wasteneys (cf. A., 1925, i, 97) has been applied to the products of peptic digestion of egg-albumin by pepsin at p_H 1·6. The amounts of the fractions present at various times up to 168 hrs. have been followed in detail. It is concluded that the process of peptic hydrolysis consists of a primary stage during which the original protein is split directly into fragments belonging to the various protein fractions, and a secondary stage, during which proteose and subproteose fractions are slowly split up into simpler fragments. Although acid metaprotein is formed from egg-albumin by the action of acid, it appears that this is not an essential step during peptic hydrolysis since such acid metaprotein is less readily hydrolysed than the denatured protein itself. W. O. Kermack.

Autodestruction of pepsin in relation to its ionisation. A. M. Goulding, H. Borsook, and H. Wasteneys (J. Gen. Physiol., 1927, **10**, 451—467).—The destruction of pepsin at a definite hydrogen-ion concentration is found to follow the law of unimolecular reaction. There is evidence that pepsin is a univalent acid (pk=6·85) or a base (pk=7·39). In the first case, the dissociated ions alone are regarded as undergoing destruction, whilst in the second case only the undissociated molecule would be destroyed. The rate of destruction of pepsin increases rapidly with the hydroxyl-ion concentration. In these experiments, the active pepsin was determined by allowing it to act for a given time on albumin at p_H 1·6, precipitating with trichloroacetic acid, and determining the nitrogen content of the filtrate.

W. O. Kermack.

Influence of bile on the digestion of protein by pancreatic juice. S. Matsukura (Proc. Imp. Acad. Tokyo, 1926, **2**, 447—448).—Digestion of protein by pancreatic juice in presence of duodenal extract begins most quickly in absence of bile, which inhibits digestion during the first few hours, but appears to be necessary for prolonged digestion.

J. M. Gulland.

Tyrosinase–tyrosine reaction. VI. Production from tyrosine of 5 : 6-dihydroxyindole and 5 : 6-dihydroxyindole-2-carboxylic acid—the precursors of melanin. H. S. Raper (Biochem. J., 1927, **21**, 89—96).—Tyrosine was incubated with tyrosinase at p_H 6—6·5 for several hrs. After completely precipitating the enzyme with acetic acid from the resulting red solution, the latter was allowed to remain in an atmosphere of hydrogen until it turned pale brown. The concentrated solution was then methylated with methyl sulphate under hydrogen and the crystalline 5 : 6-*dimethoxyindole*, m. p. 154—155°, was extracted with ether from the reaction mixture. It was identical with the synthetic compound. In the methylated alkaline solution, traces of 5 : 6-*dimethoxyindole*-2-*carboxylic acid*, m. p. 202°, were found. This latter acid, which was identical with the synthetic compound, predominates if the red solution is decolorised with sulphurous acid. 5 : 6-Dimethoxyindole was also prepared as above from the red substance obtained by treating 3 : 4-dihydroxyphenylalanine with tyrosinase (cf. A., 1926, 977). The red pigment produced from tyrosine is probably the 5 : 6-quinone of dihydroindole-2-carboxylic acid. S. S. Zilva.

The uricolytic enzyme. I. Liver perfusions. II. Destruction of uric acid by ammonia. A. Schittenhelm and F. Chrometzka (Z. physiol. Chem., 1927, **162**, 188—202, 203—218).—I. The surviving livers of the rabbit, dog, and pig oxidise uric acid to allantoin. Perfused human liver can also decompose uric acid, but no definite decomposition products could be isolated.

II. The preparation of enzyme extracts from dried ox liver by Willstätter's methods is described, the processes involving extraction by glycerol, washing, adsorption on various precipitates and colloids, and dialysis. Ammonia itself has a uricolytic action, but the uricolytic power of such extracts is not due solely to ammonia. A. Wormall.

Products of oxidation of uric acid by hydrogen peroxide. F. Chrometzka (Z. physiol. Chem., 1927, **162**, 219—222).—The acceleration by ammonia of the oxidation of uric acid to allantoin by oxygen (cf. preceding abstract) is not observed with other amines. Methyl-, ethyl-, and trimethyl-amine have no similar catalytic action, when tested at p_H 8 for 24 hrs. at 38° with a stream of air passing through the solution. These amines in 33% solution oxidise uric acid to allantoin if they are previously heated gently with hydrogen peroxide. This uricolysis may be due to some hydrogen peroxide remaining after the reaction, since hydrogen peroxide will effect the same oxidation. A. Wormall.

Preparation of yeast-juice by Buchner's method. A. Harden and F. R. Henley (Biochem. J., 1927, **21**, 196—197).—In preparing yeast juice by the grinding method from English top-yeast, it is usually advantageous to preserve the ground mass for 2 hrs. at air temperature before pressing out the juice. Preservation of the expressed yeast-juice does not produce the same effect. S. S. Zilva.

Growth of yeast. III. Influence of volume of medium employed. G. L. Peskett (Biochem. J., 1927, **21**, 104—110).—The conclusions previously arrived at by the author (A., 1925, i, 1011) were not justified by the results reported at that time. A reinvestigation of the problem, however, leads to the same conclusions. S. S. Zilva.

Influence of hydrogen-ion concentration on alcoholic fermentation. VI. E. Hägglund and T. Rosenqvist (Biochem. Z., 1927, **180**, 61—64).—Further experiments on the fermentation of pyruvic acid (cf. A., 1926, 543) confirm that the activity of carboxylase completely disappears in faintly alkaline solution. The p_H–activity curves rise very rapidly near the neutral point and then flatten out over the optimal range of p_H 3·5—6. P. W. Clutterbuck.

Reductase (hydrogenase) of yeast. V. H. von Euler and R. Nilsson (Z. physiol. Chem., 1926, **162**, 72—84).—The ability of washed dried yeast to reduce methylene-blue is restored by the addition of a hydrogen donator and a co-reductase preparation, but is not restored by the addition of a hydrogen donator alone (sodium succinate). Both reductase and co-reductase (wash-water or "Kochsaft") must be present. Fermentation sodium hexosephosphate appears to be a better hydrogen donator for yeast reductase than sodium succinate. The activating power of hexosephosphate is not due to the products of its hydrolysis by phosphatase. H. D. Kay.

Pyruvic acid as an intermediate product of alcoholic fermentation. G. Rimini (Annali Chim. Appl., 1926, **16**, 488—490).—Traetta-Mosca's results (A., 1926, 978) may indicate the formation of pyruvic acid in small proportion during the alcoholic fermentation of dextrose, but by no means prove that this acid is a product intermediate between dextrose and alcohol. The fermentation of 10% dextrose solution by fresh distillery yeast in presence of rather more brucine than is necessary to keep the liquid saturated with this base gives practically the theoretical yield of alcohol. It was not found possible to crystallise any salt of brucine from the fermented liquid after evaporation. T. H. Pope.

Specific activators of fermentation enzymes. I. H. von Euler and R. Nilsson (Z. physiol. Chem., 1927, **162**, 264—271; cf. this vol., 77).—The stability of co-zymase and co-reductase at high temperatures is studied, and these activators show a marked similarity in this respect. After heating at 100° for 1½ hrs., a highly purified co-zymase preparation retained 4·8% of the original co-zymase power and 5·7% of the co-reductase value. After heating for 1 hr. at 90°, the figures were 31% in each case. No alteration in p_H occurred in these heating processes. Dried bottom yeast loses on washing both co-zymase and co-reductase, whilst washed dried top yeast retains its co-zymase, but loses most of its power to reduce methylene-blue. This, however, is not due to the loss of the co-enzyme, but to removal of the hydrogen donators, since methylene-blue can be reduced if a hydrogen donator (hexosephosphate) is added. A. Wormall.

Enzymes, co-enzymes and biocatalysts in coproporphyrin-rich yeasts. II. H. von Euler and H. Fink (Z. physiol. Chem., 1927, **162**, 272—303; cf. A., 1926, 1176).—There is no close relationship between increases in invertase and porphyrin, since the former may increase five-fold with no marked rise in the content of the latter. Top and bottom yeasts behave differently after preliminary treatment with porphyrin; in the former case, the quantity of invertase is greatly diminished, whilst in the latter there is a rise up to two- or three-fold. Glycogen storage takes place, but the increase is about the same with top and bottom yeasts. The observation, reported in the first paper, that after drying, the co-enzymes of copro-yeasts were not extracted by washing, is investigated further. After "regeneration" of the copro-yeast in beer wort, the co-enzyme was again removed by water. The relation between coproporphyrin and the co-enzyme (co-reductase) is discussed. The copro-yeasts used contain 0·06—0·25 mg. of coproporphyrin per 30 g. of fresh yeast. The absorption bands of cytochrome could be observed to a varying extent with extracts of copro-yeasts, and these yeasts contain more total pyrrole colouring matter (coproporphyrin+hæmochromogen) than do ordinary yeasts. The relationship between porphyrin- or cytochrome-formation and the type of nitrogenous nutrients supplied is studied and briefly discussed. A. Wormall.

Action of yeast on sugars rendered optically inactive by dilute alkalis. A. Fernbach, M. Schoen, and M. Mori (Compt. rend., 1927, **184**, 168—170).—The action of the yeast of Sauterne differs from that of beer yeast on sugars rendered optically inactive by dilute alkalis; thus with dextrose the products are dextrorotatory in the former case and lævorotatory in the latter. W. Robson.

Fission of starch by *Saccharomyces sake*. K. Sjöberg (Z. physiol. Chem., 1927, **162**, 223—237).—Dihexosan, amylobiose, and an unidentified *substance* ($[\alpha]_D^{18}$+172°) were isolated. A. Wormall.

Soluble enzymes secreted by *Hymenomycetes*: antioxygenous actions superimposed on reducing actions. L. Lutz (Compt. rend., 1927, **184**, 173—174).—Experiments were carried out to verify the hypothesis that the addition of an antioxygenous substance to a reducing medium must favour reducing actions in catalysing, inversely, oxidations brought about by the living mycelium of *Hymenomycetes*. W. Robson.

Respiratory intensity of *Aspergillus niger* during development. A. Hée (Compt. rend., 1926, **183**, 1351—1353).—*A. niger* is cultivated on media containing no nitrogeneous substances or on media containing no nitrogen or carbohydrates. The dry weight of the culture falls after the second or third day, and the respiratory intensity falls to one tenth its original value by the ninth day. When there are no carbohydrates in the culture medium the respiration intensity is about one half.

L. F. Hewitt.

Imitations of moving amœbæ, infusoria, and other organic and cellular structures and forms. A. L. Herrera (Mem. R. Accad. Lincei, 1926, [vi], 2, 195—202).—A fuller account of work already published (A., 1926, 435), with photographic reproductions of the phenomena. T. H. Pope.

Reversible gelation and fixation of tissues. M. A. van Herwerden (Proc. K. Akad. Wetensch.

Amsterdam, 1926, 29, 975—978; cf. *ibid.*, 1924, 27, 867).—It is suggested that histological fixation involves an irreversible coagulation, but that there is a gradual transition reversible through a gelation of protoplasm to complete fixation. If *Paramœcium aurelia* is kept in 1% formaldehyde, death results, but in 0·01—0·1% solutions a solidification occurs which is not a fixation, but a reversible gelation, since conditions return to normal after washing the animals in ditch water. Similarly, the Brownian movement of another protozoon, *Actinophrys sol*, is stopped by adding a 0·01% formaldehyde solution and completely restored after rinsing out.

J. S. Carter.

Acids as intermediate stages in the oxidation of sugars by fungi. W. Butkewitsch (Jahrb. wiss. Bot., 1925, 64, 637—650).—Gluconic and citric acids are formed apparently directly from sugar by *Aspergillus niger*, *Citromyces glaber*, *Penicillium glaucum*, and related fungi. Low acidity favours the formation of gluconic, and high of citric acid. The general occurrence of gluconic acid indicates that it is a normal intermediate product in the aërobic oxidation of sugars. Chemical Abstracts.

Dependence of the amount of growth of fungi on the quantity of food factors. R. Meyer (Z. Pflanz. Düng., 1926, A, 8, 121—163).—Alterations in the concentration of total foodstuffs (except water) give results that indicate that Mitscherlich's law (cf. A., 1911, ii, 760) can be applied only with difficulty. The law is not strictly valid, for with varying concentrations of ammonium sulphate as the source of nitrogen the amount of growth is influenced by the hydrogen-ion concentration, whilst with sodium nitrate, differences in growth curves are obtained with different concentrations of sugar. With alterations in carbamide concentration, no agreement with the law is found. Variation in the concentration of phosphoric acid gives better agreement, but if the concentrations of two foodstuffs are varied, the results do not agree with the law. A. Wormall.

Conditions for symbiosis of nitrogen-fixing bacteria and maize. G. Truffaut and N. Bezssonoff (Compt. rend., 1926, 183, 1065—1067).—Maize may be grown on a solid medium containing no nitrogen if inoculation with *Clostridium Pastorianum*, *Azotobacter chroococcum*, *A. Vinelandii*, and *Bacillus Truffauti* be made after germination, if the plants are exposed to bright illumination and grown in sand containing up to 0·6 g. of iron per kg.

L. F. Hewitt.

Significance of gelatin for bacterial growth. B. S. Platt (Biochem. J., 1927, 21, 16—18).—Pneumococcus does not grow in peptone-water, but will do so on addition of gelatin. Optimum growth is obtained with 3% gelatin. Growth can also be obtained in absence of peptone on media containing 15% of gelatin solution autoclaved for 20 hrs. and 0·5% of sodium chloride. The concentrated washings of commercial gelatin or the washed gelatin also induce growth in peptone. The ash of "Gold Label" gelatin and of the washings or the concentrated dialysate of the washings promote growth of pneumococcus in 2% washed gelatin–peptone media. 4% of Ringer–Locke solution has a similar effect. Growth was also obtained in a 3% gelatin-peptone medium of several strains of *Bacillus diphtheriæ*, of meningococcus, and of streptococcus. The first did not grow in bouillon or peptone-water. The strains of gonococcus examined would not grow in any of these media. S. S. Zilva.

Effects of chemical and physical changes in environment on resting bacteria. J. H. Quastel and W. R. Wooldridge (Biochem. J., 1927, 21, 148—168).—Resting *Bacillus coli* was exposed to the following conditions and substances and its activation of a number of compounds determined by the methylene-blue technique; changes of temperature from that of liquid air to 77°, changes of hydrogen-ion concentration from p_H 2·2 to p_H 11, varying concentrations of sodium chloride at varying p_H and for different times, varying concentrations of sodium nitrite at varying p_H and for different times, methylene-blue, benzene, toluene, phenol, ether, chloroform, propyl alcohol, *cyclo*hexanol, colloidal ferric hydroxide, and dilute solutions of cuprous sulphate and mercuric chloride. Selectivity of destructive action on the activating mechanisms was exhibited by such treatment. A step-by-step degradation occurred. The order of sensitivity or of disappearance of the mechanisms was approximately the same in all cases. The activations of the sugars appear to take place at the more fatty or lipoidal fraction of the surface, those of substances such as succinic acid, formic acid, etc. at the less lipoidal. The activation of dextrose as a hydrogen donator seems also to bring about glycolysis. Inactivation by propyl alcohol, *cyclo*hexanol, copper, or mercury is reversible. Sodium hyposulphite has a restorative action. The results are in accordance with the hypothesis that the activations of substrates are intimately associated with surface structure (cf. A., 1926, 434).

S. S. Zilva.

Peroxide formation by pneumococcus and its relation to bacterial oxidation–reduction reactions. B. S. Platt (Biochem. J., 1927, 21, 19—25).—Aërated cultures of pneumococcus free from catalase, when grown on gelatin–peptone, produce considerably less hydrogen peroxide than when grown on gelatin–bouillon. There is no corresponding difference in the amount of growth in the two cases. Peroxide is not produced in gelatin–bouillon in appreciable amounts until near the end of multiplication of the bacteria. The addition of sodium lactate or dextrose, but not of sodium thiolactate to gelatin–peptone cultures of pneumococcus increases the production of hydrogen peroxide in this medium. The rates of growth of, and peroxide formation by, pneumococci are compared under various conditions. It is suggested that lactic acid and indirectly dextrose function as hydrogen donators in the presence of the pneumococcus, peroxide being formed when oxygen acts as hydrogen acceptor. S. S. Zilva.

Cellobiose fermentation by the coli–aërogenes group. S. A. Koser (J. Infect. Dis., 1926, 38, 506—510).—In the fermentation of cellobiose, the differentiation of intestinal *Bacillus coli* and the ærogenes–cloacæ group is distinct. With the so-called intermediate forms obtained from soil a correlation between all the tests is not obtained.

Chemical Abstracts.

Mineral nutrition of *Bacillus tuberculosis*. A. Frouin and M. Guillaumie (Bull. Soc. Chim. biol., 1926, 8, 1151—1177).—The only mineral elements essential for the growth of *B. tuberculosis* are sulphur, phosphorus, potassium, and magnesium. Potassium cannot be replaced by sodium, cæsium, or rubidium, nor magnesium by calcium, strontium, or the rare earths. The growth is increased by sodium vanadate in a glycerol medium. Salts of copper, arsenic, manganese, and zinc are almost without action, whilst those of calcium reduce the yield. The effect of salts of other metals, *e.g.*, iron, depends very largely on the other conditions of the medium. The constitution of the ash obtained by incineration of the bacilli depends on the reaction of the medium and the other conditions of growth, as well as on the mineral constituents of the medium.

W. O. Kermack.

Carbon nutrition of *Bacillus tuberculosis*. A. Frouin and M. Guillaumie (Bull. Soc. Chim. biol., 1926, 8, 1178—1197).—The influence of the addition of glycerol, certain mono-, di-, and tri-saccharides, and of salts of iron on the weight of the culture of *B. tuberculosis* obtained when grown on a medium otherwise standardised has been investigated. Glycerol, dextrose, and trehalose are found to increase the yield of culture. Iron salts always increase the yield in a glycerol medium, but in a dextrose medium only when the reaction is acid. The fat content of the bacilli is greater in media containing glycerol than in those containing dextrose. W. O. Kermack.

Generality of the distinction between two categories of fatty matter; constant element and variable element. P. Belin (Bull. Soc. Chim. biol., 1926, 8, 1081—1102).—A distinction between the two categories of fatty acids can be drawn in the case of micro-organisms as in higher animals. *Aspergillus niger* and Timothy grass bacillus, relatively poor and rich in fatty matter, respectively, both show varying powers of synthesising fats from the sugar, but not from the protein of the medium. Alteration of the medium in sugar content only produces considerable variation in the fat content (cf. Terroine and Lobstein, A., 1923, i, 633), showing the existence of a variable element. Inanition causes the fatty acid content of *A. niger* to fall to approximately 1·37% dry weight, a value independent of the initial fat content. This low limit (constant element) is irreducible and agrees roughly with the amount left after extraction of the same organisms with carbon tetrachloride or light petroleum.

A. Wormall.

Action of neon light on bacteria. A. Philibert and J. Risler (Compt. rend, 1926, 183, 1137—1139).—Cultures of staphylococcus, *Bacillus diphtheriæ*, pneumococcus, and streptococcus are sterilised by exposure to the light of a neon lamp when rendered sensitive by a solution of methyl-violet, in periods ranging from 1 to 30 min., whilst neither treatment alone has any bactericidal effect. *B. coli* was unaffected. When eosin or methylene-blue was used in place of methyl-violet, sterilisation did not occur even after exposure for 1 hr. J. W. Baker.

Secondary action of *X*-rays on micro-organisms. J. J. Trillat (Compt. rend., 1926, 183, 1304—1307).—Surface cultures of *Bacillus prodigiosus* were exposed to the radiations caused by *X*-rays impinging on metals. The effect of the irradiation increases with the atomic number of the metal. Thus bactericidal action is observed in 10 min. with bismuth, lead, gold, and platinum, in 20 min. with silver and tin, and in 35 min. with zinc, copper, nickel, and iron. Even after 1 hr., aluminium gives practically no effect. The phenomenon is ascribed to the fact that absorption of *X*-rays by elements, and hence emission of secondary radiations, increases with the fourth power of the atomic number. For effective bactericidal action, the metal must be close to the culture. L. F. Hewitt.

Chemical structure as affecting the staining and therapeutic properties of dyes. R. W. French (Stain Tech., 1926, 1, 74—77).—Toxicity resulting from the oxidation of methyl groups in certain therapeutic dyes seems to arise from the formaldehyde produced; this might be overcome by ethylation instead of methylation. In the triphenylmethane series, apparent differences in staining and bactericidal value appear to depend on differences in chemical structure. A rosaniline base is, in general, superior to pararosaniline compounds.

H. W. Dudley.

Fluorescein dyes as bacterial stains, particularly for soil preparations. H. J. Conn and W. C. Holmes (Stain Tech., 1926, 1, 87—95).—A discussion of the relative merits of 13 members of this group of dyes as stains. H. W. Dudley.

Mechanism of stain action with basic dyes. W. C. Holmes (Stain Tech., 1926, 1, 98—102).—The chemical theory of staining is discussed. Additive compounds as well as salts of the dyes may play a part in the reactions. H. W. Dudley.

Relation of age of bacteria to bacteriostatic properties of aniline dyes. J. W. Churchman (Stain Tech., 1926, 1, 103—104).—Cultures of organisms (*Bacillus coli*, *B. prodigiosus*, *B. subtilis*, and *Staphylococcus aureus*) become less resistant to gentian-violet as their age increases. This holds even for organisms which are undergoing sporulation.

H. W. Dudley.

Chemical nature of metachromasy. W. C. Holmes (Stain Tech., 1926, 1, 116—124).—The phenomena of metachromasy are analogous to the colour changes of aqueous solutions of the dyes, and probably arise from tautomeric changes of these substances. H. W. Dudley.

Thiazine dyes as biological stains. I. Staining properties of thionine and its derivatives as compared with their chemical structures. R. Haynes (Stain Tech., 1927, 2, 8—16).—Eight ethyl and methyl derivatives of thionine have been studied. A general correlation exists between the degree of ethylation or methylation of the compounds and their staining properties. Passing down the series from tetraethylthionine to thionine, there is a progressive decrease in the amount of green, and an increase in the amount of red, in the preparations; at the same time, the metachromatic effects and the intensity of nuclear staining increase. H. W. Dudley.

Rôle of insulin in protein metabolism. N. W. Janney and I. Shapiro (Arch. Int. Med., 1926, **38**, 96—108).—In fasting persons receiving dextrose and dextrose–insulin, the additional fall in nitrogen output represented 9·93—13·97% of the nitrogen output with dextrose alone. There was also a fall in blood-, urea-, and non-protein-nitrogen. The protein tissues are regarded as the seat of activity of insulin. Protein sparing by carbohydrate is increased by insulin. Diabetes may be a result of deficient protein metabolism. Chemical Abstracts.

Carbohydrate metabolism. II. Influence of methylglyoxal and other possible intermediaries on insulin hypoglycæmia. W. O. Kermack, C. G. Lambie, and R. H. Slater (Biochem. J., 1927, **21**, 40—45).—No significant difference could be observed in the time taken to recover from insulin hypoglycæmia following intravenous dihydroxyacetone administration as compared with dextrose (cf. Campbell and Hepburn, A., 1926, 979; Hewitt and Reeves, Lancet, 1926, i, 703). Methylglyoxal, sodium pyruvate, sodium lactate, glycerol, sodium citrate, and rhamnose do not cause animals to recover from insulin hypoglycæmia. The first two compounds appear to have a toxic action. S. S. Zilva.

Fate of deoxyglucose in the rabbit. L. B. Winter (Biochem. J., 1927, **21**, 54—55).—The injection of deoxyglucose into rabbits suffering from convulsions induced by the administration of insulin does not effect complete recovery, although the subsequent administration of dextrose restores the animals. Deoxyglucose does not seem to be metabolised by the animal. S. S. Zilva.

Action of insulin. I. On normal animals. E. Grafe, H. Reinwein, and H. Singer (Arch. exp. Path. Pharm., 1926, **119**, 91—101).—Fragments of liver taken from an animal after injection of insulin and suspended in Ringer solution show less glycogenolysis than do fragments from the same animal before the injection of insulin. W. O. Kermack.

Action of insulin on the permeability of the human kidney. H. Elias and J. Güdemann (Arch. exp. Path. Pharm., 1926, **119**, 119—126).—In the normal and in the diabetic subject, the minimum blood-sugar concentration at which dextrose begins to appear in the urine is not altered by the injection of insulin. This conclusion is true whether the raising of the blood-sugar concentration is effected by either peroral or intravenous administration of dextrose. W. O. Kermack.

Action of insulin on the sugar, phosphate, lactic acid, and glycogen contents of blood. A. I. Virtanen and H. Karström (Z. physiol. Chem., 1926, **161**, 218—244).—A large number of determinations of the sugar, phosphate, lactic acid, and glycogen of the blood of sheep with and without insulin are tabulated and discussed in relation to the author's theory of the mechanism of insulin action (cf., A., 1926, 760). P. W. Clutterbuck.

Phosphorus distribution in muscle and liver under different conditions, especially under the influence of hormones. Y. Oda (J. Biochem. [Japan], 1926, **6**, 179—210).—Insulin and pituitrin separately, but not together, cause an increase in the water content of the muscles. The combined phosphate and total phosphorus increase after the administration of insulin or dextrose, both in muscle and liver, but the effect of simultaneous administration is not a summation. Adrenaline and pituitrin reduce the amount of combined phosphate in muscle and liver; on simultaneous administration, there is antagonism in the muscle, but neither antagonism nor synergism in the liver. Both for muscle and liver, insulin and adrenaline or insulin and pituitrin are antagonistic in their effect on the combined phosphoric acid. The curves of the rate of autolytic splitting of phosphorus are different for muscle and for liver. Chemical Abstracts.

Effect of quinine and of some hormone preparations on the phosphoric acid hydrolysis during autolysis of muscle and liver. Y. Oda (J. Biochem. [Japan], 1926, **6**, 367—382).—Insulin, pituitrin, adrenaline, and quinine, in the concentrations used, have no effect on the rate of phosphoric acid hydrolysis in the autolysing muscle or liver-tissue. Chemical Abstracts.

Determination of the hormone content of corpus luteum preparations. Female sex-hormones. XI. S. Loewe and F. Lange (Arch. exp. Path. Pharm., 1927, **120**, 48—64).—Physiological methods are described. R. K. Cannan.

Female sex-hormones (thelytropins). XII. Oestrus-producing substances (thelykinins) obtained from the vegetable kingdom. S. Loewe, F. Lange, and E. Spohr (Biochem. Z., 1927, **180**, 1—26).—A substance having the action of thelykinin, the hormone which induces the œstrus cycle in mice, is found in vegetable sources and its distribution is investigated. Blossom is the most abundant source of plant thelykinin, female willow catkins containing up to 200 mouse units per kg. of fresh material. Vegetable thelykinin is detected also in *Nuphar luteum*. The separated stigma contains much less thelykinin (less than 14 mouse units per kg. of fresh material) than the whole blossom. *Impatiens parviflora* and *Althæa rosea*, after removal of the blossom, contain only minute quantities of the hormone. P. W. Clutterbuck.

Growth-promoting effect of irradiated fat in the diet, of direct irradiation, and of cod-liver oil. H. Goldblatt and A. R. Moritz (J. Biol. Chem., 1926, **71**, 127—137).—Whilst growth in young rats on a diet lacking vitamins-*A* and -*B* is promoted to an equal extent by addition of irradiated fat to the diet or by direct irradiation of the animals, neither of these methods is so efficacious as administration of cod-liver oil; irradiation does not prolong the life of the animals, nor does it prevent the occurrence of xerophthalmia. C. R. Harington.

Fractionation of irradiated cholesterol. I. Chemical observations. M. J. Shear and B.

Kramer. **II. Antirachitic potency of fractions.** B. Kramer, M. J. Shear, and D. H. Shelling (J. Biol. Chem., 1926, **71**, 213—220, 221—233).—I. Cholesterol was irradiated for 1—2 hrs. with ultra-violet light; on recrystallisation of the product, the mother-liquor yielded, on evaporation, 5—10% of a yellow oil, of which about 40% was not precipitated by digitonin. The oil gave a strong reaction with aniline and hydrochloric acid, as well as the Liebermann–Burchard and Salkowski reactions for cholesterol; the latter reaction was not obtained with perfectly pure cholesterol.

II. The above-described oil protected young rats against rickets when fed in a concentration of 0·1% of the diet; when dissolved in cotton-seed oil, it retained its antirachitic properties during storage for 2 months. C. R. Harington.

Glass screens for transmission of antirachitic light radiations. E. M. Luce (J. Biol. Chem., 1926, **71**, 187—190).—Growing rats were exposed to direct sunlight and to sunlight filtered through various screens, with results indicating that light of wave-length $>300\,\mu\mu$ fails to protect from rickets, whilst ultra-violet light of wave-length 240—300 $\mu\mu$ is as strongly antirachitic as full sunlight.

C. R. Harington.

Is antiscorbutic effect due to two substances ? N. Bezssonoff (Compt. rend., 1926, **183**, 1309—1310).—One half the usual dose of fresh lemon juice is sufficient to protect guinea-pigs from scurvy if 60 c.c. of milk heated at 120° for 1 hr. are administered, but if used alone, fresh milk is necessary for antiscorbutic effect. One half the antiscorbutic effect of orange juice is lost on heating at 130° for 1 hr. By fractionation with lead acetate, a crystalline product is obtained from cabbage, which in a dose of 40 mg. will protect guinea-pigs from scurvy when boiled milk is administered at the same time, whilst without the milk 160 mg. are without effect. The boiled milk may be replaced by 1·5 c.c. of boiled lemon juice. It is therefore suggested that vitamin-*C* is in reality two substances, one probably derived from the other, one being heat-stable and the other decomposed by heating. L. F. Hewitt.

Water, fatty acid, and cholesterol content of suprarenal glands of normal and scorbutic guinea-pigs. L. Randoin and A. Michaux (Compt. rend., 1926, **183**, 1055—1057).—The suprarenal glands of normal guinea-pigs contain about 68·6% of water, 5·5% of cholesterol, and 8·85% of fatty acids. When fed on diets deficient in vitamin-*C*, the water content remains constant, the cholesterol content falls as low as 2·7%, whilst the fatty acid content first falls and then increases to the normal or above normal value. The ratio of cholesterol content to fatty acid content (lipocytic coefficient) thus falls with the progress of scorbutic symptoms. L. F. Hewitt.

Influence of surface-active substances on the forms of growth of *Soor neonatorum* in respect to water-soluble vitamins. F. V. von Hahn (Kolloid-Z., 1926, **40**, 321—327).—A study of the physico-chemical conditions for the mycelial formation of *Soor neonatorum* revealed no difference between the natural, vitamin-rich products and artificial solutions of high surface activity. This supports the view that the vitaminoid state is essentially characterised by a certain surface tension.

E. S. Hedges.

Diet and reproduction. II. G. Grijns and K. de Haan (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 873—877).—A continuation of previous work (A., 1926, 546), in which the reproductive power of rats supplied with a diet from which various possible fertilising factors were absent, has been examined. No definite fertility-controlling factor has as yet been recognised, and the only progress made in this direction is that, by controlling the diet, females in the first or second generation are unable to rear their young, fertility in both sexes in so far as the production of living young is concerned being very little altered. J. S. Carter.

Apple physiology, growth, composition, and fruiting responses in apple trees. R. H. Roberts (Wisconsin Agric. Exp. Sta. Res. Bull., 1926, **68**, 1—72).—Blossom bud formation accompanies a condition of balance between the nitrogen and carbohydrate content. Apple trees may accumulate and use nitrogen reserve. The colour of the fruit varies inversely with the nitrogen content.

Chemical Abstracts.

Physiology of the nutrition of fruit trees. I. Effects of calcium and potassium starvation. C. E. T. Mann (Univ. Bristol Ann. Rep. Agric. Hort. Res. Sta., 1924, 30—45).—Deficiency of potassium leads to small apple leaves; deficiency of calcium to large ones. In dull light, transpiration is lower, and in bright sunlight higher, with leaves from trees deficient in potassium. Deficiency in potassium leads to a lower water content of gooseberry leaves.

Chemical Abstracts.

Oxygen requirements of plant roots. A. Kudryasheva (Sci. Agron. J., 1924, **1**, 48—67).—The roots of a plant require much oxygen, and consume it immediately; deficiency of oxygen leads to the formation of nitrite in the nutrient solution (Hellriegel's). Oxygen requirements per g. of dry substance are: maize, 0·38 mg., peas, 1·37 mg. The consumption is maximal at the flowering period.

Chemical Abstracts.

Carbon assimilation by plants. J. C. Bose (Scientia, 1926, **40**, 143—152).—Small traces of certain substances, particularly formaldehyde, largely increase the power of assimilation. Photosynthetic curves indicate that malic acid in the plant serves as a substitute for an external supply of carbon dioxide. The characteristic effects of different spectral regions are considered. The efficiency of the photosynthetic organ in *Hydrilla* is 7·4%. Chemical Abstracts.

Theory of the formation of lignin. W. Fuchs (Biochem. Z., 1927, **180**, 30—34).—Theoretical.

P. W. Clutterbuck.

Comparative plant chemistry. XIV. *Oenothera biennis*. R. Klapholz and J. Zellner (Monatsh., 1926, 47, 179—183).—The chemical composition of the evening primrose is in general similar to that of the related *Chamœnerium angustifolium* (A., 1924, i, 815). The air-dried leaves and flowers, respectively, contain: soluble in light petroleum, 2·45%, 4·07%; in ether, 1·77%, 3·05%; in alcohol, 17·23%, 26·50%; total water-soluble, 42·52% 41·18%; water-soluble mineral matter, 8·18%, 3·55%; soluble polysaccharides, 3·70%, 3·05%; free acid (as KOH), 4·52%, 5·31%; reducing sugars, 3·22%, 5·91%; crude fibre, 15·08%, 18·03%; nitrogen, 1·96%, 2·02%; crude protein (from nitrogen), 12·25%, 12·63%; ash, 10·54%, 6·89%. The petroleum extract of the leaves contains a phytosterol, m. p. 133° (acetate, m. p. 117°), identical with that obtained by Heiduschka and Luft (*ibid.*, 1919, i, 372) from the seeds; also (?)ceryl alcohol, m. p. 68—72°, and solid fatty acids. Phlobaphens, tannins, and invert-sugar are present in the alcohol extract, whilst the cold aqueous extract contains invertase. The polysaccharides appear to be entirely pentosans. The petals yield, in addition to the substances just mentioned, a saturated *hydrocarbon*, $C_{31}H_{64}$ or $C_{32}H_{66}$, m. p. 63°. H. E. F. NOTTON.

Presence of allantoic acid in *Phaseolus vulgaris*. R. FOSSE (Compt. rend., 1926, **183**, 1114—1116; cf. A., 1926, 438).—The crude derivative obtained by the action of an acetic acid solution of xanthhydrol on the juice of *Phaseolus vulgaris* gives no crystalline lead salt on treatment with lead acetate, but after hydrolysis the liquor gives all the reactions of allantoic acid, thus proving the presence of this acid in the sugar, since xanthyluroxanic acid (which by simple crystallisation from pyridine is converted into dixanthylallantoic acid) gives a characteristic lead salt under these conditions. When treated with xanthhydrol, the juice of *Acer pseudoplatanus* gives a precipitate which on crystallisation from pyridine yields dimethylallantoic acid. J. W. BAKER.

Respiration of tobacco leaves during drying. So-called tobacco fermentation. A. FODOR and A. REIFENBERG (Z. physiol. Chem., 1926, **162**, 1–40).—Peroxydase, oxydase, and catalase have been detected in the green, macerated leaves. In the dried leaves are found peptidase, peroxydase, catalase, and an enzyme which decomposes nicotine to organic bases and ammonia, but no oxydase. The uptake of oxygen by the leaves when placed in water in a Barcroft micro-respirometer at various stages during the drying process, is dependent on their moisture content, being least when the leaves have been thoroughly dried. Potassium cyanide greatly reduces both oxygen uptake and carbon dioxide output. Iron salts do not affect oxygen uptake, but increase the carbon dioxide output of the leaves. Mercury salts diminish oxygen uptake without affecting carbon dioxide output. The respiratory phenomena are not due to bacterial action. If air, but not if hydrogen, is drawn slowly through slightly moist tobacco in a desiccator, the temperature may rise several degrees. Maximal heat production occurs when tobacco of optimal moisture content, and compressed into the smallest possible space, is slowly aërated. Pyruvic acid and certain other organic acids are decarboxylated by tobacco leaves. H. D. KAY.

Chemical changes accompanying tuberisation in potato. J. T. ROSA (Proc. Ann. Mtg. Potato Assoc. Amer., 1924, **11**, 107—108).—In the underground stems, the dextrose and sucrose content is high prior to stolon formation, low during this period, and increases when the tubers begin to form. Starch, at first practically absent, rapidly increases in the underground stems and leaves. The total nitrogen is maximal in the early development and thereafter decreases rapidly. CHEMICAL ABSTRACTS.

Biocatalysts in meadow and pasture plants. F. BOAS and H. O. DIENER (Z. Pflanz. Düng., 1926, A, 8, 164—176).—Considerable differences are exhibited by different plants with regard to fermentation catalysts. The most active extract is obtained by immersing the hay in hot water and extracting for 6 hrs. Some of the catalysts are destroyed by heat, but part of the activity resides in the salts of the extract. Potassium chloride, even in a dilution of 1 : 1,140,000, has a noticeable effect on the fermentation. Ultrafiltration results in a partial separation, and the recombined fractions have the same activity as the original extract. A. WORMALL.

Colorimetric micro-method for determination of $p_{\rm H}$. O. A. WALTHER and J. ULRICH (Bull. Soc. Chim. biol., 1926, 8, 1106—1111).—Special precautions are taken to prevent evaporation of water and gaseous exchanges, and the method is applicable to quantities of fluid of the order of 0·1—1·0 mm.^{3} Standard amounts of the indicator and the solution are mixed in a special micro-pipette fitted with a micrometer screw and filled with mercury. A capillary tube, open at both ends, is filled with the mixture and plunged into paraffin oil. The colour is compared with that of appropriate standards in similar tubes by observation under the microscope or a lens.

A. WORMALL.

Colorimetric correction curves. S. L. WRIGHT, jun. (J. Biol. Chem., 1926, **71**, 209—212).—Correction curves for colorimetric work such as those previously published by the author (Bull. Ayer Clin. Lab., 1925, 9, 65) are largely a matter of individual observation, and should therefore be determined by each person for himself. This is particularly the case in connexion with the determination of creatinine in blood by the method of Folin and Wu (A., 1919, ii, 308).

C. R. HARINGTON.

Practical model of micro-pipette. R. WOLFF (Bull. Soc. Chim. biol., 1926, 8, 1112—1113).—A graduated capillary tube fitted with micrometer screw and measuring a total volume of 0·1 c.c. is described.

A. WORMALL.

Potentiometric determination of various cations and anions in biological research. P. D. VON NEERGAARD (Kolloid-Z., 1926, **40**, 339—340).—The influence of ions other than that of hydrogen should not be overlooked in biology.

E. S. HEDGES.