BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1928.

General, Physical, and Inorganic Chemistry.

Primary dark space of a Geissler discharge. K. B. EMELÉUS and (MISS) N. M. CARMICHAEL (Phil. Mag., 1928, [vii], **5**, 1039—1048).—Some of the properties of the primary dark space on the cold cathode of a Geissler discharge can be accounted for by an application of the equations developed by Langmuir for the positive ion sheaths present on exploring cathodes. There are, however, discrepancies which indicate that the cathode receives fast electrons from adjacent parts of the discharge which could subsequently produce a secondary electronic emission from the metal.   A. E. MITCHELL.

Emission of particles from hot platinum in air at atmospheric pressure. W. D. FLOWER (Phil. Mag., 1928, [vii], **5**, 1084—1094).—The Wilson cloud method has been employed for the ultramicroscopic examination of the large ions and nuclei emitted from a hot platinum wire in air at normal pressure. After removing the source of the nuclei it was found that the number visible increased to a maximum and then diminished, a result which is explained on the theory that at emission the nuclei are too small to be seen and subsequently coagulate. The coagulation of the nuclei has been observed and the rate of coagulation is expressed by the equation $dn/dt = -kn^2$, where n is the number of particles present and k is a constant $= 0.15 \times 10^{-8}$ cm.³/sec. This value is in fair agreement with the value 0.13×10^{-8} cm.³/sec., obtained by Kennedy for large ions and nuclei from a Bunsen flame.   A. E. MITCHELL.

Fine structure of the spectrum lines of thallium in the ultra-violet. W. MOHAMMAD and S. B. L. MATHUR (Phil. Mag., 1928, [vii], **5**, 1111—1114).—Of the twenty-one lines of thallium reported by Exner and Haschek between 6550·15 and 2580·25 Å., only eleven have sufficient intensity to be photographed by the aid of a quartz Lummer–Gehrcke plate. The fine structure of these lines has been examined and the positions of the satellites are given.   A. E. MITCHELL.

Distribution of electrons among atomic levels. E. C. STONER (Proc. Leeds Phil. Soc., 1928, **1**, 226—231).—Theoretical. It is shown that electrons may be divided into n, k groups, but a subdivision into n, k, j grouplets is not justifiable. For an n, k group for which the maximum number of electrons is z [$z = 2(2k-1)$] the X-ray sub-level scheme is appropriate when the group contains 1 or $z-1$ electrons. For other numbers of electrons, the level scheme is completely different, corresponding with other multiplicities.   W. E. DOWNEY.

Spectrum of ionised sodium. K. MAJUMDAR (Indian J. Physics, 1928, **2**, 345—354).—The spectral lines of sodium have been classified by the application of the irregular doublet law. An approximate value of 47 volts is deduced for the ionisation potential of sodium.   M. S. BURR.

Extension of the irregular doublet law to complex spectra. M. SAHA and P. K. KICHLU (Indian J. Physics, 1928, **2**, 319—342).—The data for Millikan and Bowen's irregular doublet law have been collected and tabulated, and the law has been shown to hold good in the case of complex spectra. On the basis of this law the ionisation potential of carbon should be approximately 11 volts. This has been confirmed experimentally (Fowler, Nature, 1928, **121**, 304). Predictions have also been made with regard to spectral lines which are still unknown, belonging to other elements.   M. S. BURR.

Regularities in the spectra of sexavalent elements. D. S. JOG (Indian J. Physics, 1928, **2**, 343—344).—The structure of spectra may be elucidated by comparing the spectra of successive elements which, by electric discharge, have been reduced to the same electronic configuration, e.g., O, F^+, and Na^{++}. Several lines have been identified as belonging to these elements by the help of the extension of the irregular doublet law discussed by Saha and Kichlu (cf. preceding abstract).   M. S. BURR.

Scattering of electrons by crystals. H. BETHE (Naturwiss., 1927, **15**, 786—788; Chem. Zentr., 1928, i, 154).

Excitation function of spectral lines. W. HANLE (Naturwiss., 1927, **15**, 832—833; Chem. Zentr., 1928, i, 158).—The excitation function (excitation probability in relation to the acceleration voltage of the bombarding electrons) of the mercury line 2537 Å. has been observed in the neighbourhood of the excitation potential.   A. A. ELDRIDGE.

New type of discharge in neon tubes. J. W. RYDE, L. JACOB, and B. S. GOSSLING (Nature, 1928, **121**, 794).

Rydberg term tables. F. PASCHEN (J. Opt. Soc. Amer., 1928, **16**, 231—243)—Values of $Z^2N/(m+a)^2$ are tabulated for $Z = 1$, 2, 3, and 4, Z being the number of the spectrum, N Rydberg's constant, m the order number of the term, and a the Rydberg correction.   C. W. GIBBY.

New regularities in the band spectrum of helium. G. H. DIEKE, T. TAKAMINE, and T. SUGA (Nature, 1928, **121**, 793—794).—More than 20 new

bands, and parts of other bands, have been found; most of the new bands have the $2p$ state as final state. Besides bands in which terms of a new type are involved, there were found new bands originating from the combination of Curtis' terms with the vibrational quantum number 1 and 2.

A. A. ELDRIDGE.

K-Electron ionisation by direct impact of cathode rays. D. L. WEBSTER (Proc. Nat. Acad. Sci., 1928, **14**, 339—344).—The assumptions underlying the theory of indirect K-ionisation used in previous work (this vol., 691) and here, are first tested by finding the ratio of the indirect $K\alpha$-line rays of silver to its continuous spectrum rays of the same wave-length. This should be independent of all questions of resolving power, sensitivity function, etc. The results obtained are of the right order, although not strictly accurate. The probability of direct K-ionisation by a cathode ray in silver is found to be 0·9 times the probability of an equivalent quantum emission in the continuous spectrum; the ratio is practically constant with change of voltage, and therefore must hold, not only for ordinary thick targets, but for infinitely thin targets also. The absolute probability of direct K-ionisation is also estimated with large limits of error, and found to agree with Thomas' theory. It seems probable that the process of direct ionisation is not usually an internal photo-electric effect, but rather a process of repulsion between electrons obeying laws much like the inverse square law.   A. J. MEE.

Analysis of spectra arising from quadruply-ionised tin, Sn V. R. C. GIBBS and H. E. WHITE (Proc. Nat. Acad. Sci., 1928, **14**, 345—348).—Most of the strong lines in the spectrum of Sn V have been identified. A table showing the intensities, wave-lengths, and frequencies of the identified lines is given, and the spectrum is analysed.   A. J. MEE.

Structure of some spectra with regard to recent theoretical considerations. T. L. DE BRUIN (Arch. Néerland., 1928, [iii], A, **11**, 70—153).— A comprehensive paper giving the results of researches which confirm the spectroscopic displacement law of Sommerfeld and Kossel. The arc and spark spectra of several elements were photographed, using the method of discharge without electrodes. The spectrum of potassium was examined and the existence of two characteristic spectra shown. One is yellowish-green and the other is bluish-violet. The former is due to the neutral atom, K I, the latter to the singly-ionised atom, K II, and is comparatively simple. The spectrum of K II was analysed and compared with that of neutral neon, Ne I, and neutral argon, A I. It shows some analogy to both these spectra, as it should do if the Bohr theory is correct. The structure of the spectrum is discussed in relationship to the configuration of the atom. It is also shown that the 3_3 structure is more stable than the 4_2, which is not so for the rare gases. The Zeeman effect in the case of the K II lines was examined partly for ordering the spectrum, and partly in an attempt to verify the theory of Landé and Heisenberg, but the diffuse way in which the lines split made measurements impossible. The spectra of doubly-ionised potassium, K III, and triply-ionised potassium, K IV, were difficult to study, but should be equivalent to those of non-ionised fluorine, F I, and chlorine, Cl I, and singly-ionised fluorine, F II, and chlorine, Cl II, respectively. The spectrum of fluorine was obtained by passing a discharge without electrodes through silicon tetrafluoride. The theoretical scheme for terms of F I is drawn up, and the terms found are experimentally identified. The ionisation potential of fluorine calculated from the fundamental term is found to be 16·7 volts. The spectrum of singly-ionised fluorine F II was investigated and compared with the analogous spectra of non-ionised oxygen, O I, and non-ionised sulphur, S I; the structure is shown to be similar. The spectrum of singly-ionised neon, Ne II, was analysed and shown to be analogous to that of non-ionised fluorine, whilst that of doubly-ionised neon, Ne III, is similar to that of singly-ionised fluorine. The structure of the terms of the spectra examined conforms to the new theory of Heisenberg and Hund on complex spectra. The spectra of selenium, arsenic, and indium were investigated by the same method with a view to relate them with the theory of Hund.   A. J. MEE.

Spectrum of ionised neon. T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 2—13).—180 Lines of the spectrum of ionised neon (Ne II) have been classified in a term scheme and the deepest quadruplet terms identified. The Ne II spectrum has a structure analogous to that of the F I spectrum. This is in agreement with the theory according to which the spectra of the ionised rare gases should have the same structure as the F I spectrum (cf. A., 1927, 82). In Ne II the terms have approximately double the value of the analogous terms of F I.   M. S. BURR.

Intensity measurements in the secondary spectrum of hydrogen. L. S. ORNSTEIN, W. KAPUSCINSKI, and (Miss) J. G. EYMERS (Proc. Roy. Soc., 1928, A, **119**, 83—91).—The figures given by McLennan for the intensities in the secondary spectrum of hydrogen (A., 1927, 1004) are only densities, and it is shown that, since the relations between density and intensity are not simple, McLennan's values could not be used for theoretical investigations of the secondary spectrum. The intensities of about 230 lines over the region 4500—4900 Å. have now been measured by the Utrecht method. In this region, the value of the sensitivity of the photographic plate depends strongly on the wave-length, and allowance was made for this. The method used for the analysis of closely adjacent lines is described in detail. The intensity values are compared with McLennan's densities; for moderate intensities the ratio of the results is almost constant, but no proportionality is shown for higher intensities.

L. L. BIRCUMSHAW.

Relation between mean stopping power and mean range of β-rays. E. J. WILLIAMS (Proc. Camb. Phil. Soc., 1928, **24**, 315—319).—The true rate of loss of energy or " stopping power " of β-rays is the quantity dT/dx, where dT is the mean energy lost by rays of energy T in travelling a distance dx

along their paths. The cloud method enables only the total ranges of β-particles to be observed, and in deducing the stopping power from the mean range $\bar{R}$, dT/dR is not exactly the same as dT/dx, owing to straggling. The relation between these two quantities is calculated so that the cloud method may be rigorously interpreted. For rays of 10,000 volts traversing light elements the correction is about 7%, whilst for α-rays it is negligible. C. J. SMITHELLS.

Absolute intensity measurements on the sodium flame. Duration of the excited state. L. S. ORNSTEIN and E. F. M. VAN DER HELD (Ann. Physik, 1928, [iv], **85**, 953—960).—The absolute intensity of the green mercury line from a quartz lamp was first measured and then photographic comparisons were made of the sodium flame and the yellow light from a Nitra lamp, and the green line with the green light from the Nitra lamp. For the sodium flame, 250 quanta per sec. per atom are emitted at 1970° Abs. The Einstein equation leads to the value 5×10^{-8} sec. for the period of excitation as against the values 1·6 and $3·8 \times 10^{-8}$ sec. due to Minkowski (A., 1926, 650) and Kerschbaum (A., 1926, 652), respectively. R. A. MORTON.

Methods of estimating the intensities of spectral lines. W. H. J. CHILDS (Proc. Physical Soc., 1928, 40, 132—148).—A critical discussion of several methods of spectral photometry applied to the special case of the band spectrum of helium is given. The preferred method is to photograph the line spectrum in the usual way and then calibrate the plate by illuminating the slit with a tungsten-filament lamp in such a way that on development a number of continuous spectra of progressively increasing density are obtained. From these images the relation between the intensity of light and density of image, and between plate sensitivity and wave-length, may be ascertained. Density measurements are obtained by means of a selenium cell microphotometer. C. J. SMITHELLS.

Structure of the second order spectrum of sulphur. J. GILLES (Compt. rend., 1928, **186**, 1354—1355).—The values of the combinations of the multiplets amp^4S and^4P of the S II spectrum, are deduced from those previously published (cf. this vol., 565). J. GRANT.

Certain multiplets in the spectra of Cd III and In IV. R. C. GIBBS and H. E. WHITE (Physical Rev., 1928, [ii], **31**, 776—781).—With the aid of the transitions from ^3PDF, $^1PDF(4d^95p)$ to ^3D, $^1D(4d^95s)$ already determined for Pd I and Ag II, the corresponding lines in the spectra of Cd III and In IV have been identified and tabulated; the transitions from $^3D_1$, $^3P_1$, and $^1P_1(4d^95p)$ to $^1S_0(4d^{10})$, the lowest level, have also been identified for Ag II, Cd III, and In IV. The validity of the irregular doublet law is confirmed. A. A. ELDRIDGE.

Application of the X-ray laws to optical spectra of higher rank, and the classification of Ga IV and Ge V. J. E. MACK, O. LAPORTE, and R. J. LANG (Physical Rev., 1928, [ii], **31**, 748—772).—The $(3d^94s)$ and $(3d^94p)$ levels of Ga IV and Ge V, and a tentative $(3d^{10})$ level for Ga IV have been found, and

the levels formerly classified as $^3D_1$, $^1P_1(3d^94p)$ of Zn III have been interchanged. Evidence is adduced to show that of the ^3D, $^1D(d^9s)$ the $^3D_2$ level approaches the limit $^2D_3(d^9)$, contrary to Hund's theory. Distinctions between X-ray and optical spectra in application of the X-ray laws are considered, as also is the shape of the σ_1 (first order screening number) curve for isoelectronic spectra. The irregular doublet law is not always valid. A. A. ELDRIDGE.

Arc spectrum of germanium. C. W. GARTLEIN (Physical Rev., 1928, [ii], **31**, 782—792).—The wave-lengths ($\pm 0·03$ Å.) of germanium arc lines above 1870 Å. are tabulated; the relative energy levels have been determined and transitions corresponding with 73 lines identified. The first resonance potential is 4·65 volts and the ionisation potential determined by the limit $^2P_1$ is 7·85 volts. Similarities in the arc spectra of silicon, germanium, tin, and lead are considered. A. A. ELDRIDGE.

Lowest terms in the spark spectrum of nickel and copper (Ni II and Cu II). R. J. LANG (Physical Rev., 1928, [ii], **31**, 773—775).—In the spark spectrum of nickel the lowest terms $^2D_{2,3}(d^9)$ lie 6884 and 8391 cm.$^{-1}$ below $a^4F'_5$; in that of copper $^1S_0(d^{10})$ lies 21925 cm.$^{-1}$ below a^3D_3. A. A. ELDRIDGE.

Arc and spark spectra of titanium. I. Spark spectrum, Ti II. II. Arc spectrum, Ti I. H. N. RUSSELL (Astrophys. J., 1927, 66, 283—328, 347—438).—I. All but the weakest lines have been classified; 33 doublet and 17 quadruplet terms have been identified. Three series of two members each indicate an ionisation potential of 13·6 volts. Hund's theory of the relation of spectral lines to electronic configurations in the atom is confirmed. A comparison of the spectra of Ti II and Sc I shows that Moseley's law is closely satisfied.

II. The arc spectrum is complicated; 43 singlet, 65 triplet, and 34 quintuplet terms have been identified. There are no intercombinations between singlets and quintuplets. Hund's theory is again confirmed. Seventeen series, converging to seven different limits, all terms of Ti II, have been identified; the ionisation potential is 6·81 volts. The spectra of Ti I and V II are similar in structure; comparison indicates that the ionisation potential of V II is approximately 14·1 volts. A. A. ELDRIDGE.

Zeeman effect and spectral terms in the arc spectrum of platinum. A. C. HAUSSMANN (Astrophys. J., 1927, 66. 333—346).—The Zeeman effect of 173 arc lines of platinum was investigated in the region 5500—2500 Å.; 33 of the lines could be identified from their patterns. Twelve low levels have been identified; the ground term is $^3D_3$, d^9s. There are 45 intermediate and 15 high levels. Practically all the strong lines in the arc spectrum are attributed to combinations between these levels. A. A. ELDRIDGE.

Wave-lengths of carbon, oxygen, and nitrogen in the extreme ultra-violet with a concave grating at grazing incidence. J. B. HOAG (Astrophys. J., 1927, 66, 225—232).—With a vacuum spectrograph of special design, wave-lengths from 1658 to 558 Å. for spark discharge through mag-

nesium and carbon electrodes were obtained; by passing gases through the electrodes, gaseous and metallic spectra are simultaneously obtained.

A. A. ELDRIDGE.

Secondary standards of wave-length; interferometer measurements of iron and neon lines. H. D. BABCOCK (Astrophys. J., 1927, **66**, 256—282). —Standard wave-lengths are recorded for 286 iron lines, λ 3407—6677 Å., and for 11 neon lines, λ 5852—6506 Å., measured in terms of the primary standard, 6438·4696 Å., of cadmium. The neon wave-lengths agree precisely with the values adopted as secondary standards, but the iron wave-lengths are systematically smaller than the adopted values. The differences are discussed. A. A. ELDRIDGE.

Absorption spectrum of mercury at high pressure admixed with nitrogen. H. R. MOORE (Science, 1927, **66**, 543—544).—The bands already observed (Mohler and Moore, A., 1927, 917) have been extended towards the red to 3087 Å. at 215—305°, and towards the violet to 2666 Å. at 425—530°, by the addition of nitrogen. Forty-two such bands were observed. The band at 2528 Å. was always obtained with mixtures of mercury and nitrogen, and appears to be definitely conditioned by the presence of nitrogen. Resonance broadening increases with the pressure of the nitrogen. The extension of the bands may be ascribed to the increase in concentration of Hg_2 molecules resulting from the combined effect of the nitrogen and the radiation used as a source, or they may represent the vibrational spectra of HgN_2 molecules, unstable or quasi-stable, formed between nitrogen molecules and excited mercury atoms.

A. A. ELDRIDGE.

Band spectrum of mercury excited by a high-frequency discharge. J. G. WINANS (Nature, 1928, **121**, 863—864).—The spectrum of the discharge showed the mercury arc lines and the mercury bands with maxima at 4850, 3300, 2540, and 2345 Å.; distilling vapour is necessary for the excitation of the bands 4850, 3300, and 2345 in a high-frequency discharge. The band at 4850 Å. is destroyed by local heating. The initial excited state for the band 4850 Å. differs from that of the band at 3300 Å. and from those of the bands at 2345 and 2540 Å., but the final states of the bands at 2345 and 2540 Å. are the same. A. A. ELDRIDGE.

Spectra of doubly- and trebly-ionised titanium. (Ti III and Ti IV.) H. N. RUSSELL and R. J. LANG (Astrophys. J., 1927, **66**, 13—42).—Thirty-one new lines of Ti IV and 90 lines (mostly new) of Ti III have been identified between 5492 and 423 Å.; all the former and all but four of the latter have been classified. Twelve terms are tabulated for Ti IV; the $3D$ term is the lowest, and the ionisation potential is 43·06 volts. Nineteen terms were identified for Ti III; the estimated ionisation potential is $27\cdot6\pm1\cdot0$ volts. The spectrum of Sc III is briefly discussed.

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Photography of the infra-red solar spectrum. H. D. BABCOCK (Nature, 1928, **121**, 830—831).— About 12 lines between 10000 and 10750 Å. have been observed on prismatic plates, one at 10049·8 Å. being specially conspicuous; it is evidently the fourth

member of the Paschen series of hydrogen. On grating plates a number of lines were also observed.

A. A. ELDRIDGE.

Application of the irregular doublet law to complex spectra. K. MAJUMDAR and G. R. TOSHNIWAL (Nature, 1928, **121**, 828—829).—Saha and Kichlu's application of the irregular doublet law to complex spectra (this vol., 209) is confirmed in the groups Ne, Na^+, Mg^{++} and A, K^+, Ca^{++}. The view that the spectrum of the solar corona is composed of the lines of Ca^{++} is not supported. The ionisation potential of Ca^{++} is about 52 volts.

A. A. ELDRIDGE.

Related lines in the spectra of the elements of the iron group. H. N. RUSSELL (Astrophys. J., 1927, **66**, 184—216).—The arc and spark spectra of potassium, calcium, scandium, titanium, vanadium, chromium, iron, cobalt, nickel, copper, and zinc have been classified sufficiently to illustrate the similarity of spectral groups resulting from similar electron transitions. Homologous terms and homologous lines as n varies from 1 to 12 are tabulated.

CHEMICAL ABSTRACTS.

Spectrum of ionised sodium. O. LAPORTE (Nature, 1928, **121**, 941).—By using one of the differences between pairs of lines in the Na II spectrum (Newman, this vol., 210), it is possible to arrange numerous strong lines as combinations of four s terms with ten p terms corresponding with the transition $3s^1\,{}^3P — 3p^{1\,2}\,(S,P,D)$. A. A. ELDRIDGE.

Optical characterisation of spark emission spectra. G. I. POKROWSKI (Z. Physik, 1928, **48**, 586—593).—By assuming that the energy consumed in a spark is proportional to the square of the root mean square value of the current flowing through the arc, the total intensity I of n spectral lines is shown to be related to the current i and to the absorptive power, k, of the metal vapour through which the spark takes places by the expression $I = ai^2 + b(1 - e^{-kci^2})$, where a, b, and c are constants. It is also shown that for a given value of i, I is linearly related to the width of the spark gap. Data relating to lines 5000, 5200, 5890 Å. in the spark between copper and electrodes are shown to be in agreement with the above expression. R. W. LUNT.

Active nitrogen. P. K. KICHLU and D. P. ACHARYA (Nature, 1928, **121**, 982—983).—The spectrum of active nitrogen includes a band system from 7500 to 8900 Å., doubtless originating from the N_2 molecule, and presumably analogous to A, B, α bands of oxygen. The results of McLennan, Ruedy, and Anderson (this vol., 456) are criticised.

A. A. ELDRIDGE.

New photo-electric phenomenon with thin sheets of alkali metals. R. SUHRMANN (Naturwiss., 1928, **16**, 336).—When thin sheets of alkali metals are illuminated with the mercury 240 $\mu\mu$ line, the light intensity–voltage characteristic reaches a sharp saturation value at a few volts. At the red limit (313 $\mu\mu$), however, it rises steadily with increasing potential. The same phenomenon is found but to a less degree with thicker sheets. J. W. SMITH.

Predicted ionisation potential of radon. S. C. BISWAS (Phil. Mag., 1928, [vii], **5**, 1094—1098).—It

is shown that the ionisation potential of an atom is given by the expression $I_{(volts)} = 3.83kn/\bar{r}^2$, where k and n are respectively the azimuthal and radial quantum numbers of the external electron and $\bar{r}^2$ is the mean square radius of the nk orbit. Since for elements of the same group of the periodic classification k is constant, it follows that the ionisation potentials of these elements will be proportional inversely to the square of the radius and directly to the radial quantum number. From crystal structure and other measurements it is shown that the atomic radius of radon should be 1.81 ± 0.03 Å., whence taking the quantum numbers in question as 6 and 2 the ionisation potential should be 14.0 ± 0.5 volts, a result in general accordance with the known values for krypton and xenon, but in disagreement with the predictions of Turner (A., 1924, ii, 797) and others.
A. E. MITCHELL.

Cause of loss of thermionic activity of thoriated tungsten filaments under certain voltage conditions. (Miss) A. C. DAVIES and (Miss) R. N. Moss (Phil. Mag., 1928, [vii], 5, 989—1010).—It is found that loss of thermionic activity is due to the bombardment of the filament by positive ions which originate in their turn from the electron bombardment of the grid and plate. W. E. DOWNEY.

Electron theory of metals. A. SOMMERFELD (Naturwiss., 1927, 15, 825—832; 1928, 16, 374—381).—The old electron theory of metals is discredited, but it can be rehabilitated without the adoption of new physical assumptions. The statistical treatment of the assumptions of Drude and Lorentz must be replaced by a new treatment based on the wave-mechanics. The present work is concerned mainly with the development of a wave-mechanical theory of conductivity in metals, and the variations with changes in temperature and pressure. Starting from the Pauli principle and the Fermi–Dirac statistics, it is shown that the mean velocity of an electron-gas is independent of temperature; wave-lengths in terms of de Broglie's ideas are then calculated, and after considering the Richardson and Volta effects, it is possible to develop the theory of metallic conduction so as to obtain satisfactory agreement between the observed and calculated data. A final section is devoted to the direction-dependence of conductivity and the thermal forces in unicrystalline material.
R. A. MORTON.

Electron emission in intense electric fields. R. H. FOWLER and L. NORDHEIM (Proc. Roy. Soc., 1928, A, 119, 173—181).—The phenomenon of electron emission in intense fields can be accounted for in a satisfactory quantitative way by Sommerfeld's revived electron theory of metals (see preceding abstract). Nordheim's results (this vol., 452) are extended to include the effect of an external field, using the same methods and the same underlying picture of the metal. The formula $I = CF^2 e^{-a/F}$ is established, independent of the temperature at low temperatures, in agreement with experiment. No theoretical justification is found for the general formula for the current, valid over wide ranges of temperature and field strength, suggested by Millikan and Lauritsen (Proc. Nat. Acad. Sci., 1928, 14, 45).

Exception is taken to the assertion of these authors that the conduction electrons, unlike the thermions, do not share in the thermal energy of agitation of the atoms. It is found that Sommerfeld's picture of a metal yields the formula both for strong fields and for thermionic emission, a single set of free conduction electrons distributed according to the Fermi–Dirac statistics sufficing for both purposes.
L. L. BIRCUMSHAW.

Liberation of electrons from a metal surface by positive ions. F. M. PENNING (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 14—23).—In order to get more information as to the part played by positive ions in a gas discharge, two methods have been devised for determining experimentally the number of positive ions required to liberate one electron from a metal surface. In neon, α_0, the number of electrons liberated by one positive ion at zero velocity from a copper or iron surface, is of the order of 0.05. In argon α_0 is smaller than in neon, but at a magnesium surface it is larger than at a copper surface. Measurements have also been carried out with hydrogen to compare the method with that employed by Baerwald (Ann. Physik, 1921, [iv], 65, 167), but, for a potential of 1000 volts, the value of α was only 10% of that found by Baerwald.
M. S. BURR.

Hydrogen activated by the electric discharge. A. DE HEMPTINNE (Bull. Acad. roy. Belg., 1928, [v], 14, 8—17).—See this vol., 139.

Photo-electric threshold and heat of dissociation of the potassium molecule. R. W. DITCHBURN (Proc. Camb. Phil. Soc., 1928, 24, 320—327).—Absorption curves and photo-ionisation experiments agree and give for the molecular photo-electric threshold value of potassium 2555 ± 20 Å. The energy of dissociation of the potassium molecule is $0.50_5 \pm 0.01$ volt, and the heat of dissociation 11400 g.-cal. Between 200° and 500° the fraction associated varies from 10^{-4} to 10^{-2}.
C. J. SMITHELLS.

High-frequency electric discharge at low pressures. J. TAYLOR and W. TAYLOR (Proc. Camb. Phil. Soc., 1928, 24, 259—267).—Experiments have been carried out under widely varied conditions on discharges through gases, under the influence of high-frequency oscillations (order 10^7 cycles per sec.), using tubes of the electrodeless type. The influence of the wall material is shown by the fact that on pumping down tubes not previously baked out, the order in which the discharges were first obtained on increasing the voltage was: soft glass, pyrex, and quartz. Even at the highest degree of exhaustion and with the mercury vapour (from the pumps) frozen out, faintly luminous discharges could be obtained. With a high frequency of alternation there will be no separation of charges, and the nett effect will be a periodic movement of the electrons through an atmosphere of positive ions, the observed luminosity arising from recombinations proceeding between oppositely charged particles. The discharge passes more easily in wide tubes than in narrow ones, with a dark space between the glow and the wall. The luminosity can be conducted along the tube by

moving an earthed conductor such as the hand along the outer walls. By lining the inside of a tube with metal gauze connected to a voltage supply, it is shown that the luminosity is destroyed by a uni-potential wall. Injection of slow electrons into the glow has little effect. A new type of spherical glow has been obtained in bulbs, and discharges of this kind are regarded as uniform high-temperature enclosures of electrons and positive ions maintained artificially.   R. A. MORTON.

Electrodeless discharge through gases. J. J. THOMSON (Proc. Physical Soc., 1928, **40**, 79—89).— An electrodeless discharge is produced by placing outside a glass tube containing gas at a low pressure a solenoid connected to the outsides of two Leyden jars, the insides of which are connected to the terminals of an induction coil. Rapidly alternating currents pass through the solenoid, and the electro-magnetic induction starts currents in the exhausted vessel which flow in rings co-axial with the solenoid. The theory of the discharge is discussed. There is a critical gas pressure, depending on the frequency, at which the discharge passes most easily. With heavy currents the magnetic force is greatest near the walls of the bulb and produces a condition resembling the Heaviside layer. The discharge is assisted by the action of light, which is attributed to the absorption of energy by the gas molecules rendering them more easily ionised. The effect of impurities in the bulb is investigated. Free electrons become attached to electronegative elements like phosphorus and sulphur and ionisation is reduced. Metals also hinder the discharge by combining with gas molecules which are in a more active state than normal. The normal oxides of magnesium, calcium, and zinc combine with oxygen under the influence of the discharge to form higher oxides.   C. J. SMITHELLS.

Excitation of the D-lines by the green sodium band. E. L. KINSEY (Nature, 1928, **121**, 904—905).—In accord with the views of Wood and Kinsey (this vol., 687), the green sodium band excites the D-lines in pure sodium vapour, but only in a narrow temperature range; the atomic lines appear somewhat below 400°, are maximal at 410°, and disappear above 450°. At 410° the molecules are probably only 55% dissociated.   A. A. ELDRIDGE.

Space-distribution of the photo-electrons ejected by X-rays. E. C. WATSON (Physical Rev., 1928, [ii], **31**, 728—741).—Rutherford's theory of nuclear scattering, together with the assumption that all the electrons start from the parent atom in the same direction, accord with the observed distribution of the photo-electrons ejected by X-rays.
                              A. A. ELDRIDGE.

Photo-electric effect and thermionic emission. P. W. BRIDGMAN (Physical Rev., 1928, [ii], **31**, 862—866).—A correction and extension of previous work (this vol., 213).   A. A. ELDRIDGE.

Voltage–intensity relations in the mercury spectrum. W. D. CROZIER (Physical Rev., 1928, [ii], **31**, 800—811).—Voltage–intensity curves were obtained for 20 mercury lines, when excited by elec-tron impact. There is no significant change in the

number of atoms in a given energy state as the ionisation potential is passed. The probability of different transitions down from a given energy state may not be independent of the way in which this state is excited.   A. A. ELDRIDGE.

Series and ionisation potentials of the ele-ments of the iron group. H. N. RUSSELL (Astro-phys. J., 1927, **66**, 233—255).—Series, usually of two members only, have been identified in the arc spectra of potassium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and in the spark spectra of calcium, scandium, titanium, manganese, nickel, copper, and zinc; approximate series limits are determined and tabu-lated. Four important modes of ionisation of the neutral atom and three for the second ionisation are indicated. The following principal and second ionis-ation potentials are recorded : potassium 4·32, —; calcium 6·09, 11·82; scandium 6·57, 12·80; titanium 6·80, 13·60; vanadium 6·76, 14·7; chromium 6·74, 16·6; manganese 7·40, 15·70; iron 7·83, 16·5; cobalt 7·81, 17·2; nickel 7·64, 18·2; copper 7·69, 20·34; zinc 9·36, 17·89. New high terms, arising from configurations involving a $5s$ electron, have been identified in the spectra of vanadium, man-ganese, cobalt, and ionised manganese.
                              A. A. ELDRIDGE.

Astrophysical estimates of ionisation poten-tials of iron, yttrium, and lanthanum. A. V. DOUGLAS (Nature, 1928, **121**, 906).—Ionisation potentials are estimated, from astrophysical data, to have the following values : iron, 6·6 (by comparison with scandium and titanium), 5·5 (by comparison with strontium and barium); yttrium, 6·6; lanthanum, 4·9 volts.   A. A. ELDRIDGE.

Ionisation by metastable atoms. F. M. PEN-NING (Naturwiss., 1927, **15**, 818; Chem. Zentr., 1928, i, 155).—The condition for the reduction of the sparking potential of an inert gas for large values of pd (pressure × separation of electrodes) on admixture of another gas is $V_{met} > V_{i'}$ (V_{met}=excitation potential of the metastable form of the inert gas; $V_{i'}$=ionisation potential of the admixed gas). The explanation is based on the scheme : metastable atom+foreign atom=normal atom+foreign ion. Measurements were made on neon with admixed mercury, krypton, argon, hydrogen, and nitrogen, and on argon with admixed iodine, mercury, xenon, and krypton.   A. A. ELDRIDGE.

Current density of the normal cathode fall. W. DE GROOT (Naturwiss., 1927, **15**, 818; Chem. Zentr., 1928, i, 155).—The current density was smaller in a mixture of neon (containing 30% of helium) and argon (0·1—2%) than in the separate gases; two types of discharge were observed.
                              A. A. ELDRIDGE.

Loss of charge of positive rays and the influence of neighbouring metallic walls. E. RÜCHARDT (Z. Physik, 1928, **48**, 594—599).— Polemical. A reply to Koenigsberger (A., 1927, 806).   J. W. SMITH.

Mobilities of the positive ions formed by alpha-rays in air, hydrogen, and helium. J. S. ROGERS (Phil. Mag., 1928, [vii], **5**, 881—903).—From the

experimentally observed decrease in the mobility of ions during their life it is concluded that an ion, in a very short time after its formation, has developed into a cluster. The mobility changes in definite steps. If the changes in mobility were due to the gradual addition of neutral molecules, a gradual change in the mobility with the life of the ion would be expected. This step change in mobility is unexplained.

W. E. DOWNEY.

Measurement of displacements of negative carriers in flames. E. MARX and P. KAPPLER (Physikal. Z., 1928, **29**, 261—269).—A flame is charged with solutions of alkali metal salts and the variation of the "displacement" K_2', where $K_2' = \beta K_2$ (β being the charge-number and K_2' the mobility) with the concentration c determined. K_2' varies as $(1/c)^{\frac{1}{2}}+$constant, and the magnitude $K_2' \times$ (at. wt.)$^{\frac{1}{2}}$ is the same for rubidium, potassium, and sodium at a given normality; lithium is anomalous.

R. A. MORTON.

Reflexion of electrons by a crystal of nickel. C. J. DAVISSON and L. H. GERMER (Proc. Nat. Acad. Sci., 1928, **14**, 317—322).—In continuation of previous work (A., 1927, 492), an electron beam was directed against a {111} face of a nickel crystal at various angles of incidence, and the intensity of scattering in the incidence plane measured as a function of bombarding potential and direction. Whenever the speed of the incident electrons is comprised within any of certain ranges, changing in location as the angle of incidence is varied, a sharply-defined beam of scattered electrons issues from the crystal in the direction of regular reflexion. In each of these ranges there is an optimum speed where the intensity of the reflected beam is a maximum. The phenomenon is the analogue of the regular selective reflexion of X-rays, but the Bragg formula does not hold, although there is a simple correlation between the observed positions of the maxima and the positions calculated by the Bragg formula. A. J. MEE.

Luminous beads of metal particles sputtered by disruptive discharge in magnetic field. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1928, **4**, 106—108).—Photographs are given showing the peculiar beaded tracks of metal particles sputtered in a magnetic field. Various explanations of the phenomena are offered, the most probable cause being the alternate formation and loss of an oxide film on the surface of the particle. C. J. SMITHELLS.

Relation between colour and magnetism of ions. B. MALYSCHEV (Ann. Physik, 1928, [iv], **85**, 794).—In connexion with the work of Joos (A., 1927, 94) it is suggested that the investigation of the magnetic susceptibilities of the carbonyls of paramagnetic metals in the gaseous, liquid, and solid states should prove interesting. R. A. MORTON.

Radiations emitted at the impact of hydrogen canal rays on metals. C. GERTHSEN (Ann. Physik, 1928, [iv], **85**, 881—912).—The possibility of exciting characteristic radiations by means of the impact of canal rays on metals has been investigated (cf. A., 1926, 655). Optical reflexion from a concave mirror makes possible the detection of weak rays emitted from the points of impact, but it has not proved

possible to decide whether the rays are characteristic radiations from the atoms of the surface, or whether they correspond with the excitation of the Lyman series. The effects observed by Thomson (A., 1926, 988) are ascribed to reflected canal rays. An experiment designed to separate the wave-radiation effect from the reflected positive-ray effect showed that some of the canal rays are scattered with almost unchanged velocities. These reflected rays increase in velocity as the velocity of the primary rays increases. The scattering from different materials follows the laws for the scattering of α-particles at atomic nuclei, namely, proportionality with the number of atoms per c.c., and with the square of the atomic number. R. A. MORTON.

Positive-ray analysis of water vapour ionised by impact of slow electrons. H. A. BARTON and J. H. BARTLETT, jun. (Physical Rev., 1928, [ii], **31**, 822—826).—By the use of an electromagnetic method the ions H_2O^+ and OH^+ were detected, the former being the more abundant, with small quantities of a third ion, probably H_3O^+; no negative ions were observed, and scarcely any H^+ and H_2^+ ions. The ionisation potential corresponding with H_2O^+ was 13 ± 1.5 volts, and that of OH^+ was not distinguishably different. The H_2O^+ ion is probably the primary ion. A. A. ELDRIDGE.

Detection and determination of ions in a gaseous discharge by optical methods. W. DE GROOT and L. BLOK (Physica, 1927, **7**, 315—320).—Light from a carbon arc passes through an arc formed in neon between a tungsten cathode and a nickel anode with a barium core; the light from the carbon arc is cut off in phase with an alternating current superimposed on the direct current for the barium arc, so that the absorption effects can be observed during those periods when the barium arc is extinguished. The barium lines 4934 and 4554 were observed in absorption. A positive-column discharge tube with argon and mercury vapour showed the mercury line 2847 Å. at 20° and —12°, but not at 120°. The absorption is dependent on the effective number of absorbing atoms and the thickness of the absorbing layer. For barium, the number of ions per c.c. at 3 amp. arc current is 10^{12}.

CHEMICAL ABSTRACTS.

Ionisation in positive-ion sheaths. P. M. MORSE and W. UYTERHOEVEN (Physical Rev., 1928, [ii], **31**, 827—832).—The positive-ion current to a plane auxiliary collector placed in a neon discharge is double that anticipated; the increase is probably caused by the ionisation of the metastable atoms within the sheath by radiation from the discharge. A similar increase is to be expected in helium and argon. A. A. ELDRIDGE.

Active nitrogen. J. KAPLAN and G. CARIO (Nature, 1928, **121**, 906—907).—The long life and behaviour in the presence of catalysts of active nitrogen indicates that it is atomic, and that metastable molecules are formed under the influence of the recombination of atoms to molecules. This process is considered to be accompanied by the formation of metastable atoms. This view is shown to be in accord with experimental data. A. A. ELDRIDGE.

Active nitrogen. B. LEWIS (Nature, 1928, **121**, 864—865).—Polemical and explanatory (cf. Willey, this vol., 341). A. A. ELDRIDGE.

Active nitrogen. B. LEWIS (Nature, 1928, **121**, 938—939).—On introduction of pure oxygen (1%) into glowless nitrogen immediately after discontinuing the electrodeless discharge, no glow was produced; further, subsequent subjection of the mixture to the discharge caused little or no glow. The observation accords with those of Herzberg (this vol., 457) and of Bonhoeffer and Kaminsky (A., 1927, 801). Intense nitrogen after-glows have been obtained in mixtures containing up to 57% of oxygen in the electrodeless discharge at or below 0·2 mm. pressure. At higher pressures the type of afterglow changes, until at about 1 mm. and up to 2 mm. (in air) only the continuous after-glow spectrum of oxygen is observed. A. A. ELDRIDGE.

Nitrogen after-glow. S. P. McCALLUM and W. E. PERRY (Nature, 1928, **121**, 942).—A nitrogen after-glow appears when a discharge is passed through a mixture of air and argon at low pressures; the relative proportions of the mixture may be varied over a fairly wide range. Mixtures of neon and helium are ineffective. A. A. ELDRIDGE.

Action of "active nitrogen" on iodine vapour. L. H. EASON and R. W. ARMOUR (Proc. Roy. Soc. Edin., 1928, **48**, 1—9).—The spectrum of iodine excited by active nitrogen was investigated and, in addition to the iodine line at 206 $\mu\mu$, a line at 185 $\mu\mu$ was found. In order to dissociate the iodine and raise the atom to the level of electronic energy required to emit this line, a total of 189,000 g.-cal., or 8·4 volts, is necessary. There must therefore be some form of nitrogen present capable of supplying the energy. The high energy level can be accounted for on the view that the glow is produced by the combination of atoms of nitrogen. An experiment was conducted to find what pressure of iodine vapour was required to increase the velocity of "reaction" between the iodine and the nitrogen so that simple decay could be neglected. It is concluded from the fact that the pressure of iodine required to produce practically nothing but iodine glow is of the order of 1/15th part of the active nitrogen present, and that the glow is practically instantaneous, that chemical action is very unlikely, and that the iodine receives energy and radiates it over and over again. The view is confirmed by the fact that even with pressures of iodine 1/1250th part of the partial pressure of active nitrogen, there is still a decided photographic effect due to the iodine. By attempting to measure the duration of the glow by means of a kinematographic camera it was found that when the pressures of iodine vapour and of active nitrogen were of the same order the glow did not last for more than 0·01 sec. A. J. MEE.

Chemical at. wt. determination and true at. wt. G. KIRSCH (Naturwiss., 1928, **16**, 334—335).—A discussion of the discrepancy between the chemically determined at. wt. of radium-G and that deduced from the disintegration series and of the difficulty of reconciling these with the at. wts. of lead found by Aston. J. W. SMITH.

At. wt. of actinium-lead, the last member of the actinium series. F. LOTZE (Z. anorg. Chem., 1928, **170**, 213—221).—The published at. wt. determinations with lead of purely radioactive origin, and therefore consisting of radium-G, thorium-D, and actinium-D, have been examined. Calculating the amounts of thorium-D and radium-G from the proportions of thorium and uranium, respectively, in the original minerals, the mean value of 207 is obtained for the at. wt. of actinium-D. R. CUTHILL.

Separation of isotopes of potassium. G. VON HEVESY and M. LÖGSTRUP (Z. anorg. Chem., 1928, **171**, 1—13).—By subjecting potassium to the process of ideal distillation (cf. A., 1922, ii, 149), a residue was obtained having at. wt. 39·109, corresponding with an increase of 4·8% in the proportion of the isotope K^{41}. As the radioactivity increased at the same time by 4·2%, it is concluded that this isotope is probably responsible for the radioactivity of potassium. R. CUTHILL.

Determination of isotopes by spectral lines. E. K. PLYLER (J. Elisha Mitchell Sci. Soc., 1927, **43**, 24).—The band spectra of sulphates of isotopes are multiple. Nickel, potassium, and magnesium contain, respectively, 2, 2, and 3 isotopes. CHEMICAL ABSTRACTS.

Purification of radon. L. WERTENSTEIN (Phil. Mag., 1928, [vii], **5**, 1017—1027).—An all-glass apparatus in which radon preparations of high purity may be made is described. Purification is effected by the usual reagents, copper oxide, copper, potassium hydroxide, and phosphoric anhydride, and condensing the gas by liquid air. Pressures are measured by means of a calibrated Knudsen gauge. Evacuation is effected by a mercury diffusion pump, and in order to avoid contamination with hydrocarbons from tap grease a mercury seal is employed to isolate the apparatus from the pump. Considerable difficulty was encountered in removing the last traces of carbon dioxide. It is concluded that carbon dioxide is the only gas left as an impurity. In general quantities of radon of the order of 50—100 millicuries can be concentrated by this method so that they contain only 20—50% of carbon dioxide. A. E. MITCHELL.

Ranges of the α-particles of uranium I and II. G. C. LAURENCE (Phil. Mag., 1928, [vii], **5**, 1027—1038).—A more detailed account, based on a greater number of observations, of previous work (this vol., 4) is given. The ranges of the α-particles from uranium I and uranium II were found to be respectively 2·73 and 3·28 cm., at 150° and 760 mm. These results are in close agreement with the preliminary determinations and the probable error is less than 1%. The decay constant of uranium II calculated from the above figure is $1·7 \times 10^{-12}$ sec.$^{-1}$, equivalent to a half-life period of 13,000 years. A. E. MITCHELL.

Formation of a gaseous helide of radium active deposit. D. M. MORRISON (Proc. Camb. Phil. Soc., 1928, **24**, 268—275).—On the assumption that the helium atom can exist in hydrogen-like form, in which one electron is relatively far from the nucleus, the formation of compounds corresponding with hydrides may be expected. Helium was passed over

radium active deposit in a high-frequency discharge tube and the formation of a gaseous compound detected by counting scintillations in a bulb containing a zinc sulphide screen. The effect is attributed to the formation of a radioactive helide, and not to radium emanation or impurities in the gas.

C. J. SMITHELLS.

Passage of electrons through hydrogen at low pressures. H. JONES and R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1928, 1, 239—241).—Electrons from a tungsten filament were passed through 2 cm. of hydrogen at 0·01—0·02 mm. After passing through the gas, the electrons were accelerated and a magnetic spectrum was formed. Electrons suffering inelastic collision produce radiation corresponding with a loss of 12·2 and 9·1 volts. The interpretation of these results is discussed. W. E. DOWNEY.

Passage of electrons through slits. R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1928, 1, 242—245).—Using the technique previously described (cf. preceding abstract) and an oxide-coated filament, lines were obtained at 3·9, 9·6, 11·4, 19·8, 22·6, 26·4, 32·3, 38·7, and 45·0 volts loss. When pure platinum was used as emitter, the spectrum was much simpler, giving lines only at 4·0 and 7·5 volts loss. Various possible causes of these " lines " are discussed.

W. E. DOWNEY.

Scission of hydrogen molecules by electronic collision, and chemical detection of the atoms produced. K. E. DORSCH and H. KALLMANN (Naturwiss., 1927, 15, 788—789; Chem. Zentr., 1928, i, 154—155).—The formation of atoms by electronic collision in hydrogen takes place directly, and (above the ionisation potential) indirectly, thus : $H_2^+ + H_2 = H_3^+ + H$. The atoms are detected by the reduction of lead chloride to lead. A. A. ELDRIDGE.

Saha theory and the conductivity of flames containing alkali metal vapours. H. A. WILSON (Proc. Roy. Soc., 1928, A, 119, 1—11).—Theoretical. The expression for the equilibrium constant of the reaction $M = M^+ + e$ (where M is an atom of an alkali metal and e an electron) in terms of quantities which can be measured is independent of the fraction f of the salt reduced to metal in the flame and of the fraction q of the negative ions which are free electrons in the flame. The calculation of the equilibrium constants by Noyes and the author (A., 1923, i, 112) is therefore unaffected, even if the fractions f and q are not equal to unity as assumed. There are strong reasons for believing that in flames at about 2000° Abs. the fractions f and q are constants independent of the concentration of the solution sprayed into the flame, and it is probable that at this temperature f and q are both nearly equal to unity. The relative conductivities of the alkali metals in flames at about 2000° Abs., as found by different observers, are tabulated, and are found to be in rough agreement with Saha's theory of the ionisation of metallic vapours at high temperatures. Zachmann's values for the relative conductivities of sodium and lithium are probably erroneous. L. L. BIRCUMSHAW.

Activation of hydrogen by electric discharge. G. A. ELLIOTT (Nature, 1928, 121, 985).—A brief discussion. A. A. ELDRIDGE.

Particles of high velocity in the chromosphere. R. W. GURNEY (Month. Not. Roy. Astron. Soc., 1928, 88, 377—379).—A discussion of the kinetics of the rapidly moving particles in the chromosphere.

J. W. SMITH.

The Debye–Hückel theory and stellar atmospheres. J. A. GAUNT (Month. Not. Roy. Astron. Soc., 1928, 88, 369—377).—Mathematical. Whilst showing some indications in favour of the Debye–Hückel theory, the reasoning developed is claimed to indicate that statistical mechanics provides no firm basis for the use of Boltzmann's theorem on an atomic scale. A summary is also given of an abortive attempt to distinguish between bound and free electrons in the manner suggested by Eddington.

J. W. SMITH.

Statistical interpretation of quantum mechanics. A. E. RUARK (Proc. Nat. Acad. Sci., 1928, 14, 328—330).—An experiment is suggested to decide between the views of Born and of Darwin on the meaning to be attached to the probability functions occurring in wave mechanics. A. J. MEE.

Theory of Hartree's atomic fields. J. A. GAUNT (Proc. Camb. Phil. Soc., 1928, 24, 328—342).—Mathematical. The expressions for the total energy of the atom are theoretically more sound than those for the separate X-ray terms, although of less practical value. Hartree's wave-functions (this vol., 216) are shown to be good approximations. R. A. MORTON.

Rotation of the nitrogen nucleus. R. DE L. KRONIG (Naturwiss., 1928, 16, 335).—A discussion of the kinetics of the nitrogen atom. J. W. SMITH.

Statistical deduction of the properties of the elements. E. FERMI (Atti R. Accad. Lincei, 1928, [vi], 7, 342—346).—From a statistical analysis of the electrons surrounding the nucleus considered as a completely degenerated gas, the general characteristics and some of the anomalies of the periodic classification of the elements can be predicted.

R. W. LUNT.

Rutherford satellite theory. G. SENTILE (Atti R. Accad. Lincei, 1928, [vi], 7, 346—349).—Arguments are advanced to show that nuclear systems discussed in Rutherford's theory are unstable and that the theory is therefore invalidated.

R. W. LUNT.

Atomic constants and the properties of matter. M. BORN (Z. physikal. Chem. Unterr., 1927, 40, 241—252; Chem. Zentr., 1928, i, 285).—A discussion. A. A. ELDRIDGE.

Ultra-violet absorption spectrum of cod-liver oil. J. W. WOODROW (Phil. Mag., 1928, [vii], 5, 944).—Using a photo-electric spectrophotometer, three ultra-violet bands have been found in cod-liver oil. The maxima of these bands occur at 2700, 2800, and 2900 Å. These bands coincide with those of ergosterol as determined by Heilbron and others (A., 1927, 381; this vol., 92). W. E. DOWNEY.

New radiation. C. V. RAMAN (Indian J. Physics, 1928, 2, 387—398).—A new type of fluorescence has been observed which appears to be universal, since about eighty different liquids which were examined all showed the effect. It differs from ordinary fluor-

escence, being of an entirely different order of intensity and requiring a very powerful incident beam of light to make it visible. It is also polarised almost to the same extent as ordinary scattered light, whereas ordinary fluorescence is usually unpolarised. The new radiation, in fact, appears to occupy a position between scattering and fluorescence. Spectroscopic examination shows that each line in the incident spectrum gives rise to at least two lines in the scattered spectrum, one in the original or unmodified position, and a second in a position of longer wave-length, thus showing a striking analogy with the Compton effect in the X-ray region. There is a marked similarity between the spectra obtained with different liquids. When the wave-length 4358 Å. only was used, most liquids showed, in the spectrum of the scattered light, a bright line in the neighbourhood of 5000 Å., the position of which was practically the same for chemically similar liquids such as pentane, hexane, and octane. There was, however, a recognisable difference in the position of the modified line when other liquids, such as benzene or water, were used. In many liquids the scattered spectrum shows, in addition to sharp lines, a continuous spectrum which is less markedly polarised than the former. The origin of the radiation is discussed, and whether it is an exclusively molecular effect or is related in any way to thermodynamics. The effect has also been observed with gases and vapours and with solids such as crystal ice and optical glass. Some experiments with carbon dioxide vapour, and with mixtures of carbon disulphide and methyl alcohol, indicate that the modified scattered radiations from the different molecules are not incoherent with one another. M. S. BURR.

Near infra-red absorption bands of some hydrocarbons. J. BARNES and W. H. FULWEILER (J. Amer. Chem. Soc., 1928, 50, 1033—1035).—The two strongest absorption bands of pentane, decane, and tetradecane exhibit doublets, the frequency difference at 0.92μ being 7×10^{12} sec.$^{-1}$ and that at 0.75μ, 8×10^{12} sec.$^{-1}$ Weak single bands at 0.81μ and 0.97μ were also observed. The 0.874μ band of benzene and the 0.877μ band of toluene are also doublets with a frequency difference of 3×10^{12} sec.$^{-1}$ S. K. TWEEDY.

Beats produced when rotating and vibrating anisotropic molecules diffuse visible or ultra-violet light. J. CABANNES (Compt. rend., 1928, 186, 1201—1202).—The new radiations discovered by Raman (this vol., 101, 348) may be considered as optical beats due to the variation of the amplitude of vibration of an optically anisotropic molecule owing to its rotation, or to the harmonic vibration of one of its atoms. This involves a displacement towards the violet of the rays of the diffusion spectrum produced from the fluid by means of monochromatic light (cf. Rocard, this vol., 571). J. GRANT.

"Phosphorescing" liquid. S. VAVILOV and V. LEVSCHIN (Naturwiss., 1927, 15, 899—900; Chem. Zentr., 1928, i, 161).—The luminosity of a solution of uranyl sulphate in sulphuric acid continues for 10^{-5} to 10^{-4} sec. after illumination, and fades approximately exponentially. Rise of temperature, addition of water, or increase of concentration shortens the duration of luminosity. A. A. ELDRIDGE.

Sulphide phosphors. I. SCHAPER (Ann. Physik, 1928, [iv], 85, 913—952).—The methods of the Lenard school have been applied to antimony phosphors and to magnesium sulphide phosphors. Calcium sulphide–antimony phosphors show three principal emission bands; the emission is green at the ordinary temperature with a maximum at 530 μμ (α) in some phosphors and 510 μμ (δ) in others. A lavender-blue emission in the region 420—510 μμ, with a maximum at 450 μμ (β), occurs on heating. With some phosphors an orange emission γ occurs at 580—650 μμ, maximum 600 μμ, at the temperature of liquid air. Comparison of bismuth and antimony phosphors indicates close resemblances; e.g., the γ band is shown well at $-180°$ in both cases and the maxima are at 595 and 600 μμ, respectively. The β bands are both obtained between 200° and 400°, but the maxima are at 522 μμ for bismuth and at 465 μμ for antimony. The α and δ bands occur best at 20°, and the wave-lengths are 470, 450, 443 for bismuth and 530, 510 for antimony. Similar temperature effects are shown with strontium sulphide–antimony phosphors; the maxima are as follows, bismuth data being in brackets : α 555 [520], δ 535 [420], β 480 [535], γ 620 [630] μμ.

The phosphorescence in magnesium sulphide has been investigated for the following metals, the figures in brackets indicating the wave-lengths in μμ of the principal bands : bismuth [443], antimony [531], manganese [665], copper [535], silver [460], lead [530]. The samarium, praseodymium, and neodymium phosphors have also been studied. Comparison shows that the wave-lengths of the maxima of corresponding bands with a heavy metal phosphor increase as a rule in the order magnesium, calcium, and strontium sulphides as the basis of the phosphor. The dielectric constant of a phosphor depends to a marked extent on the temperature at which the preparation is carried out.

A number of contributions to the analysis of the different phosphorescence processes have also been made. R. A. MORTON.

Oscillation quantum of the mercury molecule. H. KUHN (Naturwiss., 1928, 16, 352—353).—Rayleigh (A., 1927, 1122) has recorded a series of symmetrical emission bands for mercury in the region 2350—2290 Å., merging into a continuous spectrum stopping at 2270 Å. Superposed on the band structure is a much finer structure with a small initial spacing of about 20 cm.$^{-1}$ It is suggested that the small spacing corresponds with the oscillation quantum of the normal molecule, whilst the larger period represents the oscillation quantum of the excited molecule. R. A. MORTON.

Swan band spectrum of carbon. W. E. PRETTY (Proc. Physical Soc., 1928, 40, 71—78).—The Swan band spectrum was obtained in carbon monoxide and in the carbon spark in the absence of hydrogen. A discussion of the results of experiment and theory leads to the conclusion that the emitter of the Swan band system is the molecule of carbon C_2. This conclusion has been reached independently by Shea (this vol., 104). C. J. SMITHELLS.

Extinction coefficient of mixtures of ferric chloride and organic acids in the ultra-violet as experimental evidence in favour of the formation of unstable intermediate compounds. II. J. C. GHOSH and B. N. MITRA (J. Indian Chem. Soc., 1928, **5**, 191—202).—The rise in the extinction coefficient when ferric chloride is mixed with various organic acids, which it oxidises in the presence of light, has been determined in the way previously described for uranyl salts (this vol., 14). The results may be explained by supposing that there is an equilibrium in solution between ferric chloride and acid as reactants and an intermediate complex formed by the loose combination of one molecule of each of the reactants, and by assuming a definite value of the molecular extinction coefficient, for each wave-length, for the intermediate complex so formed. The following acids have been studied : formic, acetic, propionic, oxalic, malonic, succinic, glycollic, lactic, tartaric, citric, and mandelic. The value of K, the dissociation constant of the intermediate complex, is approximately double that of the corresponding uranyl salt complex (*loc. cit.*). The values of the molecular extinction coefficients of the intermediate compounds are also correspondingly greater. Certain regularities were observed between the values of K and the constitution of the acids ; *e.g.*, K diminishes with each addition of CH_2 and increases as the hydrogen atom of a methyl group is replaced by carboxyl, or when it is replaced by a hydroxyl group. M. S. BURR.

Fluorescence spectrum of sodium vapour in the vicinity of the D lines. R. W. WOOD and E. L. KINSEY (Physical Rev., 1928, [ii], **31**, 793—799).—Radiation of wave-length 5100—5250 Å. excites the D lines in sodium vapour mixed with hydrogen, air, or nitrogen at 2—3 mm. Apparently excitation of the molecule first occurs, followed by collisions of the second kind with atoms or by dissociation into a normal and an excited atom. The conditions governing the appearance of a fluorescence band group previously studied (Wood and Galt, Astrophys. J., 1911, **33**, 72) were investigated. A. A. ELDRIDGE.

Quenching of mercury resonance radiation by foreign gases. M. W. ZEMANSKY (Physical Rev., 1928, [ii], **31**, 812—821).—A relation between the quenching and the number of impacts of the second kind per sec. per c.c. is obtained for all foreign gases on the basis of Milne's theory of the diffusion of imprisoned resonance radiation, it being assumed that the number of impacts of the second kind per sec. per c.c. is proportional to the number of excited mercury atoms per c.c. The reaction velocity near the incident face of the absorption cell is proportional to the 0·6 power of the pressure, a result which suggests that the dissociation of the foreign gas is catalysed by adsorbed metastable mercury atoms. A. A. ELDRIDGE.

Luminescence excited by X-rays in colloidal alkaline-earth salts. C. H. BOISSEVAIN and W. F. DREA (Physical Rev., 1928, [ii], **31**, 851—857).—Gelatinous calcium, strontium, or barium fluoride precipitated in presence of excess of metal ions, but not of fluoride ions, is luminescent in X-rays, particularly after the precipitate has been heated to redness. By washing with dilute alkali solution the positively-charged colloids are converted into negative colloids and cease to exhibit luminescence. When precipitated in presence of excess of tungstate ions, calcium or barium tungstate (negative colloid) exhibits similar luminescence. The presence of impurities diminishes the luminescence. It is suggested that the luminescence is due to a thin layer of metallic oxide formed from the double layer of ions which is adsorbed on the surface of the colloidal particles. A. A. ELDRIDGE.

Infra-red reflexion spectra of sodium chlorate and sodium bromate. G. LASKI (Z. Krist., 1927, **65**, 607—614 ; Chem. Zentr., 1928, i, 8).—The characteristic frequency is $25\,\mu$ for sodium chlorate and $23\,\mu$ for sodium bromate ; both substances exhibit absorption between 40 and $120\,\mu$, with a maximum at $83\,\mu$ and $82\,\mu$, respectively. A triangular configuration is postulated for the chlorate and bromate radicals. A. A. ELDRIDGE.

Observed relative intensities of Stark components of H_a. J. S. FOSTER and (MISS) M. L. CHALK (Nature, 1928, **121**, 830—831).—The discrepancy between Schrödinger's calculated and Stark's observed intensities for the parallel components of H_a is apparently due merely to experimental error. A. A. ELDRIDGE.

Infra-red emission of carbon dioxide. C. R. BAILEY and K. H. LIH (Nature, 1928, **121**, 941).—Analysis of the emission spectrum of burning carbon monoxide shows that most of the carbon dioxide bands have shifted towards the longer wave-lengths, and so become exact multiples of a frequency, $\nu = 16 \times 10^{11}$, in the far infra-red. A. A. ELDRIDGE.

Pure rotation spectrum of ammonia. R. M. BADGER (Nature, 1928, **121**, 942).—The absorption spectrum of gaseous ammonia between 55 and $130\,\mu$ is unexpectedly simple ; six lines approximately equally spaced in the frequency scale are represented by the equation $1/\lambda_m = 19{\cdot}957m - 0{\cdot}00508m.^3$ The molecule is relatively elastic and stretches considerably in higher rotational states. A. A. ELDRIDGE.

Absorption spectra of silver bromide and silver chloride films. J. EGGERT and R. SCHMIDT (Z. Physik, 1928, **48**, 541—544).—The absorption spectra of thin sheets of microcrystalline silver bromide and silver chloride have been investigated photographically. The converging frequencies in the long-wave region were found to be $480\,\mu\mu$ for silver bromide and $400\,\mu\mu$ for silver chloride. The amount of silver liberated from the bromide under the action of the light (10^{-5} to 10^{-3} per mille) caused no perceptible change in the absorption spectrum. J. W. SMITH.

Molecular spectrum of sulphur. B. ROSEN (Z. Physik, 1928, **48**, 545—555).—In continuation of work previously recorded (A., 1927, 608) the absorption and emission bands of the S_2 molecule in the blue-violet and ultra-violet regions have been examined. These were in agreement with the formula previously deduced. J. W. SMITH.

Homopolarity of the hydrogen halides. V. KONDRATJEW (Z. Physik, 1928, **48**, 583—585).—The probability that hydrogen iodide, on absorption of light of a suitable wave-length, yields a hydrogen atom and an excited iodine atom (cf. Franck and Kuhn, A., 1927, 711) is held to indicate that hydrogen iodide is a homopolar molecule. In the cases of hydrogen chloride and hydrogen bromide, the dissociation energies calculated from the infra-red vibration spectra according to the method of Franck and Kuhn are shown to be in good agreement with the values obtained from thermochemical data. Hence it is concluded that the molecules of all the hydrogen halides are homopolar in character. J. W. SMITH.

Limit of photoelectric sensitivity of ammonium amalgams in the long wave-length region. SANDER and NITSCHE (Z. Elektrochem., 1928, **34**, 244—246).—The photoelectric sensitivity limit of ammonium amalgam lies at a lower wave-length than those of potassium and sodium, the order being ammonium, sodium, potassium. H. F. GILLBE.

Dielectric constant of benzil. L. SAINT-ANTOINE (Compt. rend., 1928, **186**, 1429—1431).—For solutions of benzil in benzene, ε increases almost proportionally with the concentration, but decreases with a rise in temperature. For molten benzil (m. p. 94°) it varies from 13·04 at 95° to 12·12 at 120°. It was measured with an accuracy of 3—4% from the change in wave-length produced when a cylindrical air-condenser was immersed in the liquid concerned, the resonance between a resonator and an oscillator being determined from the wave-lengths of the oscillations of the latter when its frequency was varied (cf. De Mallemann, A., 1927, 1130).
J. GRANT.

Change of the dielectric constant of liquid helium with temperature. Provisional measurements. M. WOLFKE and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 81—89).—A compensation method for determining the dielectric constant of liquid helium is described. Two series of provisional measurements have been made between 1·80° and 4·21° Abs. and, in each case, a discontinuity was observed, which may be related to the discontinuities noted in other physical properties between these temperatures. The possibility of experimental error is not, however, excluded.
M. S. BURR.

Disappearance and reversal of the Kerr effect. C. V. RAMAN and S. C. SIRKAR (Nature, 1928, **121**, 794).—Observations on the Kerr effect with octyl alcohol confirm Raman and Krishnan's theory of electric birefringence in liquids (cf. A., 1927, 397).
A. A. ELDRIDGE.

Spectrochemical observations on azo-compounds. K. VON AUWERS and P. HEIMKE (Ber., 1928, **61**, [*B*], 1030—1036).—Observations on methyl and ethyl azo*iso*butyrate give the value $D=3\cdot179$ for the unconjugated –N:N– group, which is in good agreement with the datum $D=3\cdot266$ deduced by Lochte, Noyes, and Bailey (A., 1922, i, 329) from experiments on azo*iso*propane. Observations on purely aromatic azo-compounds are hampered by the difficulty of obtaining homogeneous products by reduction of nitro-compounds in alkaline solution since these usually contain varying amounts of azoxy-substances; homogeneous azo-derivatives are obtained by treating pure hydrazo-compounds with the necessary amount of bromine. The colour of the substances usually inhibits measurement except with the H_a and sometimes the yellow He line. In cases where the high m. p. of the compound necessitates the use of a solvent, quinoline is found very serviceable. The specific exaltations for azobenzene and its homologues are grouped closely round the mean value +3·05. This high value is due to the structure of the substances, since the value of EE_D^{20} for the analogously constituted m-methylstilbene is +3·1; the twice-broken, treble conjugations C:CR·C:C·CR:C and C:CR·N:N·CR:C are therefore spectroscopically equivalent. Entry of a hydroxyl or an alkoxyl group into the azobenzene molecule invariably increases these exaltations, but the action of the groups is unequally strong and depends on their position. The following data, amongst others, are recorded for the homogeneous substances : methyl azo*iso*butyrate, $d_4^{17\cdot3}$ 1·0365, $n_a^{17\cdot3}$ 1·43335; ethyl azo*iso*butyrate, $d_4^{18\cdot9}$ 0·9932, $n_a^{18\cdot9}$ 1·42831; phenylazoethane, $d_4^{21\cdot9}$ 0·9628, $n_a^{21\cdot9}$ 1·53133; azobenzene, $d_4^{78\cdot1}$ 1·0362, $n_a^{78\cdot1}$ 1·62662; m-methylazobenzene, $d_4^{17\cdot6}$ 1·0658, $n_a^{17\cdot6}$ 1·64822; oo'-dimethylazobenzene, $d_4^{65\cdot3}$ 1·0215, $n_a^{65\cdot3}$ 1·61804; mm'-dimethylazobenzene, $d_4^{66\cdot2}$ 1·0123, $n_a^{66\cdot2}$ 1·61519; o-methoxyazobenzene, d_4^{100} 1·0728, n_a^{100} 1·62652; p-ethoxyazobenzene, $d_4^{99\cdot6}$ 1·0400, $n_a^{99\cdot6}$ 1·62355; benzeneazothymol, $d_4^{100\cdot2}$ 1·0328, $n_a^{100\cdot3}$ 1·63169; benzeneazothymol ethyl ether, d_4^{100} 0·9791, n_a^{100} 1·59345; n-propyl p-hydroxybenzoate, $d_4^{102\cdot1}$ 1·0630, $n_a^{102\cdot1}$ 1·50503; n-propyl anisate, d_4^{100} 1·0054, n_a^{100} 1·47977. Measurements are also recorded for certain of the compounds dissolved in quinoline, absolute alcohol, or propyl butyrate. The *ethyl ether* of *benzeneazothymol*, m. p. 85°, has not been described previously. H. WREN.

Spectrochemistry and constitution of azoxy-compounds. K. VON AUWERS and P. HEIMKE (Ber., 1928, **61**, [*B*], 1037—1041).—Homogeneous azoxy-compounds are most readily prepared by oxidising azo-compounds with hydrogen peroxide. The following data, amongst others, are recorded for the homogeneous substances : azoxybenzene, d_4^{26} 1·1590, n_a^{26} 1·65103; oo'-azoxytoluene, $d_4^{99\cdot9}$ 1·0548, $n_a^{99\cdot9}$ 1·57686; mm'-azoxytoluene, $d_4^{21\cdot6}$ 1·1136, $n_a^{21\cdot6}$ 1·63345; α-p-bromoazoxybenzene, $d_4^{99\cdot9}$ 1·4068, $n_a^{99\cdot9}$ 1·64967; β-p-bromoazoxybenzene, d_4^{100} 1·4138, n_a^{100} 1·64497; α-p-ethoxyazoxybenzene, $d_4^{99\cdot7}$ 1·1082, $n_a^{99\cdot7}$ 1·62363; β-p-ethoxyazoxybenzene, $d_4^{100\cdot1}$ 1·1068, $n_a^{100\cdot1}$ 1·61348; p-ethoxyhydrazobenzene, $d_4^{100\cdot5}$ 1·0556, $n_a^{100\cdot5}$ 1·57491; p-phenetidine, $d_4^{15\cdot9}$ 1·0652, $n_a^{15\cdot9}$ 1·55715. Observations for certain compounds in quinoline are also given. The data strongly support the constitution assigned to azoxy-compounds by Angeli. The behaviour of oo'-azoxytoluene is, however, exceptional and may possibly indicate the presence of a three-membered ring. H. WREN.

Valency and refraction equivalents. K. VON AUWERS (Ber., 1928, **61**, [*B*], 1041—1049; cf. Strecker and Spitaler, A., 1926, 1082).—Any change in the spectroscopic constants of a substance cannot

be attributed solely to a single component of the molecule, but is due to the sum of the actions exercised by two atoms combined with one another. From this point of view the molecular refractions of a series of azo- and azoxy-compounds are compared, thus leading to the conclusion that the atomic refraction of quinquevalent nitrogen is lower than that of tervalent nitrogen, since the entering oxygen atom never increases the molecular refraction of the compound to the extent expected from doubly-bound oxygen. On the other hand, great exaltation of the molecular refraction is observed when an oxygen atom is added to a benzylideneamine or an oxime O-ether; the increase is in all cases greater than the atomic refraction of carbonyl oxygen, particularly so with mixed aliphatic aromatic substances. Spectroscopic data support the constitutions $\begin{smallmatrix} CMe \cdot CMe \\ \| \quad \| \\ N \cdot O \cdot N \vdots O \end{smallmatrix}$ and $CPh \vdots N \vdots O$ for dimethylfurazan and benzonitrile oxide, respectively. Diminution in the atomic refraction of carbon with increasing valency is shown by comparison of ethyl carbonate and carbon monoxide diethylacetal (cf. Scheibler, A., 1926, 711). Less striking results are obtained by comparison of carbylamines and carbimides, thus supporting the view that the terminal carbon atom of the former is not pronouncedly bi- or quadri-valent and that therefore the effect of the entering oxygen atom is only partly balanced by the change in character of the carbon atom. With carbylamines and thiocarbimides the increase in molecular refraction corresponds approximately with the refraction equivalent for S''; conclusions with regard to dispersion cannot be reached.

The following data, amongst others, are recorded : o-chlorobenzylideneaniline, $d_4^{14 \cdot 6}$ 1·1857, $n_{He}^{14 \cdot 6}$ 1·65689; benzonitrile, $d_4^{11 \cdot 8}$ 1·0109, $n_{He}^{11 \cdot 6}$ 1·53258; methylcarbimide, $d_4^{14 \cdot 9}$ 0·9744, $n_{He}^{14 \cdot 9}$ 1·37400; ethylcarbimide, $d_4^{15 \cdot 7}$ 0·9065, $n_{He}^{5 \cdot 7}$ 1·38262; phenylcarbimide, $d_4^{11 \cdot 6}$ 1·1010, $n_{He}^{11 \cdot 6}$ 1·54032; phenylthiocarbimide, $d_4^{20 \cdot 3}$ 1·1303, $n_{He}^{20 \cdot 3}$ 1·64974; benzonitrile oxide, $d_4^{12 \cdot 2}$ 1·2190, $n_{He}^{12 \cdot 2}$ 1·59687. H. WREN.

Magnetism and the structure of some simple and complex molecules. D. M. BOSE (Phil. Mag., 1928, [vii], 5, 1048—1067).—The author's modification (A., 1927, 805) of Hund's theory of paramagnetism has been employed for the calculation of the magnetic moments of molecules containing elements of the first transition group. Up to manganese the agreement between calculated and observed values is good, but the simple salts of the ferromagnetic elements give values considerably in excess of those predicted, the deviation being apparently associated with the addition of the sixth, seventh, and eighth electrons to the M_3 shell of the central atom. In certain fourfold co-ordination compounds the predicted magnetic moments are in close agreement with observed values, and it is concluded that in these compounds the valency shell of eight electrons contributed by the four atomic groups forms an octet shell outside the core of the central atom. In sixfold co-ordination compounds it is concluded that if there are vacancies in the M_3 shell of the central atom for four electrons, then four of the twelve shared electrons occupy this shell, whilst the remaining eight

form an octet shell round the core, and if the M_3 shell cannot accommodate all four electrons these move in orbits outside the octet shell. It is shown that the co-ordination linkings contributed by the atomic groups usually found in co-ordination compounds can be accounted for satisfactorily on the new theory. A. E. MITCHELL.

Electronic theory of valency. V. Molecular structure of strong and weak electrolytes : (a) **Complete ionisation.** T. M. LOWRY (Phil. Mag., 1928, [vii], 5, 1072—1080).—From the electronic theory of valency previously developed (A., 1923, ii, 480, 848; A., 1925, ii, 15) it follows that compounds in which neutralisation of the ionic charges is prevented by the laws of valency generally behave as strong electrolytes in solution, whilst if a salt is dissolved in a medium of low dielectric constant the resulting solution will have a low conductivity and abnormal variations of conductivity with dilution are to be expected. It is suggested that the high conductivity of some fused salts is a result of the formation of multi-charged ionic aggregates, whilst the low conductivity of others is attributed to the breaking down of the crystal lattice into neutral doublets on fusion. On the theory of complete ionisation the term hydrolysis can have no significance unless the hydrogen or hydroxyl ion of water can be fixed by one of the ions of the salt with formation of a covalent compound. A. E. MITCHELL.

Electric moment and space-orientation of atoms in some *para*-derivatives of benzene. J. W. WILLIAMS (Physikal. Z., 1928, 29, 271—272).— The assumption that *para*-substituents lie in the plane of the benzene ring leads to the view that with equal substituents the symmetrical molecule should exhibit no electric moment. This expectation is fulfilled in the cases of p-xylene, p-dichlorobenzene, and p-dinitrobenzene, since the values for the electric moment are less than 0.3×10^{-18} (e.s.u.). For quinol diethyl ether and quinol diacetate the values are, however, 1·7 and 2.2×10^{-18}, respectively. This result indicates that the substituents need not necessarily lie in the plane of the benzene ring ; either the OR-groups may be bent away from the plane or the oxygen atoms may remain in the plane with the ethyl groups out of alinement. R. A. MORTON.

Dipole moment of symmetrical compounds, and *cis–trans*-isomerism at " single " linkings. A. WEISSBERGER (Physikal. Z., 1928, 29, 272—273).— The demonstration (A., 1927, 9) that compounds of the type $C(OR)_4$ exhibit a dipolar character and that the valencies of the carbon atom may be regarded as directed towards the corners of a tetragonal pyramid opens up the possibility of a new type of enantiomorphism. The existence of a considerable electric moment in certain compounds of the type $C_6H_4a_2$ (cf. preceding abstract) likewise makes possible a type of *cis–trans*-isomerism not involving double linkings. It is suggested that the yellow and colourless benzil derivatives studied by Schönberg and his co-workers (1922, *et seq.*) and hitherto regarded as $\alpha\beta$-diketones and isomeric peroxides may be enantiomorphs of this kind. R. A. MORTON.

The shared-electron chemical linking. L. PAULING (Proc. Nat. Acad. Sci., 1928, **14**, 359—362).—London's theory of the formation of valency linkings is equivalent in simple cases to G. N. Lewis' theory of the shared electron pair. A number of new results have been obtained in extending London's simple theory, taking into account quantitative spectral and thermochemical data. A sensitive test to determine whether a compound is polar or non-polar is put forward, and it is concluded that hydrogen fluoride is polar, whilst the chloride, bromide, and iodide are probably non-polar. If quantisation can be changed, as it can in the case of some elements in the first row of the periodic system where the interchange energy resulting from the formation of shared-electron linkings is large enough to bring it about, very stable shared-electron linkings are possible. Hence the stable shared-electron linkings of saturated carbon compounds, and the relatively stable double linkings of carbon. The tetrahedral arrangement of the four linkings of quadrivalent carbon can be shown to be the stable one as a result of the resonance phenomenon. A. J. MEE.

Electrostatic explanation of complex formation. A. E. VAN ARKEL and J. H. DE BOER (Rec. trav. chim., 1928, **47**, 593—605; cf. A., 1927, 189).—After a discussion of the application of Kossel's theory of the chemical linking as a purely electrostatic phenomenon (Ann. Physik, 1916, [iv], **49**, 229) made by numerous authors, the problem of complex formation is considered. Strong polarisation of the outer ions of a complex ion may be due to a small radius of the central atom which causes it, or also to a polarisation of this central atom itself. In the latter case the electrical field of ions which surround the central atom induces a dipole in the central atom which acts on the outer ions of the complex ion, thus strengthening the linking. A dipole can arise in the central atom only if the polarisability of this central atom is so great that an unsymmetrical arrangement of the outer ions results, as is the case with H_2O, NH_3, NH_4^+. The complexes formed by ammonia fall into two principal groups, (1) to which compounds obtainable only as solids belong, e.g., $[Na(NH_3)_6]I$, which loses ammonia completely on dissolution in water, and (2) the compounds in which, in aqueous solution, the ammonia is present in the cation, e.g., $[Co(NH_3)_6]Cl_3$. In group (1) the hydrates are more stable than the ammonia complexes, whilst in group (2) the relation is reversed. Since the electric dipole of the ammonia molecule is smaller than that of the water molecule and furthermore the radius is somewhat larger, the stronger union of water molecules is to be expected. The behaviour of compounds of group (2) may be explained by a deformation of the whole ammonia molecule. An increase in the dipole already present would result, so that as the deformability of the ammonia molecule is greater than that of the water molecule the increase in the dipole in the case of ammonia is greater than in that of water. In the case of non-polarisable central ions there is a definite distance between the central ion and water or ammonia molecule at which the energies of formation are equal. If in a given instance the distance is smaller than the critical value then the ammonia complex is the stable compound and, if greater, the hydrate. An approximate calculation of this critical distance is made.

H. INGLESON.

Electron theory of valency based on an extension of the Bohr–Stoner electron distribution in atoms. O. STUHLMAN, jun. (J. Elisha Mitchell Sci. Soc., 1927, **43**, 19).—Stoner's modification of the Bohr electron distribution in atoms is extended and co-ordinated with ionisation and critical potential data. Anion valency is attributed to the action of the completed doublet levels, and cation valency to the action of the external levels acting in conjunction with the incomplete paired levels.

CHEMICAL ABSTRACTS.

Hypothesis of valency deflexion. C. K. INGOLD and J. F. THORPE (J.C.S., 1928, 1318—1321).—A reply to the criticism of the Thorpe–Ingold hypothesis of valency deflexion made by Hückel (Fortschr. Chem., 1927, **19**, [4]). H. INGLESON.

Complex compounds. F. EPHRAIM (Helv. Chim. Acta, 1928, **11**, 431—436).—In order to account for the formation of complex compounds, an electrostatic field valency is postulated in addition to the ordinary electro- and co-valent linkings. The theory is developed on the basis of the octet model of the atom and is applied to the case of the constitution and isomerism of the metal ammines. F. J. WILKINS.

Law of molecular forces. A. W. PORTER (Trans. Faraday Soc., 1928, **24**, 108—111).—Theoretical. Difficulties in calculating intermolecular forces are discussed. L. F. GILBERT.

Molecular numbers. P. VINASSA (Gazzetta, 1928, **57**, 178—180).—It is held from an extended survey of compounds that the law of molecular numbers is valid for most chemical compounds naturally occurring and otherwise; the known exceptions to the law are tabulated. R. W. LUNT.

Spontaneous division of drops of microscopic dimensions. N. VON RASCHEVSKY (Z. Physik, 1928, **48**, 513—529).—A former theory (cf. this vol., 474) is extended to cases where diffusion processes and chemical changes occur in a drop, the rate of growth of which is very small. The conditions under which such a drop can split are deduced. The stability of polyphase drops is also discussed. J. W. SMITH.

Scattering of electrons by crystals. H. BETHE (Naturwiss., 1928, **16**, 333—334).—It is shown that the true analogues of the reflected electron beams observed by Davisson and Germer (A., 1927, 492) are the X-ray beams of next shorter wave-length, and not those of longer wave-length as suggested by them. J. W. SMITH.

Positions of X-ray spectra as formed by a diffraction grating. A. W. PORTER (Phil. Mag., 1928, [vii], **5**, 1067—1071).—It is pointed out that for accurate X-ray spectral measurements with diffraction gratings it is insufficient to apply the usual methods of ordinary spectroscopy applicable to Fraunhofer spectra, but that a factor, correcting for the lack of parallelism of the X-ray beam, must be applied to

wave-lengths determined in the ordinary way. For conditions of nearly grazing incidence this factor is shown to be $(1 + 3X^2/20l_0{}^2)$, where X is the length of the grating and l_0 is the shortest distance between the source and the grating. A. E. MITCHELL.

Apparent irregularities in experiments with heterogeneous X-ray beams, with special reference to the J-phenomenon. R. T. DUNBAR (Phil. Mag., 1928, [vii], **5**, 962—989).—Two experimental methods designed to observe the J-discontinuities in the absorption of scattered heterogeneous X-radiation failed to show any such discontinuities. It is thereby shown that the irregularities observed by Barkla are probably due to the assumption that a heterogeneous beam should give nearly the same results as a homogeneous beam, the latter having an absorption coefficient equal to the half-value absorption coefficient of the former. W. E. DOWNEY.

Diffraction of X-rays by means of line gratings. Spectrography of the intermediate region. J. THIBAUD (Physikal. Z., 1928, **29**, 241—261).—A full account is given of researches which have already been briefly reported (A., 1925, ii, 176; 1926, 333, 651; 1927, 286, 803). It is shown that tangential gratings with 200 lines per mm. permit the investigation of X-rays in air, and ultra-violet rays down to 140 Å. in a vacuum. A new type of vacuum spectrograph is described and data on the spark spectrum of copper are given. The gap between X-rays and the extreme ultra-violet has been bridged by the use of an improved vacuum spectrograph with a tangent grating ruled with 1180 lines per mm. Wave-lengths in the region 17·7—65·0 Å. together with their origins are given for various elements. The continuous spectrum and the K-absorption limit have been studied for carbon, nitrogen, and oxygen.

For wave-lengths near 17 Å. the line grating and the crystal lattice methods are in good accord, whilst at about 70 Å. a definite discrepancy arises, due, it is shown, to refraction of the rays by the material (fatty acid) composing the lattice. Oil-sensitised (non-Schumannised) plates record rays between 600 and 100 Å.

The lines of advance in this field are indicated.
R. A. MORTON.

Relation between chemical constitution and X-ray diffraction in liquids. I. Mono- and di-substituted benzene derivatives. P. KRISHNAMURTI (Indian J. Physics, 1928, **2**, 355—364; cf. Sogani, A., 1927, 924, 1129).—A number of o-, m-, and p-disubstituted benzene derivatives have been subjected to X-ray examination. The diffraction haloes for the o- and m-compounds have two distinct rings. In the o-compounds the outer ring increases in brightness as the sizes of the substituents are increased. In the corresponding m-compounds, however, the rings are smaller, but the outer ring increases in brightness relatively to the inner more than in the case of the o-compounds. Only one broad ring is obtained for p-compounds, and this diffuses outwards. Substitution in the first carbon group of the side-chain produces no interference effects tending to the formation of two rings. Benzene derivatives with a single long side-chain show a similarity to the corresponding aliphatic derivatives. Ethyl benzoate is similar to acetic acid, since both of them show a faint inner ring. M. S. BURR.

X-Ray diffraction in carbon tetrachloride (liquid). C. M. SOGANI (Indian J. Physics, 1928, **2**, 377—386).—The diffraction photographs of liquid carbon tetrachloride obtained with the Cu K_a rays have been studied. The pattern shows an inner ring which is sharper than for any other organic liquid hitherto examined and is explained by the nearly spherical form of the molecule. Separated from the inner ring by a clear space is a diffuse outer ring. There is, however, a fair amount of scattering at small angles which is to be ascribed to the compressibility of the liquid. The Bragg spacing, 5·3 Å., for the inner ring agrees well with the value of $(m/d)^{1/3}$, namely, 5·43 Å., where m is the mass of a molecule and d the density. The spacing for the outer halo is 2·9 Å. The presence of the second ring is discussed in relation to a similar phenomenon in the case of mercury and argon which are monatomic, and it is suggested that the second ring, which, in general, is considered to be due to a pronounced asymmetry of the molecule, is in this case merely a second order effect. A possible alternative explanation is that it may be due to the shape of the molecular F-curve. There is an analogy between the X-ray diffraction in liquids with spherical molecules and the diffraction of visible light by homogeneous chromatic emulsions. M. S. BURR.

Direct and indirect characteristic X-rays: their ratio as a function of cathode-ray energy. D. L. WEBSTER (Proc. Nat. Acad. Sci., 1928, **14**, 330—339).—The work of a previous paper (A., 1927, 803) on the ratio of direct rays to total indirect X-rays produced from any ordinary X-ray target is extended. The apparatus was reconstructed to obtain greater accuracy and the same method was used as in the previous work. The calculation was carried out in practically the same way as before, except that the assumption that all the primary continuous spectrum X-rays originate in the surface is replaced by the assumption that they originate at a depth equal to the average depth as measured by the absorption limit method. The value of the ratio of direct rays to total incident rays for silver is found to be almost constant, the data giving 1·83 at 35 kilovolts, and 1·96 at 80 kilovolts. The probable error is high, amounting to 10—20%. The variation of the ratio is not sufficient to vitiate current comparisons of observed line intensities with theories.
A. J. MEE.

X-Ray examination of saturated dicarboxylic acids and amides of the fatty acid series. E. HENDERSON (Proc. Roy. Soc. Edin., 1928, **48**, 20—27).—In continuation of former work (A., 1927, 612) several additional normal saturated dicarboxylic acids have been investigated by means of X-rays, the results being in agreement with the earlier work. In order to study the effect on crystal structure of expanding the molecule without altering the distance between the carboxyl groups, the mono- and di-alkylmalonic acids were investigated. The d_1 spacing increases by 1·0—1·3 Å. per CH_2 group added, and it

is concluded that this d_1 spacing is a measure of the length of the molecule, and that there is only one molecule between successive reflecting planes. The fact that in long-chain compounds having a "chemically active" terminal group, e.g., carboxyl, successive reflexion planes are separated by the length of two molecules oriented in opposite directions can be explained by assuming that the two molecules are held together by forces due to free partial valencies of the terminal group. In the case of the malonic acids the two carboxyl groups mutually saturate each other so that there is insufficient residual affinity to attract another molecule. This theory was tested by examining the fatty acid amides by means of X-rays, when it was found that successive reflexion planes were separated by the length of two molecules placed end to end and oppositely oriented. In the case of dialkylmalonic acids the angle between the alkyl groups diminishes as the series is ascended. The theory of Müller and Shearer regarding the nature of the chain structure of long-chain compounds is discussed, and it is shown that whilst this theory assumes that the tetrahedral angle of the carbon atom will be maintained throughout the chain, this cannot be so. The molecule will probably be spiral in form.

A. J. MEE.

Excitation of soft X-rays. II. O. W. RICHARDSON and F. C. CHALKLIN (Proc. Roy. Soc., 1928, A, **119**, 60—83; cf. ibid., 1926, A, **110**, 247).—The gap left between 130 and 200 volts in the investigation on iron is now filled up, and the range is extended from 600 to 720 volts. The apparatus has been improved and is capable of greater sensitiveness. Three discontinuities are observed between 600 and 720 volts, and eight between 130 and 200 volts. All the known observations of critical potentials of iron obtained by various observers are tabulated, and very satisfactory agreement is found between the different values. Rollefson's claim to have found a number of critical voltages of iron in the low-voltage region which follow a Rydberg series (cf. A., 1924, ii, 216) is discussed, and the existing data are critically examined. Thomas' values for iron, cobalt, nickel, and copper (cf. A., 1925, ii, 336; 1926, 1186) are used to determine A and b in the equation $V(n) = A - b/n^2$. The experimental evidence for the reality of the series is strong in the case of iron, cobalt, and nickel, but much less decisive in the case of copper. In a discussion of the theoretical interpretation of such a classification the difficulty raised by the high value of the constant b is emphasised. This is 2420 volts for iron and 2357 volts for cobalt and nickel, and corresponds with an attracting centre with about 13 times the electronic charge. This fact, and a large number of otherwise unco-ordinated facts, might be explained by assuming that in the case of iron, cobalt, and nickel, at any rate, it is possible for an electron to function as a series electron in relation to the structure bounded by the completed L shell without being profoundly affected by the surrounding electrons. In order to test whether the discontinuities under investigation are instrumental or are real properties of the materials, the emission from a carbon target as successive layers of tungsten are gradually deposited on it has been examined. The various deposited inflexions are not

equally interdependent, but can be classified in groups such that the members of each group appear and disappear, or strengthen and weaken, together independently of the other groups. Four groups of critical voltages were obtained, one group being due to tungsten, whilst the majority of the inflexions found must be attributed to contamination (possibly nickel). As a result of the present investigations, some of the critical potentials given in the former paper (loc. cit.), are reconsidered. In the case of carbon, the weak inflexion at 265·0 volts is probably due to tungsten, and the strong inflexion at 81·2 volts is due to an impurity which may be nickel.

L. L. BIRCUMSHAW.

Intensity of reflected X-rays and the distribution of electrons in crystals. G. E. M. JAUNCEY and W. D. CLAUS (Physical Rev., 1928, [ii], **31**, 717—727).—A reply to Havighurst's criticisms (this vol., 224). By trial a reasonable Bohr model of the chlorine ion has been found which gives modified F values at all angles in good agreement with the experimental values. The Fourier analysis method of unravelling atomic structure is still considered invalid.

A. A. ELDRIDGE.

K-Absorption edges of potassium and chlorine in various compounds. J. M. NUTTALL (Physical Rev., 1928, [ii], **31**, 742—747).—Experiments were performed with sylvine, orthoclase, lepidomelane, and phlogopite. The fine structure of the potassium edge extended from 3429 to 3365X, or over a range of about 67 volts, and that of chlorine from 4383 to 4341X, or about 27 volts. The view that the ejected electrons stop in an outer orbit appears inadequate to explain the complicated structure of the edges.

A. A. ELDRIDGE.

Physical purity and powder röntgenograms. N. H. KOLKMEIJER (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 151—154).—X-Ray powder spectrograms have been made of mixtures of the white and grey modifications of tin, in order to determine the extent to which the physical purity of a substance, or freedom from its enantiomorph, may be tested. The composition of the mixtures was previously determined by density measurements. The results show that, with a normal exposure, an admixture of as much as 10% of a second modification might be unnoticed. The bearing of this result on Levi's conclusion (A., 1924, ii, 860), that yellow and red mercuric oxide are crystallographically identical, is discussed.

M. S. BURR.

Scattering by free gratings and the statistical significance of the distribution of grating spectra on the interference of plane waves. A. WINTNER (Z. Physik, 1928, **48**, 495—512).—Mathematical.

J. W. SMITH.

X-Ray investigation of the structures of the oxides of iron. H. GROEBLER (Z. Physik, 1928, **48**, 567—570).—Ferric oxide was reduced to different stages by carbon monoxide at 800° and the X-ray spectra of the products were examined. It was shown that ferrosoferric oxide can contain only 5% of ferrous oxide in solid solution. Above this percentage the ferrous oxide forms a second solid phase. With 39% of ferrosoferric oxide present the magnetite

structure breaks down and until pure ferrous oxide is reached the crystal structure of the latter persists. The solubility of iron in ferrous oxide is only very slight. J. W. SMITH.

Is crystal reflexion of X-rays entirely a classical phenomenon? G. E. M. JAUNCEY and W. D. CLAUS (Nature, 1928, **121**, 983).

Influence of relative ionic sizes on the properties of ionic compounds. L. PAULING (J. Amer. Chem. Soc., 1928, **50**, 1036—1045).—Some of the results of a theory which expresses the interionic forces in a crystal in terms of the radii of the ions are considered. Many crystal properties depend both on the " radius sum," i.e., the distance between neighbouring ions, and also on the " radius ratio," i.e., on the relative sizes of the cation and the anion. The latter quantity accounts for many irregularities in the properties (e.g., m. p., b. p.) of the alkali halides formerly attributed to deformation phenomena, and is of significance in all crystal properties depending on the crystal energy. S. K. TWEEDY.

Production and absorption of the K-rays of aluminium. F. HOLWECK (Compt. rend., 1928, **186**, 1203—1205).—The absorption coefficients of rays produced from a water-cooled aluminium anode with an incandescent cathode in a highly evacuated metallic tube provided with an aluminium window are 550 and 7400 (approximately) for wave-lengths slightly greater and less than the K-discontinuity, respectively. This gives a value of about 13 for the ratio J, which is in agreement with that found (14) from the values obtained for the absorption in air at voltages above the critical potential using an aluminium filter 15 μ thick, and from the absorption coefficient of the soft rays of oxygen and nitrogen. J. GRANT.

Röntgenographic examination and eutropic relations of alkaline-earth fluorides. F. THILO (Z. Krist., 1927, **65**, 720—722; Chem. Zentr., 1928, i, 150).—The following values for calcium, strontium, and barium fluorides, respectively, are recorded : a (Å.) 5·45, 5·81, 6·20; $d_{calc.}$ 3·18, 4·24, 4·83; n 1·434, 1·438, 1·475; solubility (mg. in 1 litre of water at 18°) 16, 117, 1630. A. A. ELDRIDGE.

Structure of quartz. B. GOSSNER (Zentr. Min. Geol. Paläont., 1927, A, 329—338; Chem. Zentr., 1928, i, 152—153).—The unit cell, containing three molecules, of quartz has a 4·89, c 5·46 Å. The most probable atomic co-ordinates of β-quartz are : Si $(\frac{1}{2}, 0, 0)$, $(\bar{1}{2}, \bar{1}{2}, \frac{1}{3})$, $(0, \frac{1}{2}, \frac{2}{3})$; O $(v\ \bar{v}, \frac{5}{6})$, $(2\bar{v}, \bar{v}, \frac{1}{6})$, $(v, 2v, \frac{1}{2})$, $(2v, v, \frac{1}{6})$, $(\bar{v}, v, \frac{5}{6})$, $(\bar{v}, 2\bar{v}, \frac{1}{2})$, where $v=$ 0·197. Conversion into α-quartz is accompanied by a slight variation of these co-ordinates. A. A. ELDRIDGE.

Lattice constants of skapolite and apophyllite. B. GOSSNER (Zentr. Min. Geol. Paläont., 1927, A, 338—342; Chem. Zentr., 1928, i, 153).—Skapolite (mixed crystals of various plagioclases) and apophyllite (the unit cell of which contains 2 mols. of $8CaSiO_3[K_2H_2SiO_4,7H_4SiO_4],4H_2O$) have, respectively, a 17·26, 12·71 Å., c 7·65, 15·86 Å. ; d 2·65, 2·36; space-group C_{4h}^5 or C_{4h}^6, D_{4h}^1 to D_{4h}^{16}. A. A. ELDRIDGE.

Broadening of Debye lines with cold-worked metals. U. DEHLINGER (Z. Krist., 1927, **65**, 615—631; Chem. Zentr., 1928, i, 157).—With cold-worked silver, copper, tantalum, and α-brass the $K\alpha$ doublet is not resolved, whereas with cold-worked aluminium and zinc it is sharp. Hence periodic strain and distortion may be a cause of broadening of Debye–Scherrer lines. A. A. ELDRIDGE.

Charged spheres, the photo-electric effect, and the fluorescence spectra of X-rays. L. DÉCOMBE (Compt. rend., 1928, **186**, 1291—1293).—The production of the characteristic and continuous X-ray spectra is explained on the assumption that all monochromatic X-radiation of given frequency is due to the beats arising from the pulsatory frequencies of two cathodic electrons considered as small pulsating spheres, one of which is brought to rest by impact, whilst the other has a restricted speed less than that of impact. The explanation is also applied to the photo-electric effect of X-rays, to resonance, and to the Compton effect. J. GRANT.

Hemihedry of zinc blende and X-ray reflexion. S. NISHIKAWA and K. MATUKAWA (Proc. Imp. Acad. Tokyo, 1928, **4**, 96—97).—Friedel's law that hemihedrism due to lack of a centre of symmetry cannot be revealed by the X-ray diffraction method was tested in the case of zinc blende. Tungsten L radiation, the spectral lines of which cover the range including the K critical absorption limit for zinc atoms, was reflected from (111) and ($1\bar{1}1$) polished surfaces. Differences in the intensity of the lines were noticed, which might, however, be due to difference in the degree of polish. Preliminary experiments using a cleavage plane also showed differences in the relative intensities. C. J. SMITHELLS.

Structure of cyanite, Al_2SiO_5. W. H. TAYLOR and W. W. JACKSON (Proc. Roy. Soc., 1928, A, **119**, 132—146).—The crystal structure of cyanite has been determined by a qualitative method, based on the estimation of the relative intensities of a large number of reflexions obtained in a series of single-crystal rotation photographs. The crystal belongs to the pinacoidal class of the triclinic system, the space-group being C_i^1, and has a 7·09, b 7·72, c 5·56 Å. ; α 90° 5·5', β 101° 2', γ 105° 44·5'. There are four molecules in the unit cell. The structure is based on a slightly distorted cubic arrangement of close-packed oxygen atoms, the silicon and aluminium atoms being distributed uniformly among the interstices of the oxygen assemblage so that independent tetrahedral SiO_4 groups are formed, whilst each aluminium atom lies at the centre of an octahedron having an oxygen atom at each of the corners. The very perfect cleavage parallel to (100) is explained by the existence of widely-spaced planes, parallel to (100), densely packed with silicon, aluminium, and oxygen atoms; similarly, the less perfect but fairly distinct cleavage parallel to (010) is explained by the existence of sheets densely packed with silicon and aluminium atoms, widely spaced and parallel to (010). No such densely-packed layers can be distinguished parallel to (001), corresponding with the fact that no (001) cleavage occurs. The unusually large variation of hardness in different directions on the (100) face is attributed to

the existence of the cleavage parallel to (010). It should be possible to extend this explanation to include examples of hardness variation of much smaller amount.　　　　L. L. BIRCUMSHAW.

Crystal structure of the alkali metals and of strontium. F. SIMON and E. VOHSEN (Z. physikal. Chem., 1928, **133**, 165—187; cf. this vol., 223).—Lithium has a body-centred cubic lattice, the constant at 100° Abs. being 3·46 Å. The face-centred cubic lattice of strontium, stable at low temperatures, has a lattice constant at 100° Abs. of 6·03 Å. Powder measurements indicate the existence of a hexagonal form at lower temperatures. Calcium at the ordinary temperature exhibits the face-centred cubic lattice, whilst zinc and cadmium show one modification only both at the ordinary and at higher temperatures.　　　　H. F. GILLBE.

Crystal structure of lead phosphate and pyromorphite. F. ZAMBONINI and A. FERRARI (Atti R. Accad. Lincei, 1928, [vi], **7**, 283—291).—From X-ray measurements by the rotating crystal and by the Debye–Scherrer method it is shown that these two substances have essentially the same type of structure, and that therefore they cannot have the complex ion structure assigned to them by Abegg, Bodländer, and Werner.　　　　R. W. LUNT.

Crystal structure of lithium iodide trihydrate. S. B. HENDRICKS (Amer. J. Sci., 1928, [v], **15**, 403—409).—The crystal structure of lithium iodide trihydrate has been determined by the use of Laue and spectrum photographs. The space-group and resulting atomic configuration are the same as those of the triethylammonium halides. The unit cell contains two molecules of lithium iodide trihydrate and has $d_{100}=7\cdot45$ Å. and $d_{001}=5\cdot45$ Å.　　F. J. WILKINS.

Molecular structure and scattering of X-rays. G. W. STEWART and M. MANNHEIMER (Z. anorg. Chem., 1928, **171**, 61—72).—Previous work on the diffraction of X-rays by organic liquids is summarised (cf. A., 1927, 1015; this vol., 224).　　R. CUTHILL.

New type of crystal fine structure. Crystal structure of hexamminecobaltic iodide. H. HENTSCHEL and F. RINNE (Ber. Sächs. Ges. Wiss., math.-phys. Kl., 1927, **79**, 3—4, 5—54; Chem. Zentr., 1928, i, 152).—The crystal structure of hexamminecobaltic iodide is a combination of the rock salt and fluorspar types. The elementary cell contains four molecules; $a=10\cdot91$ Å. The distance Co—N is 1·64—1·91 Å. The lattice is face-centred.　　A. A. ELDRIDGE.

Uncommon common salt. A. F. DUFTON and C. G. WEBB (Nature, 1928, **121**, 942).—Crystals of sodium chloride formed in a gel prepared by addition of sodium silicate to hydrochloric acid were cubes with hollow faces and bevelled edges, the form being (110).　　A. A. ELDRIDGE.

Constitution of silver subfluoride. II. E. BRODY and T. MILLNER (Z. anorg. Chem., 1928, **172**, 84—86; cf. this vol., 223).—Polemical.　　　　H. F. GILLBE.

Constitution of silver subfluoride. C. DEL FRESNO (Z. anorg. Chem., 1928, **172**, 256—264).—Theoretical. The possibility of the existence of

silver subfluoride is demonstrated, but the process of addition of fluorine to the silver fluoride lattice, as described by Brody and Millner (this vol., 223), is not possible.　　　　H. F. GILLBE.

Crystal group of pentaerythritol; the tetrahedral carbon atom. A. SCHLEEDE and A. HETTICH (Z. anorg. Chem., 1928, **172**, 121—128).—By observations with the tube electrometer and study of the etching by methyl alcohol, it has been established that pentaerythritol belongs to the S_4 group of symmetry. It is thus not pyramidal but tetrahedral, in agreement with the classical stereochemistry of van 't Hoff and Le Bel.　　　　H. F. GILLBE.

Diffraction of de Broglie waves by crystal gratings. E. E. WITMER and L. ROSENFELD (Z. Physik, 1928, **48**, 530—540).—Mathematical.　　　　J. W. SMITH.

Magnesium; its etching and structure. H. B. PULSIFER (Amer. Inst. Min. Met. Eng., Tech. Pub., 1927, No. 42, 17 pp.).

Twinning in beryllium, magnesium, zinc, and cadmium. C. H. MATHEWSON and A. J. PHILLIPS (Amer. Inst. Min. Met. Eng., Tech. Pub., 1928, No. 53, 8 pp.)

Twinning in copper and brass. A. J. PHILLIPS (Amer. Inst. Min. Met. Eng., Tech. Pub., 1928, No. 56, 10 pp.).

Cause of translation striæ and translation strain-hardening in crystals. M. J. BUERGER (Amer. Inst. Min. Met. Eng., Tech. Pub., 1928, No. 54, 14 pp.).—The phenomenon of slipping by blocks in a deformed crystal of a " pure " metal is due to atoms of impurities which, scattered regularly through the space lattice, distort it, producing planes of varying degrees of weakness. When separation of distorted shearing planes occurs, during slip, more than atomic linkings will allow, cleavage occurs.　　　　CHEMICAL ABSTRACTS.

Characteristic infra-red vibrations of certain crystals of the rock-salt type. L. G. CARPENTER and L. G. STOODLEY (Phil. Mag., 1928, [vii], **5**, 823—832).—Mathematical. Using the data of Lennard-Jones for the force fields of atoms and ions, the frequency of the characteristic infra-red vibration of sodium chloride and potassium chloride, bromide, and iodide, respectively, has been calculated.　　　　W. E. DOWNEY.

Optical properties of the highly refractive isostructural compounds of magnesium, calcium, strontium, and barium with oxygen, sulphur, selenium, and tellurium. M. HAASE (Z. Krist., 1927, **65**, 509—587; Chem. Zentr., 1928, i, 10—11).—The following refractive indices are recorded: magnesium oxide (d 3·579+0·002), n_D 1·7366±0·001, n_{Tl} 1·7416+0·0005, n_c 1·7335±0·001; calcium oxide n_D^{20} 1·838±0·002, n_{Tl} 1·845±0·003; strontium oxide n_{535} 1·880, n_{570} 1·875, n_{600} 1·8675, n_{630} 1·863, n_{656} 1·8565±0·001; barium oxide n_{590} 2·002±0·001, n_{557} 1·989±0·002, n_{589} 1·980±0·001, n_{650} 1·960+0·004; the value for beryllium oxide increases with rise of the temperature of preparation from the nitrate; magnesium sulphide n_D 2·26±0·07; calcium sulphide n_{520} 2·161, n_{589} 2·137, n_{633} 2·124,

n_{656} 2·120±0·002; strontium sulphide n_{540} 2·122, n_{570} 2·114, n_{595} 2·105±0·003, n_{656} 2·087±0·005; barium sulphide n_D 2·155±0·005; magnesium selenide n_D >2·42; calcium selenide n_{555} 2·292, n_{589} 2·274, n_{620} 2·261, n_{656} 2·245±0·002; strontium selenide n_{540} 2·252, n_{565} 2·236, n_{589} 2·220, n_{620} 2·208, n_{656} 2·190±0·003; barium selenide n_{560} 2·289, n_{589} 2·268, n_{620} 2·252, n_{675} 2·230; calcium telluride n_D >2·51; strontium telluride n_D 2·408±0·004, n_G 2·367±0·005; barium telluride n_D 2·440±0·005, n_G 2·379±0·003 (lattice constant a 6·82±0·02 Å.). A. A. ELDRIDGE.

Crystallography, especially optical, of some organic compounds. S. RÖSCH (Z. Krist., 1927, 65, 680—711; Chem. Zentr., 1928, i, 9).—A study of p-toluoylacetophenonenol, $C_6H_4Me \cdot C(OH)\colon CHBz$, and dibenzoylmethanol, $CPh(OH)\colon CHBz$.
A. A. ELDRIDGE.

Crystallography of dicyanodiamide. E. BAIER (Z. Krist., 1927, 65, 719; Chem. Zentr., 1928, i, 26).—Dicyanodiamide, monoclinic, has $a:b:c = 1·0021:1:0·4854$, $\beta = 90° 31'$; axial plane (010), $n_{\beta D}$ 1·5492. A. A. ELDRIDGE.

Resistance to shear in metal crystals. G. I. TAYLOR (Trans. Faraday Soc., 1928, 24, 121—125; cf. A., 1927, 1017).—X-Ray examination of compressed aluminium in which all the distortion was due to slipping parallel to a 111 plane (cf. Proc. Roy. Soc., 1926, A, 111, 529) showed that all parts of the material which had rotated through angles greater than 2° had rotated about the transverse direction in the plane of slip. This direction of rotation is the same as that which might be expected if the detached portions of the crystals acted as rollers between the slip planes. The theory of rotation of material in the neighbourhood of regions of stress concentration is discussed. L. F. GILBERT.

Pyrophoric lead. G. R. LEVI and A. CELERI (Atti R. Accad. Lincei, 1928, [vi], 7, 350—355).—Pyrophoric lead has been prepared by heating the tartrate, citrate, oxalate, and formate under paraffin; the product is purified by washing with benzene. The amount of active lead has been determined from measurements of the volume of hydrogen liberated when the substance is treated with hydrochloric acid; the highest concentration is reached in the product from lead formate. X-Ray measurements of pyrophoric lead have shown that its crystalline structure is identical with that of ordinary lead. R. W. LUNT.

Determination of mol. wt. of saturated vapours of pure liquids and their mixtures by the displacement method. M. S. VREVSKI (Z. physikal. Chem., 1928, 133, 357—361).—See this vol., 18.

Resistance of sputtered films. R. S. BARTLETT (Phil. Mag., 1928, [vii], 5, 848—859).—It is found that the ageing of sputtered films depends on the temperature to which the film is raised. The resistance of the film decreases to a minimum value and then increases as the temperature is further raised. Occluded gas is the main cause of the high specific resistance of new films and of the decrease with ageing brought about by outgassing. A state of tension in the film, produced by unequal coefficients of expansion of film and backing, opens or closes gaps in the film as the temperature changes, giving rise to the low or negative temperature coefficients of resistance found in the experiments. W. E. DOWNEY.

Disturbance of the superconductivity of mercury by a magnetic field. W. J. DE HAAS, G. J. SIZOO, and H. K. ONNES (Arch. Néerland., 1928, [iii], A, 11, 1—47).—The hysteresis effect in the disturbance of superconductivity which has already been found in the case of tin (cf. A., 1927, 11, 717) was also found for mercury. The effect was observed in all cases examined. Whilst the increase of resistance as the field was increased was regular in the majority of instances, the return to a state of superconductivity as the field was diminished occurred in a series of jumps, the number and extent of which varied for the different resistances used. It is supposed that the difference in the intensities of field when these discontinuities occur is due to the different orientation of crystals in relation to the field. The hysteresis effect, and also the discontinuities in the curve, were obtained both in transverse and in longitudinal fields, although the position of the discontinuities was different in the two cases. The area of the hysteresis diagram varies with temperature. The relationship between the temperature and the strength of the field when the resistance has been half restored can be expressed by a straight-line graph. It is also shown that when a superconductor is placed in a magnetic field of sufficiently great intensity the resistance curve shows no anomalies. A. J. MEE.

Influence of pressure on the electrical conductivity of gold up to 1000 atm. A. MICHELS and P. GEELS (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 50—55).—A continuation of previous work (A., 1927, 99). A bridge method has been used for measuring resistances. Measurements have been made at temperatures between 15° and 40°, approximately, and at 50 atm. pressure intervals between 0 and 250 atm., but at 200 atm. intervals between 250 and 1000 atm. The results are tabulated. The tempering of hard-drawn wire for a considerable time at 40° appears to cause a marked reduction in the pressure effect. Bridgman's results are criticised (cf. A., 1926, 565). M. S. BURR.

Theory of electrostriction and its experimental control. G. BRUHAT and M. PAUTHENIER (Compt. rend., 1928, 186, 1289—1291).—The isothermal and adiabatic electrostrictions have been calculated in terms of directly measurable quantities, and the agreement with the results obtained experimentally by means of the Lorentz–Lorenz formula has been shown to be fairly good in the few cases for which data are available. J. GRANT.

Electrical conduction from the viewpoint of wave mechanics. W. V. HOUSTON (Z Physik, 1928, 48, 449—468).—Mathematical.
J. W. SMITH.

Birefringence and dichroism of thin layers of iron obtained by distillation. M. CAU (Compt. rend., 1928, 186, 1293—1295).—Determinations of the optical rotations and ellipticities of thin layers of iron of various thicknesses, formed on the walls of an evacuated glass container by distillation from an

electrically-heated iron wire, indicate the existence of a birefringence accompanied by dichroism, the principal directions of which are parallel and perpendicular, respectively, to that of the original wire. The effect ceases when the deposit is removed, and is due to the magnetic field of the heating current, in which the atoms of vapour tend to orient themselves in positions which are retained after deposition and are unaffected by a magnetic field placed parallel to the deposit. J. GRANT.

Refractive index and specific mass of liquid and of viscous sulphur. P. MONDAIN-MONVAL and P. SCHNEIDER (Compt. rend., 1928, **186**, 1356—1357; cf. this vol., 479).—r_L has been calculated from the values of n and d between 120° and 200°. At 160°, a change of slope was obtained on the r_L–temperature diagram, which was made up of two nearly straight lines. J. GRANT.

Extension of Dulong and Petit's law to gaseous compounds and mixtures. A. PRESS (Phil. Mag., 1928, [vii], **5**, 832—834).—Theoretical. It is shown that for gaseous compounds and mixtures the formula $2\alpha = C_v M(\gamma-1)$ holds, where α is a constant. W. E. DOWNEY.

Preliminary isotherms of ethylene. C. A. CROMMELIN and H. G. WATTS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 1059—1061).—Isotherms for ethylene have been determined at 20·18°, 10·17°, 0·10°, and −1·36°. The observations have been represented by Onnes' empirical equation of state and values for the first three coefficients, A_A, B_A, and C_A, calculated, succeeding coefficients being neglected. The results are in good agreement with Amagat's values, but differ from those of Masson and Dolley (A., 1923, ii, 462). M. S. BURR.

Accurate measurements of the specific heat of solid substances between 0° and 1625°. II. Specific heat of platinum and tungsten. F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 1069—1088).—By a method previously described (this vol., 469), the specific heats of platinum between 0° and 1625° and of tungsten between 0° and 1300° have been determined. In the case of tungsten a correction had to be applied at the higher temperatures for the oxides formed. The values of the atomic heat of platinum at constant volume, calculated from those at constant pressure, increase practically linearly with temperature, although they have already reached a value $3R$ below 0°. Similar results are obtained in the case of tungsten, the value $C_v=3R$ being reached at about 400°. The results cannot be explained by any heat of transformation, since no allotropic modification is obtained in either case. The results seem to throw doubt on the theories postulating the existence of a limiting value of $3R$ for the atomic heat at constant volume, and they are not explained by any extension of these theories. M. S. BURR.

Relation between specific heat and temperature. A. DENIZOT (Bull. Soc. Amis Sci. Poznan, 1926, **2**, 1—3).—In the temperature range where the atomic heat is approximately 6, the specific heat of many elements is proportional to log T. CHEMICAL ABSTRACTS.

Latent heat of fusion and vibration frequency. W. HERZ (Z. anorg. Chem., 1928, **170**, 237—240).—Whilst among the non-metals the value of the quotient of the latent heat of fusion per g. by the vibration frequency may lie between 1×10^{-12} and 1×10^{-11}, the range of variation shown by the metals, with the exception of mercury, aluminium, and beryllium, which are abnormal, is only about 3.5—7.5×10^{-12}. The values for many salts also lie within this latter range, but calcium chloride and alkali metal salts give figures about twice as great. R. CUTHILL.

Evaporation of rhombic sulphur. G. AMINOFF (Z. Krist., 1927, **65**, 632—635; Chem. Zentr., 1928, i, 3).—Sulphur spheres were evaporated at 100°, and the surfaces formed were measured goniometrically. Plane evaporation surfaces are formed, corresponding with the principal crystal faces. A. A. ELDRIDGE.

Simplified formulæ for specific heats of gases and solids, especially of explosion products. N. YAMAGA (Proc. Imp. Acad. Tokyo, 1928, **4**, 102—105).—Using Eucken's formula for the specific heat of gases in a simplified form, $C_v = nR + m\varphi(\theta/T)$, the values of n, m, and θ have been deduced for the gaseous products of explosions at temperatures of 3000—4000°. The rotational specific heat of monatomic gases is taken as 0, for polyatomic gases the atoms of which are arranged linearly R, and for other gases $\frac{3}{2}R$, which determines n. θ is chosen to accord with observed specific heats. The specific heats of solids produced in explosions are deduced from the Nernst–Lindemann equation. C. J. SMITHELLS.

Two different liquid states of helium. W. H. KEESOM and M. WOLFKE (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 90—94).—The data for the variation of the various physical constants of helium with temperature seem to suggest that helium can form two different liquid phases. From the specific heat data of Dana and Onnes (A., 1927, 101), a heat of transformation of helium I to helium II of 0·13 g.-cal./g. may be deduced. The heating and cooling curves of liquid helium have been studied, and these show a slight halt at 2·3° Abs. at a pressure of 38 mm. No change in the appearance of liquid helium at this temperature was observed. Liquid helium II is stable at the lower temperature and has a lower density, a greater heat of vaporisation, and a smaller surface tension than liquid helium I. A triple point such as liquid I–liquid II–vapour has, previously, been observed only with more complex substances which have a mesomorphic phase. M. S. BURR.

Specific heat of carbon dioxide. Correction. W. H. McCREA (Proc. Camb. Phil. Soc., 1928, **24**, 290).—The suggestion embodied in an equation of a previous paper (cf. A., 1927, 1122) that the molecule of carbon dioxide might exist in two forms is now shown to be untenable. C. J. SMITHELLS.

Measurement of the kinetic heat effect in air, hydrogen, and argon. K. RÜCKER (Ann. Physik, 1928, [iv], **85**, 831—865).—In the Gaede molecular pump an oriented motion is superimposed on the random motions of the molecules. Besides causing a high vacuum, the oriented motion causes a kinetic heat effect (Gaede effect). Accurate measurements

have now been obtained for the Gaede effect in air, hydrogen, and argon and the data have been interpreted theoretically (cf. Weber, Z. Physik, 1924, **24**, 267). R. A. MORTON.

Liquid state. W. HERZ (Z. anorg. Chem., 1928, **170**, 233—236).—For many liquids, both associated and non-associated, the values of $z/\gamma^{1/6}$ and $Z/B^{1/3}$, where z is the number of molecules per c.c., γ the surface tension, and B the internal pressure, vary very little with change in temperature.
R. CUTHILL.

Fundamental pressure-coefficient of helium. W. H. KEESOM and (MISS) VAN DER HORST (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 970—979).—The pressure coefficient of helium between 0° and 100° has been determined in two different gas thermometers of volume 108 c.c. and 355 c.c., respectively. The mean value, when all corrections are made, is 0·0036611, with a maximum possible uncertainty of 2×10^{-7}. This is in close agreement with the value deduced by Cath and Onnes (Arch. Néerland., 1922, [iii], A, **6**, 1) from the difference of the fundamental pressure coefficients for the international helium and hydrogen thermometers. M. S. BURR.

Vapour tensions of liquid ethylene. C. A. CROMMELIN and H. G. WATTS (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 1057—1058).—Determinations of the vapour pressure of liquid ethylene have been made between 7·90° and —69·27°. The error of the measurements is about 0·025%.
M. S. BURR.

Salt-like hydrides. III. M. PROSKURNIN and J. KASARNOVSKI (Z. anorg. Chem., 1928, **170**, 301—310; cf. A., 1927, 718; this vol., 595).—Densities of hydrides of the alkali metals have been determined as follows : sodium, 1·38±0·04; potassium, 1·47; rubidium, 2·60±0·07; cæsium, 3·42±0·1. From these figures it appears that combination with hydrogen is accompanied by a contraction of the metal lattice by an amount which increases with increase in the atomic volume of the metal; this effect is even more pronounced than with the hydrides of the alkaline-earth metals. The molecular volumes of both groups of hydrides approximate to those of the corresponding fluorides, and the lattices may consequently be assumed to be of the rock-salt type. On this basis, the radius of the H' ion is calculated to be 1·45 Å. R. CUTHILL.

Physical properties of acetic anhydride and related substances and their constitutional significance. D. C. JONES (J.C.S., 1928, 1193—1200).—The mol. wt. of acetic anhydride in benzene and cyclohexane has been determined cryoscopically. In the latter solvent the ratio M(found)$/M$(calc.) varied from 1·09 at a concentration of 0·355 g./100 g. of solvent to 1·54 at 2·947 g. %. At a concentration of 5·33 g. % the invariant point, 2·269°, is reached where solid cyclohexane is in equilibrium with two liquid phases. In benzene, the mol. wt. is normal up to a concentration of 3·8% with a slight tendency to increase at higher concentrations. The values for the " association factor " in the case of aniline and acetic anhydride dissolved in cyclohexane are very similar in solutions of about the same concentrations.

On the assumption that the mol. wt. of acetic acid is 120, the values for the acid are much smaller than those for the anhydride in corresponding solutions. The determinations of the temperature coefficients of molecular cohesion and mol. surface energy by Walden and Swinne (A., 1913, ii, 299) for acetic acid, acetic anhydride, aniline, etc. confirm the conclusion reached from the f.-p. determinations, that acetic anhydride and aniline behave as " normal " liquids, whereas the acid gives about half the calculated values.

Values for the parachors of acetic, propionic, n-butyric, and n-valeric acids are calculated and compared with those observed. Acetic anhydride gives a mol. volume value which might be expected if it were a ketonic ester. A study of the effect of groups containing oxygen on the solubility in water of aliphatic compounds containing four atoms of carbon might lead to the view that acetic anhydride contains a carbonyl and an ester group. It is concluded that there must be a marked conjugation between the three atoms of oxygen in the molecule of acetic anhydride which does not behave as if a free carbonyl group were present. The parachor is known to be insensitive to structural changes which produce large effects on properties such as solubility or chemical reactivity. H. INGLESON.

Molecular and atomic volumes. XVIII. Volume of ammonia in crystalline ammonium salts. W. BILTZ and G. BALZ (Z. anorg. Chem., 1928, **170**, 327—341; cf. this vol., 572).—By a comparison of the molecular volumes of ammonium salts of inorganic acids with those of the corresponding isomorphous salts of the alkali metals, the volume of the ammonia molecule in these compounds is found to be about 20, and is thus equal to the zero volume. In the salts of several organic acids, also, the volume is 20, but in the salts of the higher fatty acids the volume may be about 28. With dibasic acids, the first molecule of ammonia taken up retains its zero volume, but in the case of the lower aliphatic dibasic acids the second molecule undergoes a contraction.
R. CUTHILL.

Density of sodium azide. E. MOLES (Anal. Fís. Quím., 1928, **26**, 133—135).—A correction and redetermination. Pure sodium azide has d_4^{24} 1·8473±0·0004.
R. K. CALLOW.

Internal pressure and thermal vibrations of solid substances. E. N. GAPON (J. Russ. Phys. Chem. Soc., 1927, **59**, 933—949).—The internal pressure of elements, binary compounds, salts, and complex compounds is discussed. Two formulæ for the internal pressure of solid substances are derived and applied to the calculation of the internal pressures of copper, cadmium, lead, magnesium, aluminium, thallium, gold, and carbon. The results are in fairly good agreement with those calculated by the formulæ of Traube and Richardson. The relationship between internal pressure and coefficients of expansion and compression of elements and binary compounds is obtained and it is shown that the latter can be evaluated if the internal pressure is known. From considerations of internal pressure and association in the solid state an expression is derived by

which the association can be calculated and by the application of which it is shown that the alkali metals are associated in the solid state. Six formulæ for the vibration of elements are deduced and verified. A. RATCLIFFE.

Free-space numbers. II. W. HERZ (Z. anorg. Chem., 1928, **171**, 14—17; cf. A., 1925, ii, 185).—For a number of liquids the ratio of the excess of the critical volume over the zero volume to the product of the critical volume by the free-space number at the critical temperature has a value of about 0·87; the value rises slowly on ascending a homologous series. It thus appears that even at 0° Abs. there are spaces between the molecules. R. CUTHILL.

Vapour pressures of pure substances, and of binary mixtures. Vapour pressures of mercury and graphite. J. J. VAN LAAR (Z. anorg. Chem., 1928, **171**, 42—60).—By applying the method of thermodynamic potential to the equilibrium between a liquid and its vapour, there are derived the equations $L = a_1/v_1 + RT$ and $\log p = -L/RT + \log a_1/v_1^2$, where L is the total molecular heat of evaporation, a_1 is one of the constants in van der Waals' equation for the liquid, v_1 the molecular volume of the liquid, T the temperature, R the gas constant, and p the vapour pressure. By combining these relations there results the equation $\log p = -a_0/v_0 RT + \log (a_0/v_0^2) - \alpha_0 T$, where a_0, v_0, and α_0 are the values, extrapolated to $T = 0$, of a_1, v_1, and the coefficient of expansion, respectively; if b in the equation of state is a function of v, the term $\log (a_0/v_0^2)$ becomes more complex. This equation is in satisfactory agreement with the experimental figures for p for mercury from $-40°$ to $1480°$, the critical temperature; the value 4·60 is deduced for the critical density and 1150 atm. for the critical pressure. Applying the above equations to graphite (cf. A., 1921, ii, 17), it appears that the b. p. is about 5300° Abs., the critical temperature about 8000° Abs., and the critical pressure about 1500 atm. Starting from the relation previously developed for the molar potentials of the components of a binary liquid mixture (A., 1925, ii, 866) an expression is derived for the vapour pressure of such a mixture. This is capable of accounting for Weissenberger's experimental data (cf. A., 1926, 465) without the assumption of compound formation; such deviations as occur seem to be attributable to association. R. CUTHILL.

Fundamental state of the helium atom. E. A. HYLLERAAS (Z. Physik, 1928, **48**, 469—494).—Mathematical. J. W. SMITH.

Compressibility isotherms of hydrogen, nitrogen, and a 3 : 1 mixture of these gases at temperatures between 0° and 400° and at pressures to 1000 atm. E. P. BARTLETT, H. L. CUPPLES, and T. H. TREMEARNE (J. Amer. Chem. Soc., 1928, **50**, 1275—1288).—Compressibility data for the above gases are recorded. The additive volume rule holds fairly well at 300°, but not below, and the additive pressure rule holds within 2% if it is defined as follows : at constant temperature the pressure exerted by one constituent of a gaseous mixture equals the product of its mol. fraction and the pressure it would exert as a pure gas at a molecular concentration equal to the molecular concentration of the mixture. Practical applications of the data recorded are given. S. K. TWEEDY.

Changes in refractive index and density in binary mixtures. L. COUNSON (Arch. Sci. phys. nat., 1928, [v], **10**, 136—141).—A theoretical deduction is given of Pulfrich's law (Z. physikal. Chem., 1889, 561) according to which the variations of density and refractive index are always in the same direction. The proof is more rigid than that of de Lattre (A., 1927, 616) and leads to the same expression, $(dD/D)/(dn/n) = 6n^2/(n^2 - 1)(n^2 + 2)$, where dD and dn are, respectively, the variations in density and refraction. The right-hand side of this expression is always positive. W. A. RICHARDSON.

Viscosity isotherms of binary mixtures. G. TAMMANN and M. E. PILLSBURY (Z. anorg. Chem., 1928, **172**, 243—255).—The four main types of binary viscosity isotherms are discussed, and new data are recorded for the viscosity of methyl alcohol–water mixtures at temperatures between 0° and 30°. The curves exhibit the normal maximum at about 41% of methyl alcohol, and by cooling this mixture to about −50° to −60° crystals of ice separate; no separation of a crystalline hydrate of methyl alcohol is observed. From the corresponding maximum-viscosity mixtures of acetic acid and water and of propionic acid and water, crystals of the single components separate on cooling, whereas ethyl alcohol–water mixtures containing from 34 to 43% of alcohol yield transparent crystals of a tetrahydrate. H. F. GILLBE.

"Volume adjustment" in solutions. F. WRATSCHKO (Pharm. Presse, 1927, **32**, 355—358, 399—402; Chem. Zentr., 1928, i, 292—293).—Tannin (15%) in aqueous solution has d 1·4373, in alcohol (30%) 1·3717, (60%) 1·3611, (90%) 1·3260. Differences in density for solids and their solutions are also recorded. A. A. ELDRIDGE.

Diffusion of zinc in copper and in copper–zinc mixed crystals at 350°. Diffusion in the solid state. W. KÖHLER (Zentr. Hütten- u. Walzwerke, 1928, **31**, 650—657; Chem. Zentr., 1928, i, 467).—Mean diffusion coefficients are : copper–zinc, 0·000033 cm.²/day; α-brass–zinc, 0·000039 cm.²/day; β-brass–zinc, variable. A. A. ELDRIDGE.

Hardness of alloys. A. MALLOCK (Nature, 1928, **121**, 827).—Curves correlating the hardness with the composition of alloys of lead with antimony, tin, and bismuth are recorded. A. A. ELDRIDGE.

Age-hardening of silver–aluminium alloys rich in aluminium. M. HANSEN (Naturwiss., 1928, **16**, 417—419).—The hardening at 100°, 150°, 175° and the influence of time has been examined for 12 quenched alloys of aluminium containing 0·5—12% of silver. An alloy with 6% of silver shows the greatest percentage increase in hardness, whilst the most favourable temperature is about 150°. R. A. MORTON.

Reflective powers of some eutectic alloys in relation to their micro-structures. G. ANDO (Mem. Coll. Sci. Kyoto, 1928, A, **11**, 43—84; cf. Chikashige and others, A., 1926, 896).—The reflective

powers of the binary alloys silver–copper, copper–cadmium, cadmium–tin, cadmium–bismuth, bismuth–tin have been investigated in their dependence on wave-length and composition. The reflective power is usually minimal at the eutectic point. When, however, the reflective powers of the two components differ considerably, the minimum tends to deviate towards the side of the weaker component.

J. S. CARTER.

Significance of the crystal regions α, α+β, β in the system copper–zinc in the hot-working of alloys. W. MAYER (Metallbörse, 1927, **17**, 2357—2358, 2469—2470, 2525—2527; Chem. Zentr., 1928, i, 401—402).—All copper–zinc alloys of the regions α, α+β, β can readily be worked hot, except M 66 (66% Cu). The grain size is also of decisive significance. Copper–aluminium alloys are also considered.

A. A. ELDRIDGE.

Interatomic forces in metals and alloys. R. F. MEHL (Amer. Inst. Min. Met. Eng., Tech. Pub., 1928, No. 57, 16 pp.).—For elements of nearly equal atomic number the compressibilities vary inversely with the interatomic forces; the compressibility is independent of deformation and grain size. Data on the compressibility of alloys are tabulated and discussed. The theory that martensite consists largely of ferrite and finely-divided cementite is supported. The relation between the hardness, compressibility, and zinc content of brasses was studied. The atomic volume of an element in alloys is not constant. The electron distribution around the atom periphery produces some slip resistance. CHEMICAL ABSTRACTS.

Manganese–copper alloys, and the improvement of their physical properties. F. HEUSLER [with E. DÖNNGES] (Z. anorg. Chem., 1928, **171**, 146—162).—The alloy of copper containing 9—10% of aluminium and 14% of manganese (B., 1923, 405) is too hard to be of much practical value, even when in the soft state. A much more useful product is obtained, however, if the amount of manganese is reduced to 4—5%, the tensile strength after rolling then being 74 kg./sq. mm., and the extension 15%; this alloy can also be hardened. Alloys of manganese and copper only, or alloys of copper containing 5—15% of manganese and only 4—5% of aluminium, contain between 20° and 600° only the characteristic α-crystals, and therefore cannot be improved. Alloys of copper with more than about 2% of manganese and more than 1% of silicon may be improved ("Isima bronzes"); these may be hardened immediately after being sand-cast without being first reheated, and are never ferromagnetic. The changes in hardness, electrical conductivity, and volume of specimens of these bronzes and also of alloys of manganese, aluminium, and copper on ageing have been followed. R. CUTHILL.

Analysis by means of X-rays and crystal structure of alloys. Constitution of cadmium–magnesium alloys. G. NATTA (Annali Chim. Appl., 1928, **18**, 135—188).—A summary is given of the work done so far on the X-ray investigation of metallic alloys. By means of the powder method, tempered alloys of cadmium and magnesium have been investigated, as well as alloys which have been heated and also those spontaneously transformed by long keeping at the ordinary temperature. In the tempered alloys there are two types of solid solution, viz., those of cadmium in magnesium and of magnesium in cadmium. In alloys which have been cooled rapidly the two types exist together for a very large range of composition, and in the 50% alloy the intensities of the lines of the two lattices are approximately equal. With the introduction of magnesium the cadmium lattice is deformed without following Vegard's law, the length of the unit cell increasing from 2·98 to 3·01 Å. as the magnesium varies from 0 to 40 at.-%, the axial ratio decreasing at the same time from 1·89 to 1·875. Similarly, the magnesium lattice is deformed by the introduction of cadmium atoms, the length of the unit cell decreasing from 3·22 to 3·155 Å. for 15 at.-% of cadmium. By means of the Laue method, alloys containing not more than 50% of cadmium have been examined. Up to almost 30 at.-% of cadmium the alloys are ideal solid solutions; beyond this composition the alloys consist of solid solutions having regular distributions of the atoms and very large elementary cells with dimensions which are multiples of those of the magnesium lattice. The solid solutions of magnesium in the cadmium lattice containing a large percentage of magnesium also show lines which are not always in agreement with those of pure cadmium, indicating a regular arrangement of the magnesium atoms. The compound CdMg does not exist except as a solid solution in the magnesium lattice with the cadmium atoms arranged regularly. O. J. WALKER.

Miscibility relations of acetic anhydride. D. C. JONES and H. F. BETTS (J.C.S., 1928, 1177—1192).—The mutual solubility of mixtures of acetic anhydride with carbon disulphide, *cyclo*hexane, and a saturated petroleum fraction, decane, respectively, has been studied. The mean-concentration curves were also determined by an independent method. For the *cyclo*hexane and petroleum mixtures the mean curves are linear, but for the carbon disulphide mixtures the mean diameter is slightly curved, the curvature not being due to impurities. The three systems show good agreement with the theory of corresponding states in the phase which is rich in the less polar constituent, but in the other phase the deviations are large at lower reduced temperatures. The effect of moderate amounts of acetic acid on the critical solution temperature is small in all cases, but it is possible to detect 0·1% of acetic anhydride in acetic acid from critical solution data. The position of acetic anhydride in the internal pressure series is discussed in the light of the solubility results. The critical solution temperatures for the mixtures with carbon disulphide, *cyclo*hexane, and petroleum are, respectively, 29·83°, 52·45°, and 85·50°, and the critical concentrations of acetic anhydride (weight %) are, respectively, 36·17, 47·33, and 52·11.

W. A. RICHARDSON.

Dissolution velocity of oxygen in sodium hydroxide, sodium carbonate, and hydrochloric acid solution. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1928, **3**, 98—101).—The velocity of dissolution of oxygen when air is passed into sodium hydroxide,

sodium carbonate, or hydrogen chloride solution has been calculated from the oxidation velocities of sodium hydroxide and stannous chloride. H. F. Gillbe.

Solubility of *m*-nitroaniline in water. J. H. Walton and T. G. Finzel (J. Amer. Chem. Soc., 1928, **50**, 1508—1510).—Previous results (cf. Carnelley and Thomson, J.C.S., 1888, **53**, 782; Sidgwick, *ibid.*, 1921, **119**, 1013) were probably vitiated by the presence of finely-divided solid matter. The solubility increases from 0·03% at 0° to 1·23% at 83·4°. Analysis of the solutions was effected by the sodium nitrite and titanium chloride methods.

H. E. F. Notton.

Solubility of chloropentamminerhodium dichloride in water and hydrochloric acid, and that of ammonium chloropalladate in ammonium chloride solution. S. F. Shemtschushni (Ann. inst. platine, 1927, **5**, 364—365).—Saturated (25°) aqueous chloropentamminerhodium dichloride contains 0·828% of salt; when the solvent is 2·61, 4·51, or 10·56% hydrochloric acid the values are 0·086, 0·021, and 0·007%, respectively. Saturated aqueous (28·22%) ammonium chloride dissolves 0·26% of ammonium chloropalladate. Chemical Abstracts.

Influence of alkali nitrates on the solubility of lead nitrate. I. G. Malquori (Gazzetta, 1928, **58**, 203—208).—In order to determine to what extent hydration of ions and formation of complex salts affect the solubility relations, the isotherms of the systems $LiNO_3$–$Pb(NO_3)_2$–H_2O and $CsNO_3$–$Pb(NO_3)_2$–H_2O at 25° have been studied. The results when combined with the data of Glasstone and Saunders (J.C.S., 1923, **123**, 2134) for sodium and potassium nitrates show that the solubility of lead nitrate increases in the order $Li<Na<K<Cs$. The most highly hydrated lithium ion lowers the solubility of the lead nitrate to the greatest extent. The tendency to form complex nitrates, which increases the solubility of lead nitrate, increases from lithium to cæsium, so that ion hydration and complex formation oppose one another in their effect on solubility.

O. J. Walker.

Solubility of salts in saturated solutions of other salts. I. I. Krasikov and I. T. Ivanov (J. Russ. Phys. Chem. Soc., 1928, **60**, 561—563).—Solubility effects due to the influence of a common ion are of very frequent occurrence. Exceptional behaviour is shown by mercuric chloride, which is far more soluble in chloride solutions than in pure water, by chlorides, which have the same solubility in mercuric chloride solutions as in water, and by potassium and strontium nitrates, the solubilities of which in solutions of sodium and potassium nitrate, respectively, are the same as in water. In the absence of a common ion, a diminution in solubility is frequently met with, but the solubility for sodium, potassium, and barium nitrates in mercuric chloride solution is the same as in water. If the saturated solution of one salt lowers the solubility of another, the saturated solution of the second salt will similarly affect the solubility of the first.

R. Truszkowski.

Dissolution of metals in molten salts. W. Eitel and B. Lange (Z. anorg. Chem., 1928, **171**, 168—180).—From observations on the Tyndall effect and ultramicroscopic examination it appears that solutions of lead in molten lead chloride are not of colloidal but of molecular nature. A similar conclusion is also reached from a thermodynamical examination of surface tension data. It is very probable that dissolution occurs owing to the formation of compounds of the type $Pb_n,PbCl_2$, so that in the solutions there is very little free lead. The colour of the solutions is due to the free molecules of metal, as is also the colour which frequently appears when the pure chloride is melted. If the molten solutions are chilled, the free lead produced by dissociation of the compound may separate in particles of microscopic or ultramicroscopic dimensions.

R. Cuthill.

Effect of electrolytes on the distribution of acetic acid between benzene and water. R. Mittra (J. Indian Chem. Soc., 1928, **5**, 209—219).—The influence of lithium, sodium, potassium, and barium chlorides, potassium nitrate, sodium oxalate, and lithium, sodium, and potassium sulphates on the partition of acetic acid between benzene and water has been investigated. *E.M.F.* measurements were made to determine the change in activity of the hydrogen ion on the addition of neutral salts. From the results obtained the relative effects of the neutral salts can be discussed only qualitatively. All the salts, except sodium oxalate and potassium sulphate, cause an increase in activity, which increases with concentration. The two exceptions produce a negative effect at lower concentrations. By vapour-pressure measurements, McBain and Kam (J.C.S., 1919, **115**, 1332) have shown that sodium sulphate also has a negative effect on the activity of the acetic acid molecule at still lower concentrations of the acid. It appears, therefore, that the negative effect decreases in the order, potassium sulphate, sodium sulphate, and lithium sulphate. It is probable that, at sufficiently low concentrations of the acid, the negative effect may be observed with all sulphates and is to be ascribed to the sulphate ion only. The cations have the power to produce positive activation in the order $Li>Na>K$. The hydrogen-ion activity decreases with increasing concentration of sulphate, which is contrary to the effect produced by the other salts examined. The formation of the HSO_4 ion probably plays a part. Potassium nitrate has little effect on either the acetic acid molecule or the hydrogen ion. The activating effect of the chlorides on the acetic acid molecule is again in the order $Li>Na>K$. Barium has much the same effect as potassium. The chlorides also increase the activity of the hydrogen ion. The activating effect of an electrolyte on the acetic acid molecule does not necessarily run parallel with its effect on the hydrogen ion. It is probable that the so-called agreement with the Debye equation is more or less fortuitous, the investigations quoted in support being too limited in scope. Factors such as the existence of undissociated molecules in aqueous solution, or the ion association of Bjerrum and the hydration of ions, are not negligible, even at concentrations of the order of $0·01N$.

M. S. Burr.

Applicability of Chakravarti and Dhar's adsorption equation. M. N. CHAKRAVARTI and N. R. DHAR (Kolloid-Z., 1928, **45**, 12—21).—The authors' adsorption equation is applicable to the following cases of adsorption : silver salts by silver iodide, acids and alkali by humic acid, a number of acids and the arsenite ion by ferric hydroxide, hydrochloric acid by hide power, acetic acid by carbon, iodine in various solvents by wood charcoal, salts of various valencies by barium sulphate and by wood charcoal. Experimental curves obtained by other investigators in experiments on adsorption by barium sulphate and by wood charcoal are shown to be in agreement with the authors' adsorption equation, which is considered to fit the experimental data better than the general adsorption equation. The experiments with barium sulphate indicate that the adsorbed layer does not exceed one molecule in thickness, in agreement with Langmuir's theory. The equation requires a maximal adsorption, and this has been realised experimentally. The results show that the values of the adsorption coefficient, α, and the constant, K, depend on the chemical nature of the adsorbent and are independent of its method of preparation and age, whilst the maximal adsorption, A, decreases with age and also varies with the method of preparation. E. S. HEDGES.

Adsorption of iodine by charcoal in some mixtures of organic solvents. J. TRIVIDIC (Compt. rend., 1928, **186**, 1358—1360).—The fixation of iodine by charcoal in the mixtures water–alcohol (80%), benzene–toluene (1 : 1), chloroform–carbon tetrachloride (1 : 3), and toluene–alcohol (1 : 3) follows Freundlich's rule (cf. this vol., 471). The results are not in agreement with the conclusions of Schilov and Pevsner (A., 1926, 238). J. GRANT.

Relationship between the velocity of adsorption of hydrogen by palladium, iron, and nickel, and the orientation of the crystals. G. TAMMANN and J. SCHNEIDER (Z. anorg. Chem., 1928, **172**, 43—64).—The chemical as well as the elastic properties of metals are considerably influenced by cold working. The colour of gold–silver and gold–copper alloys tends to become more yellow as the metal is rolled, whilst the dissolution velocity of iron in acids diminishes. Further, the degree of working to which iron, palladium, or nickel is subjected influences very greatly the velocity with which gaseous and electrolytically evolved hydrogen is adsorbed, a great variety of effects being observed. Hard palladium does not adsorb hydrogen at 150°, whilst the electrolytically developed gas is adsorbed by the hard and soft metal with practically the same velocity. Iron and nickel, on the other hand, adsorb gaseous hydrogen at 200—300° much more rapidly and to a greater extent when hard than when soft; the reverse holds for electrolytic hydrogen. After α-iron has completely undergone the γ-transformation it no longer adsorbs gaseous hydrogen at 300°. The velocity of adsorption of gaseous hydrogen by palladium at 150° depends on the crystal orientation in the surface of the metal, being the greater the larger the number of eicositetrahedral planes in the surface layer. The number of such planes decreases after heating to a higher temperature, and the adsorption velocity shows a corresponding diminution. The effect is less marked for the adsorption of electrolytic hydrogen. Similar circumstances influence the rate of adsorption on iron and nickel, the velocity being greatest for the octahedral planes. The velocity of adsorption by a palladium sheet which contains dissolved hydrogen is diminished by the action of air on the surface, but is unaffected if the sheet is free from hydrogen. The production of water molecules in the lattice is probably the cause of this phenomenon. H. F. GILLBE.

Rate of absorption of water by bakelite. H. G. LEOPOLD and J. JOHNSTON (J. Physical Chem., 1928, **32**, 876—878).—When the percentage increase in weight is plotted against the quotient time of immersion in water/(half-thickness of sheet)^2, a single curve is obtained for all the sheets of brown bakelite examined. The rate of penetration of water into this type of bakelite is negligible for ordinary atmospheric conditions. Yellow bakelite gained in weight for two days when immersed in water and then steadily lost weight, yielding phenol to the water in which it was immersed. L. S. THEOBALD.

Adsorption phenomena in solutions. XII. Electroendosmosis. (FRAU) L. ORLOVA (Z. physikal. Chem., 1928, **134**, 345—352; cf. Schilov and Tschmutov, this vol., 581).—Further experimental support is given for the view suggested by Kruyt (A., 1918, ii, 289) that charged surfaces in contact with dilute electrolyte solutions first adsorb the ions of like charge and thereby increase their charge. The effect of increasing concentrations of acids, alkalis, and salts on electroendosmosis through negative kaolin diaphragms and positive alumina diaphragms has been investigated. The curves representing this effect for the negative diaphragms show a more or less distinct maximum, whilst for the positive diaphragms the curves show a minimum in several cases. The charge of the positive surface is more easily reversed in sign, and it is therefore more unstable. The characteristic shape of the curves can in general be explained by supposing that two types of adsorption are superimposed on one another, viz., a primary adsorption of ions, which gives rise to the charge on the surface and increases it, and a secondary adsorption of the oppositely charged ions, which manifests itself as molecular adsorption and decreases the primary charge on the surface. O. J. WALKER.

Behaviour of magnesium hydroxide towards aqueous mercuric chloride solutions and salts of tervalent arsenic. M. RAKUSIN and E. IZKIN (Trans. Sci. Chem.-Pharm. Inst., 1926, **16**, 109—114; Chem. Zentr., 1928, i, 93).—Magnesium hydroxide readily adsorbs mercuric chloride and Fowler's (arsenite) solution, and is thus an antidote; sodium cacodylate is not adsorbed. Aluminium hydroxide adsorbs Fowler's solution but not sodium cacodylate. A. A. ELDRIDGE.

Action of caffeine on the water absorption of colloids. J. SZELÖCZEY (Magyar Orvosi Arch., 1927, **28**, 626—638).—Caffeine lowers the temperature at which gelatin passes from the gel to the sol condition, increasing the quantity of free water and decreasing that of imbibed water. The decrease of

water absorption is not directly proportional to the concentration of caffeine; it depends on the p_H, but not on the concentration. CHEMICAL ABSTRACTS.

Active silicic acids (silica gel). E. BERL and H. BURKHARDT (Z. anorg. Chem., 1928, **171**, 102—125).—The properties of several silica gel preparations have been examined. Although considerable differences were shown by the various specimens in respect of the heat of wetting by water and by benzene, the adsorption curves for crystal-violet dissolved in "tetralin" were nearly all very closely similar (cf. A., 1925, ii, 507; Mecklenburg, *ibid.*, 530). From the adsorption isotherms for water vapour, it appears that the water content of the gels, as well as the size of their pores, plays an important part in their activity. By mixing solutions of sodium silicate and aniline hydrochloride, gels have been obtained which, in respect of the adsorption of water vapour, were much more active than the other preparations, which included a commercial product prepared by Patrick's method (B., 1919, 363). To obtain the best results, the reactants should be at considerable dilutions, excess of hydrochloric acid must be avoided, and the gel should not be washed until 24 hrs. after precipitation is begun. Contrary to the statements contained in B.P. 205,081 (B., 1925, 169), the activity of silica gels is diminished by subjecting them to high pressure. R. CUTHILL.

Effect of addition of small amounts of metals of alkalis and alkaline earths on the capillarity constant of mercury. F. OPPENHEIMER (Z. anorg. Chem., 1928, **171**, 98—101).—The surface tension of mercury is reduced by small amounts (0·005—0·05%) of sodium, calcium, or lithium, the depression increasing with increase in the concentration of foreign metal. The surface tension of bromoform, on the other hand, is raised by ethyl diazoacetate. It thus appears that there is some connexion between the surface tension and the velocities of the reactions studied by Fraenkel, Wengel, and Cahn (this vol., 717). R. CUTHILL.

Colloidal theory of surface tension. S. RAY (Kolloid-Z., 1928, **45**, 9—12).—Existing views of the nature of surface tension are criticised. A new theory of surface tension, adopting the concepts of charged particles in vogue in colloid chemistry, is evolved, according to which the rise of liquid in a capillary tube is due to the electrical attraction between the charged gas molecules and the charged liquid molecules. Depression of the liquid in a capillary (as in the case of mercury) indicates an electrical repulsion between the particles. The theory is applied to the behaviour of the capillary electrometer. E. S. HEDGES.

Unimolecular films. S. E. SHEPPARD and R. L. KEENAN (Nature, 1928, **121**, 982).—When the thickness of the film of an aqueous solution of a substance on mercury is calculated by assuming that the density of the solute is the same as that of the substance in bulk and is plotted against the concentration, a point is reached at which the thickness becomes independent of the concentration. The value for cellulose nitrates from acetone is 3—5 Å., for stearic acid from ether at 25°, 22—24 Å., for oleic acid 11·2 Å., for elaidic acid 12·2 Å., and for n-decoic acid 13·6 Å.

Thus the fatty acids are apparently oriented in unimolecular films, approaching closest packing, whilst the "high-molecular" substances appear to have a casual, porous, net-like structure, or a molecular dimension which cannot be the length of the molecule, but may be the thickness of a polymeric chain or sheet. The latter view is preferred. Proteins from water give values of the order 6—7 Å.
A. A. ELDRIDGE.

Surface layer of liquids and the size of molecules. S. G. MOKRUSCHIN (J. Physical Chem., 1928, **32**, 879—881).—Evidence supporting the author's view concerning the structure of the surface layers of liquids (A., 1927, 1128) and the formula for calculating molecular diameters (A., 1924, ii, 820) is advanced. The density of the surface layer should be less than that of the liquid in bulk.
L. S. THEOBALD.

Disinfectant action. II. Relations of phenols and amines to proteins. E. A. COOPER and J. MASON (J. Physical Chem., 1928, **32**, 868—875; cf. A., 1927, 203).—Adsorption effects predominate in the aqueous systems picric acid–serum-albumin, salicylsulphonic acid–gelatin or albumin, ethylamine–gelatin, and aniline–gelatin, the ratio of the acid or amine taken up to that remaining in solution decreasing in all cases when the initial concentration of the solution increases. Hydrazine hydrate is not absorbed by gelatin and hydroxylamine hydrochloride shows a maximum absorption at low concentrations with egg-albumin. Germicidal and inhibitory power are not definitely related to the solubility in or adsorption by proteins in the colloidal state, but when the latter are not in the sol condition, bactericidal action and adsorption (or solubility) run parallel. Adsorption data are given.
L. S. THEOBALD.

Influence of some colloidal substances on the rate of absorption of carbon dioxide by neutral sodium carbonate solutions. P. RIOU and L. LORTIE (Compt. rend., 1928, **186**, 1543—1546; cf. A., 1927, 311).—Increasing additions of peptone, pepsin, soluble starch, or gelatin to solutions of sodium carbonate $(3·7 \times 10^{-2} — 14·8 \times 10^{-8}$ g.-mol./100 c.c.) rapidly decrease the rate of absorption of carbon dioxide at 20° up to a concentration of about 0·125%, after which there is usually no change. The viscosity is therefore not the only factor affecting the rate of absorption.
J. GRANT.

Selective permeability of membranes. Influence of the mobility of the ions on the polarisation. (MLLE.) CHOUCROUN (Compt. rend., 1928, **186**, 1548—1551; cf. A., 1927, 931).—If unequally concentrated solutions of the same electrolyte are separated by a "charged" membrane (*e.g.*, prepared from an acid or alkaline solution of gelatin) the membrane shows appreciable polarisation only when the ion having the same sign has a mobility almost equal to or greater than that of the other ion involved. The polarisation is measured by the difference in the *P.D.* for the liquid couple with and without the membrane.
J. GRANT.

Osmosis of ternary liquids. Experimental. I and II. F. A. H. SCHREINEMAKERS and B. C. VAN B. WALTER (Proc. K. Akad. Wetensch. Amster-

dam, 1928, **31**, 113—124, 169—178).—I. A system of two ternary liquids in osmotic contact with one another through a membrane permeable by each of the three substances, previously discussed theoretically (this vol., 233), has been investigated experimentally. The liquids taken were aqueous solutions of sodium carbonate and sodium chloride, respectively, and for the membrane both parchment and pig's bladder were used. The results are tabulated and the direction of real and apparent osmosis is indicated.

II. The apparent osmosis of systems VI—XII, made up of $Na_2S_2O_6 + BaS_2O_6 + H_2O$, is discussed. The experimental data are given for a collodion membrane alone, a parchment membrane, and a collodion membrane with a deposit of copper ferrocyanide. The sodium dithionate in these systems behaves in the same way as the sodium chloride in the systems I—V previously examined. The change of barium dithionate in the system VI is the only example of an abnormal change of concentration in the systems I—XII.　　　　　M. S. BURR.

Equilibria between double sulphates and aqueous sulphuric acid. I. C. MONTEMARTINI and L. LOSANA (Notiz. chim.-ind., 1927, **2**, 551—556; Chem. Zentr., 1928, i, 175).—The curves which represent the expansion of solutions of aluminium sulphate, aluminium and sodium sulphates, chromium and potassium sulphates, and aluminium chloride on heating show breaks at 73°, 66°, 77°, and 63°, respectively; the cooling curves are below the former, and are uniform. For solutions of aluminium nitrate, chromium nitrate, ferric sulphate, and ferric and potassium sulphates both sets of curves show points of inflexion. The $E.M.F.$ of the cell $Al_2(SO_4)_3$ (dissolved cold)|Al or Pt|$Al_2(SO_4)_3$ (boiled) reaches zero after 1 month. The viscosity of heated aluminium sulphate and potassium chromium sulphate solutions is still not constant after 25 days. In the presence of increasing quantities of sulphuric acid the points of inflexion of the dilatation curves are shifted towards lower temperatures. The solubility of aluminium sulphate in sulphuric acid solutions differs according as the solution is saturated at 12·5° or is saturated at 100° and maintained at 12·5° for 4 days.

　　　　　A. A. ELDRIDGE.

Physical properties of aqueous hydroxybenzene solutions. L. E. SWEARINGEN (J. Physical Chem., 1928, **32**, 785—793).—The density, viscosity, index of refraction, and surface tension of aqueous solutions of phenol, pyrocatechol, resorcinol, quinol, and pyrogallol have been measured at 25°. The densities can be represented by the equation $D = mC + D_0$, where C is the molar concentration. The value of m is 0·0075, 0·0230, 0·0210, 0·0210, and 0·0350 for the substances in the above order. Excepting surface tension, the number and position of the hydroxyl groups have no marked influence on the physical property concerned. The lowering of the surface tension diminishes from phenol to pyrogallol.

　　　　　L. S. THEOBALD.

Preparation of chloride-free colloidal ferric oxide from ferric chloride. C. H. SORUM (J. Amer. Chem. Soc., 1928, **50**, 1263—1267).—Stable ferric hydroxide sols, free from chloride and nitrate ions, were prepared by dropping ferric chloride solution into boiling water and dialysing the product for some days in water at 90—97°. Dialysis for 5 weeks failed to induce coagulation.　　　　S. K. TWEEDY.

Slow hydrolysis of ferric chloride. E. HEYMANN (Z. anorg. Chem., 1928, **171**, 18—41).—The nature of the changes which occur in solutions of ferric chloride on keeping has been examined. With a freshly-prepared solution, the whole of the products of hydrolysis pass through an ultrafilter, but the degree of dispersity decreases with increasing age, the proportion of the iron finally in the colloidal state increasing with rise in temperature and with decrease in salt concentration. That this quantity may correspond with an actual equilibrium appears possible from the fact that if a chloride solution is heated at 80° for 45 min., whereby the hydrolysis is almost completed, and then aged at 20° or 37°, the amount of colloid ultimately approximates to that corresponding with the final temperature. On the other hand, there is less chlorine in the colloid produced at 80° than in those produced at the lower temperatures, and the amount does not change on cooling. The increase in conductivity of the chloride solutions with age runs parallel with the colloid content except immediately after the solution has been prepared, when the conductivity increases the more rapidly, as would be expected in view of the initial high degree of dispersity of the products of hydrolysis. The micelles themselves possess a measurable conductivity, but although with increasing age of the solution they increase in quantity their relative contribution to the conductivity of the system diminishes. This may be due in part to changes in dispersity, yet chemical changes are also involved, since the amount of chlorine falls at the same time, the composition of the final product of slow hydrolysis corresponding, not with a hydroxide, but with an oxychloride. It appears likely that the first product of hydrolysis is an oxychloride of the type $FeCl_3, nFe(OH)_3$, where n is probably less than 9. The molecules of this compound tend to associate, i.e., coagulate, and react with water with elimination of hydrogen chloride and formation of secondary oxychlorides which increase in complexity until their molecules attain colloidal dimensions. The original equilibrium is consequently disturbed, and more and more ferric chloride is hydrolysed. In this way, the present results receive a satisfactory explanation; they are definitely in conflict, however, with the views of Wagner (A., 1914, ii, 349).　　R. CUTHILL.

Ferrous hydroxide. E. DEISS and G. SCHIKORR (Z. anorg. Chem., 1928, **172**, 32—42).—Ferrous hydroxide sol cannot be prepared by direct dialysis of ferrous chloride solution, as little hydrolysis appears to take place. By passing gaseous ammonia into ferrous chloride solution in complete absence of oxygen a pure white, pulverulent precipitate is obtained, resembling in appearance calcium hydroxide. By repeated centrifugal separation and washing of the precipitate with air-free water a stable sol is obtained which is colourless by reflected and red by transmitted light, the concentration being about 4 g./litre. A stable sol cannot be obtained by the use of aqueous

ammonia solution. The colloidal particles are positively charged, and the coagulating powers of a number of anions have been determined. The brown liquid obtained by mixing ferrous and ferric hydroxide solutions rapidly changes to a green colour, and finally turns black with complete precipitation of the colloid. The green substance probably results from the combination of one molecule of ferrous hydroxide with one of ferric hydroxide, but attempts to isolate the compound have been unsuccessful.

H. F. GILLBE.

Colloidal barium sulphate. W. A. LOTT (J. Amer. Pharm. Assoc., 1928, **17**, 454—456).—Three methods for the preparation of barium sulphate in the form of a reversible colloid are described. The following gives the best preparation : 60 g. of barium hydroxide are mixed with water to a paste and glacial acetic acid is added until neutral to phenolphthalein ; 16·2 g. of 96% sulphuric acid are diluted with 65 g. of alcohol and cooled to 0° and the mixture is added to the concentrated barium acetate solution at 65° while stirring rapidly. The resulting colloidal solution is dried in a vacuum desiccator at 60°. The dried barium sulphate is readily peptised with water and the colloidal solution passes completely through a No. 5 Whatman filter and remains stable for several days. A small excess of soluble barium salt is present in the colloid and is necessary for its formation, but the product is no more toxic to white mice or guinea-pigs than ordinary precipitated barium sulphate. The colloid is peptised by the adsorbed barium ions and without them the particles are immediately agglomerated. E. H. SHARPLES.

Preparation of a lead selenide hydrosol. J. BROOKS (J. Physical Chem., 1928, **32**, 698—708).—Lead selenide sols have been prepared by the passage of hydrogen selenide into a solution of lead acetate and gelatin (5%), and into a suspension of lead carbonate in the acetate and gelatin, with the addition of sodium hydrogen carbonate in both cases to neutralise the acetic acid formed. With the first method, the percentage conversion into hydrosol decreases as the initial concentration of lead acetate is increased above a certain limit, an effect which is attributed to the presence of the acetate ion or acetic acid during the process of formation. The velocity of growth of nuclei is unaltered whilst the rate of formation of nuclei is decreased, and this aspect is treated quantitatively. The rate of stirring in the first method has little effect on the yield of colloid, but in the second method the yield is decreased at rapid rates. Addition of the hydrogen carbonate in this case also coagulates a small amount of the colloid formed. The sols can be concentrated by long boiling, or preferably by the precipitation of the lead and gelatin with a saturated solution of ammonium sulphate, removal of this reagent by washing in the cold, and the subsequent redispersion of the sols in warm water. L. S. THEOBALD.

Conductivity of copper hydrosols. H. D. MURRAY (J.C.S., 1928, 1235—1239).—Measurements have been made of the conductivity of copper sols (prepared by Bredig's method) with the addition of various electrolytes. The copper particles behave as

if coated with cupric hydroxide, which saturates the dispersion medium, giving a solution which is too concentrated to permit of the study of the ion equilibrium at the surface of the particles.

W. A. RICHARDSON.

Colloidal clay. A. DEMOLON and G. BARBIER (Rev. gén. Colloid., 1928, **6**, 29—31).—The colloidal elements of soils may be classified as those which determine its texture, and those which determine its buffering and adsorbing powers etc. Removal of electrolytes from brick-clay induces complete dispersion of the argillaceous material. The rate of flow of a clay suspension is connected with the concentration of the clay by a hyperbolic curve, and the addition of an electrolyte to a completely peptised colloidal solution increases the viscosity considerably, the chloride and nitrate of a particular metal having the greatest effects. These increments may be correlated with the permeability of the corresponding coagulum and indicate the production of aggregates of varying sizes, of which those due to flocculating salts are the largest and most rigid, and have maximum permeability. Adsorption by clay follows the laws of true adsorption, and is characterised by equilibria which depend on the final p_H value. The amount of metallic cations fixed increases with the final p_H value independently of their nature. The ionic exchanges peculiar to zeolitic silicates also depend on the colloidal structure. The chemical composition of alluvial clay is similar to that of halloysite. J. GRANT.

Examination of sols produced by peptisation of oxides of iron with silicic acid sol. A. FODOR and A. REIFENBERG (Kolloid-Z., 1928, **45**, 22—31 ; cf. A., 1927, 620).—Ignited ferric oxide is peptised by silicic acid sol to a brick-red sol which scatters light strongly. The sol bears a negative electrical charge and is partly coagulated by hydrochloric acid, whilst the coagulation by aluminium chloride is in accordance with an "irregular series." Ferrous oxide is also peptised by colloidal silicic acid to a green sol, which is oxidised slowly in the air and rapidly by hydrogen peroxide to a yellow ferric oxide sol. The particles of this sol are negatively charged, but the sol differs from the preceding one in relative viscosity and alkali-fixing capacity ; the sol is readily coagulated by hydrochloric acid and the irregular series phenomenon is shown with aluminium chloride. A third sol, prepared by direct admixture of ferric hydroxide sol and colloidal silicic acid, is negatively charged, but differs from the preceding sols in size of the particles, in relative viscosity, and in its coagulation, the irregular series being exhibited with both hydrochloric acid and aluminium chloride. In all three cases, the ferric hydroxide can be separated from the silicic acid by addition of sodium hydroxide or neutral salts. E. S. HEDGES.

Influence of mercaptan on the life-period of colloidal solutions of sulphur. E. IWASE (Kolloid-Z., 1928, **45**, 31—36).—The stability of colloidal sulphur dispersed by the non-electrolyte ethyl mercaptan has been examined. Sols were prepared by pouring 10 c.c. of a solution of sulphur in alcohol into a series of vessels each containing 90 c.c. of aqueous ethyl mercaptan in progressively increasing

concentration. On keeping it was found that the preparations containing either insufficient or an excess of ethyl mercaptan settle more rapidly than those containing intermediate quantities. The stability curve thus passes through a maximum, and the life-period of colloidal sulphur at the maximum position is at least three times that of colloidal sulphur containing no ethyl mercaptan. Differences between the dispersion of sulphur by electrolytes and by ethyl mercaptan are pointed out and discussed.

E. S. HEDGES.

Rôle of dielectric constants, polarisation, and dipole moment in colloid systems, especially in non-aqueous dispersoids. I. Wo. OSTWALD (Kolloid-Z., 1928, **45**, 56—82).—Recent work is discussed and the data for about 250, mainly organic, liquids are recorded. The different values obtained for dipole moments by different methods of measurement and the deviations of these from the requirements of the various theories are also considered. "Single moments," obtained in the vapour state or dilute solution, are differentiated from "mass moments," obtained from the massive liquid. Consideration of the relation between polarisation values, dipole moments, and chemical nature leads to the following conclusions. Simple hydrocarbons show little orientation polarisation or only small permanent dipole moments. Halogenated hydrocarbons give large dipole moments. For simple alcohols, the moment rises with increasing number of CH_2 groups, thus varying antibatically with the dielectric constant. Aldehydes and ketones have very high moments, whilst ethyl ether has a middle value somewhat greater than 1. Amines and other nitrogenous bases have high dipole moments. Fatty acids, although incompletely investigated, give values greater than 1. In the three chloroacetic acids, the moment decreases with increasing number of chlorine atoms. The dipole moments of esters lie mostly between 1 and 2, and an increase is observed when the acid radicals form a homologous series. The moments of highly associated liquids (water, nitrobenzene, acetone) vary greatly with the method of determination, but the values are mainly high. The highest values are obtained with nitro-compounds (nitrobenzene 3·8, o-dinitrobenzene ca. 6, 2 : 5-dinitrotoluene ca. 4·5, dinitronaphthalene ca. 6). Various polarisation values are treated statistically and graphically as functions of the dielectric constant and for most of them, and more particularly for the dipole moment, a maximum is obtained for medium values of the dielectric constant. This result does not seem to be connected with the association of liquids of high dielectric constant. E. S. HEDGES.

Relation of some colloids to iodine and possible application to the titration of colloids. W. ENGELHARDT (Kolloid-Z., 1928, **45**, 42—46).—Colloidal gold (prepared by fourteen different methods) is rapidly dissolved by a solution of iodine in potassium iodide with formation of the complex salt $KAuI_2$. With potassium iodide, colloidal gold dissolves slowly and with alcoholic iodine solution it forms a dark precipitate. The behaviour of a number of other colloids with these reagents was examined and gave

the following general results. Colloidal gold, silver, copper, mercury, cadmium, zinc, lead, bismuth, antimony, arsenic, and tellurium react readily with iodine in potassium iodide. Colloidal selenium reacts slowly under these conditions, and only when the iodine is in large excess. Colloidal boron, carbon, sulphur, platinum, palladium, rhodium, manganese, and iron do not react with iodine. When these elements are arranged in their positions in the periodic table, a nearly straight line can be drawn, separating those elements which are affected in the colloidal state by iodine from those which are not so affected. Most colloidal metal hydroxides do not react with iodine, whilst the majority of colloidal metal sulphides do so. It is suggested that colloids which do not contain reducing matter may be titrated by adding excess of iodine and titrating back with sodium thiosulphate. E. S. HEDGES.

Formation of filaments of ferric oxide by evaporation of colloidal solutions. P. BARY (Compt. rend., 1928, **186**, 1539—1541).—The residue from the evaporation at 50—60° of colloidal solutions of the compound $nFe_2O_3,Fe_2Cl_6,aq.$ obtained by prolonged dialysis of ferric chloride solution, takes the form of filaments of ferric oxide oriented radially and concentric with the base of the vessel. The actual pattern depends on the conditions of the experiment, and is due to the capillary action of the walls on the supposedly rod-shaped colloidal particles.

J. GRANT.

Optical examination of substances with powder- or thread-like structure. G. P. VORONKOV and G. I. POKROVSKI (Kolloid-Z., 1928, **45**, 1—7).—The optical properties of substances having a powder- or thread-like structure are discussed from a theoretical point of view, and spectro-photometric observations with light normally reflected from a number of disperse systems are recorded. The dispersion media (air, water, glycerol, anisole, and carbon disulphide) were so chosen that they absorb light almost equally but have different refractive indices. The disperse phases were chalk, powdered glass, mica, filter-paper, and talc. The experimental results are in agreement with the theory, and it is considered that the procedure may be developed so as to provide a general method for the optical characterisation of heterogeneous substances. E. S. HEDGES.

Structure formation in colloidal solutions. H. ZOCHER (Collegium, 1928, 203—208).—Concentrated vanadium pentoxide sols form spiral-shaped drops. There are two phases, one of which appears in polarised light and under the microscope to consist of spiral drops with their axes mainly in one direction. This phase is referred to as the "tactosol," and the second phase as the "atactosol." The structure of benzopurpurin "tactosol" is similar, but that of ferric hydroxide "tactosol" shows layers surrounded by cylindrical drops of the unarranged sol. The "tactosol" consists of alternate layers of colloid particles and water. D. WOODROFFE.

Colloidal state and cohesion at the time of solidification. J. ERRÉRA (Trans. Faraday Soc., 1928, **24**, 162—164; cf. A., 1925, ii, 362).—For frequencies less than 10^6 the dielectric constant of

solids produced from liquids having permanent dipoles rises sharply to a maximum near the point of fusion, after which it falls. The existence of colloidal structures in solids in the neighbourhood of the point of fusion is suggested (cf. Joffé, Rept. Physical Inst. Leningrad, 1926).

This hypothesis is in accordance also with the observation that the rise of dielectric constant, which is believed to be due to the polarisation of colloidal particles, becomes less and less as the frequency is increased, suggesting that the conditions do not provide sufficient time for the relaxation of the particles.   L. F. GILBERT.

Photophoresis in liquids. S. RAY (Kolloid-Z., 1928, **45**, 7—9).—A description is given of experiments with emulsions of oil in water and with suspensions of sulphur in which streaming of the particles was caused by illumination of the system from one side.   E. S. HEDGES.

Physico-chemical study of gum-arabic. A. W. THOMAS and H. A. MURRAY, jun. (J. Physical Chem., 1928, **32**, 676—697).—The base-combining capacity, the osmotic pressure, and viscosity of solutions of gum-arabic purified by precipitation with alcohol and electrodialysis have been studied in their dependence on p_H. The equivalent weight of the arabic acid found by titration with sodium and barium hydroxides is 1200 approximately, and 1000 when varying concentrations of alkali and acid are used in measuring base-combining capacity. The nature of the titration curve and this agreement between equivalent weights indicate that arabic acid is a relatively strong acid. The osmotic pressure-p_H curves for sodium and barium arabates show maxima at p_H 4·25 and 3·35, respectively, with no evidence of an isoelectric point. Viscosity is lowered by the addition of neutral salts. The Donnan theory of membrane equilibrium accounts qualitatively for the results obtained in the measurements of osmotic pressure and viscosity.   L. S. THEOBALD.

Viscosity and hydratation. IV. Properties of liquid formed during syneresis and the theory of syneresis. S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 467—483).—The liquid which separates in the syneresis of geranin and of benzopurpurin gels contains small quantities of these dyes which are present as single and double molecules respectively. The remaining gel is composed of hydrated colloidal particles of geranin, every molecule of which is bound with 2043 mols. of water. Addition of sodium chloride to geranin solutions diminishes the solubility of the latter, but increases the proportion of colloidal particles of the dye in solution, as a result of which the viscosity of the solution increases. Thus the action of this electrolyte is first to induce aggregation of molecules into colloidal particles, which, as the concentration of sodium chloride is increased, are then coagulated as a hydrated gel.
                          R. TRUSZKOWSKI.

Acid fixation and swelling of fibrin. I. E. VOIT. **II. Swelling of native fibrin in dilute hydrochloric acid.** F. SCHULDENZUCKER. **III. Water- and acid-fixing power of fibrin coagulated by boiling in water.** F. LOCHMÜLLER (Z. Biol.,

1928, **87**, 269—278, 279—291, 292—306).—I. General review.

II. The quantity of hydrochloric acid which combines with fibrin immersed in a fixed volume of solution increases rapidly at first with increase in the concentration of acid, then more slowly, and finally approaches a limit. The maximum swelling of the fibrin increases with increase in the amount of acid absorbed, but reaches a maximum and then decreases and finally approaches a limiting value. Under the conditions of the experiment some hydrolysis is caused by the acid and this must be considered in interpreting the results. It is concluded that acid fibrin has a swelling power nine times as great as that of neutral fibrin.

III. Fibrin denatured by boiling with water behaves very similarly to native fibrin when it is placed in contact with hydrochloric acid in respect of the amount of acid with which it combines, the chief difference being that the fixation of acid increases more slowly with concentration of acid. On the other hand, the maximum amount of swelling is much less, being only one seventh of that of native fibrin. Hydrolysis of the protein takes place to some extent and has a maximum value at that concentration of acid at which maximum swelling occurs. Experiments on the uptake of water by quartz sand, talc, and starch are described as well as some properties of purified fibrin.   W. O. KERMACK.

Deaminised gelatin. Z. C. LOEBEL (J. Physical Chem., 1928, **32**, 763—778).—The behaviour of a gelatin deaminised by Hitchcock's method (A., 1923, i, 1244) has been compared with that of isoelectric, ash-free gelatin prepared according to Loeb. The isoelectric point of the deaminised product lies at p_H 4·0. The optical rotation, viscosity, surface tension, and foaming have been studied as functions of p_H. The viscosity-p_H curves at 10°, 25°, and 50° of solutions prepared at 50° and 75° are all similar in shape. Each curve shows minima at p_H 4·0 and 7·3, and maxima at p_H 2·9, 6·5, and 7·9. The rise on the alkaline is greater than that on the acid side of the isoelectric point. The corresponding curves for 25° and 50° for solutions of ordinary gelatin prepared at 75° show that a minimum occurs at the isoelectric point, that the rise on the acid side is greater than on the alkaline, and that deamination shifts the isoelectric point to the acid side. The optical rotation at 10°, and the foaming of deaminised gelatin at the ordinary temperature, are at a maximum at p_H 4·0, whilst surface tension is at a minimum. The last results agree with those recorded by Bogue (A., 1922, i, 782) and Johlin (A., 1925, ii, 388), and conform to the theory of an adsorption film. The titration curves of gelatin and of the deaminised product with sodium hydroxide indicate that the hydroxyl groups which replace the amino-groups in deamination are acidic. A change in slope for deaminised gelatin at p_H 7·5 corresponds with one for gelatin at p_H 7·7, the second point of abrupt change in the properties of gelatin. Further, the difference in base-combining capacity of the two substances is equivalent to their difference in nitrogen content, and the value of the former for deaminised

gelatin is indicated to be 9.7×10^{-4} equiv./g., the larger value accounting for the greater viscosity on the alkaline side of the isoelectric point. The second point of abrupt change in properties is discussed.

L. S. THEOBALD.

Double refraction of caoutchouc in the deformed and undeformed state. M. KRÖGER (Kolloid-Z., 1928, **45**, 52—56).—Crude caoutchouc becomes doubly refractive on keeping. Lateral extension gives rise to biaxial positive double refraction. Vulcanisation produces uni- or bi-axial positive double refraction, whilst lamellar deformation results in weak biaxial negative double refraction.

E. S. HEDGES.

Properties of "pure" cellulose as a colloid. P. P. VON WEIMARN (Rep. Imp. Ind. Res. Inst. Osaka, 1927, **8**, 21—39).—See this vol., 474.

Relation between elastic properties and structure of organic fibres. R. O. HERZOG (Naturwiss., 1928, **16**, 420—421).—For amorphous materials, $D\eta = \alpha\Phi\delta^2/6$, in which D is the coefficient of "inner" diffusion, η is the viscosity of the gel, and α a constant for a given material, δ is the diameter of the colloid particle, and Φ the torsion modulus. An attempt has been made by comparing the fibre diameter of various natural and artificial fibres to test the relation and to decide whether the elastic properties are to be ascribed to the crystallites or to the crystallite aggregates (secondary particles). Although further investigation is needed the latter alternative is probably to be preferred.

R. A. MORTON.

Equilibrium of nitrogen and hydrogen with ammonia in a corona discharge. G. L. WENDT and J. E. SNYDER (J. Amer. Chem. Soc., 1928, **50**, 1288—1292).—At $28.5°$ and 733 mm. 4.1% by vol. of ammonia exists in the equilibrium mixture. According to calculation, the same conditions are realised thermally at $270°$ and possibly at $2500°$. Corona discharge thus appears to activate various molecular species with an enormous increase in the reaction velocity.

S. K. TWEEDY.

Equilibria relations for the water-gas reaction in the temperature interval 300—$1000°$. B. NEUMANN and G. KÖHLER (Z. Elektrochem., 1928, **34**, 218—237).—The reaction $CO + H_2O \longrightarrow CO_2 + H_2 + 10090$ g.-cal. has been investigated from $300°$ to $1000°$ using an alloy of 94% Co, 5% Al, and 1% K as catalyst. Down to $355°$ complete equilibrium is attained, whereas at $295°$ it is incomplete. At temperatures below $500°$ it is necessary to employ a catalyst having the composition 94% Fe, 5% Al, and 1% K in order to hinder side reactions, principally methane formation. Equilibrium in these circumstances can be obtained at temperatures down to $400°$, being incomplete at $365°$. At $310°$ higher hydrocarbons make their appearance. Above $400°$ the equilibrium constants determined for the two opposing reactions are in very close agreement. A new expression calculated for the reaction isochore yields curves which correspond well with those derived from the experimental data. The integration constant I calculated from the equilibrium constants shows almost perfect agreement with the sum of the chemical constants of the vapour-pressure equation obtained by taking I_H, as 3.685; the agreement is less satisfactory if Fried's value of 3.385 be employed. Combination of the integration constants for the formation of water vapour and of carbon dioxide yields for that of the water-gas reaction the value $+0.82 \pm 0.12$, which approximates closely to that determined experimentally, viz., $+0.84 \pm 0.04$. If the water-gas constant be calculated from the water vapour and carbon dioxide constants by means of Hofmann's or Eastman's expressions no agreement exists with the experimental value. Furthermore, calculation from the data for the system iron–oxygen–hydrogen, assuming the correctness of Eastman's data for the system iron–oxygen–carbon, yields a curve which agrees with the experimental figures except for the iron oxide–iron equilibria.

H. F. GILLBE.

Equilibrium in the reaction, $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$. R. N. PEASE and P. R. CHESEBRO (J. Amer. Chem. Soc., 1928, **50**, 1464—1469).—Equilibrium has been approached from both sides at $505°$, using a nickel–thorium catalyst. The mean experimental value, $K_{p(atm.)} = 0.037$, agrees closely with that calculated from the free energy equation for this reaction (Lewis and Randall, "Thermodynamics"). The presence of about 1% of carbon monoxide in the effluent gases is shown to be accounted for by the reactions $CH_4 + H_2O \rightleftharpoons CO + 3H_2$, and $CO_2 + H_2 \rightleftharpoons CO + H_2O$ (cf. Neumann and Jacob, A., 1925, ii, 532).

H. E. F. NOTTON.

Cryoscopic study of benzene solutions. J. M. PETERSON and W. H. RODEBUSH (J. Physical Chem., 1928, **32**, 709—718).—The f.-p. depressions of dilute solutions of methyl alcohol, ethyl alcohol, water, toluene, acetic acid, and benzoic acid in benzene have been measured by a new and more accurate method. The vapour densities of the solutes have been calculated from the f.-p. data by means of a thermodynamic relation. Excepting methyl alcohol and acetic acid, the f.-p. depression is a linear function of concentration for dilute solutions. The apparent mol. wt. of water and ethyl alcohol are independent of concentration and are, respectively, 18.1 and 46.4. Some association is indicated in the case of ethyl alcohol, and acetic acid behaves as a typical associated vapour. Except for benzoic acid, Henry's law may be assumed to hold in the more dilute solutions and further, where the f.-p. depression indicates polymerisation, an abnormal vapour density actually exists, which is shown to be a necessary consequence of the first conclusion. The interpretation of f.-p. data in connexion with the question of association is discussed.

L. S. THEOBALD.

Cryoscopic mol. wt. determination of glycogen in liquid ammonia. L. SCHMID, E. LUDWIG, and K. PIETSCH (Monatsh., 1928, **49**, 118—121).—Determination of the mol. wt. of various samples of glycogen by cryoscopic measurements in liquid ammonia, using a platinum resistance thermometer to measure the depression of the f. p., have been made. The mean value of the mol. wt. is 180.

J. W. BAKER.

Molecular association regarded as a phenomenon of molar concentration. G. G. Longinescu and (Mlle.) G. Chaborski (Bul. Soc. Romane Stiin., 1928, **30**, 3—29).—It is suggested that the various phenomena usually ascribed to the existence of association, e.g., abnormally small f.-p. depressions, are not so much a consequence of an actual polymerisation of the molecules as of a particularly high value of the molar concentration, C_m, i.e., the number of g.-mol. of the substance per litre. From the density data for a large number of organic liquids and solids, it appears that normal non-associated liquids have a value of about 10 for C_m. If, then, the degree of association of a particular liquid is taken as given by the quotient of its molar concentration by 10, the resulting values are in satisfactory agreement with those calculated from other physical properties, e.g., surface tension. Instances of abnormally large f.-p. depressions where no electrolytic dissociation can possibly occur are readily accounted for by C_m being less than normal, without it being necessary to postulate the existence of a non-electrolytic dissociation (cf. Walden, A., 1911, ii, 97). R. Cuthill.

Refraction and dissociation of electrolytes. I. In water. E. Schreiner (Z. physikal. Chem., 1928, **133**, 420—430).—From measurements of the molecular refraction at 18° in respect of the sodium D line and the hydrogen C and F lines of aqueous solutions of trichloroacetic acid and its sodium and lithium salts, the degree of dissociation of the acid has been calculated, the results being in satisfactory agreement up to concentrations of about 2 g.-mol./litre with the values obtained from conductivity data, when these are corrected for interionic forces and viscosity. For both hydrogen chloride and lithium chloride in aqueous solution the molecular refraction decreases with increasing concentration, the relation between these quantities being so similar in the two cases as to suggest that if the salt is completely ionised so also is the acid. In any case, the experimental data are not such as to permit of a calculation of the degree of dissociation of the acid. It seems probable that in respect of refraction molecules formed by association of ions behave like a mixture of the free ions. R. Cuthill.

Calculation of electrolytic dissociation constants from electrical conductivity. W. Nernst (Sitzungsber. preuss. Akad. Wiss., 1928, 4—8).—The alkali halides are said to be only partly ionised and it is shown that the fraction of non-ionised molecules may be calculated with considerable accuracy from the change of molecular conductivity with concentration. H. F. Gillbe.

Condition of silver chloride and other sparingly soluble substances in gelatin. A. C. Chatterji and N. R. Dhar (J. Indian Chem. Soc., 1928, **5**, 175—181).—Experiments on the electrical conductivity of silver chloride, formed in gelatin solutions by the interaction of silver nitrate and potassium chloride, indicate that only a very small proportion exists as ions, so that, instead of forming a supersaturated solution, the greater part of it is present in the colloidal state. Similar conclusions may be reached with regard to silver chromate. From the experimental results of Bolam and MacKenzie with silver chromate in gelatin (A., 1926, 678), there appears to be no definite relationship between the amount of silver present in the non-ionic condition and the quantity of gelatin present. Their $E.M.F.$ measurements show that the amount of silver present in the ionic condition for silver chromate in gelatin is, in most cases, below 40%. The hydrogen ions present in gelatin promote the dissolution of silver chromate, but not of silver chloride. Hence the amount of free silver ions present in the case of silver chloride is much less than in that of silver chromate. M. S. Burr.

Complex formation in solutions of stannous chloride and of stannous bromide. M. Prytz (Z. anorg. Chem., 1928, **172**, 147—166).—The normal potential of Sn/Sn``, determined from measurements with stannous perchlorate solutions, is 0·1359 volt. Measurements of the potential in 0·01M-stannous chloride and bromide solutions indicate that the activity of the stannous ion decreases rapidly as that of the halogen ion increases. The following constants have been calculated : $[SnCl`]/a_{Sn``}\cdot[Cl']=32$ ; $[SnCl_2]/[SnCl`][Cl']f'^2 = 5·5$ ; $[SnCl_3']/[SnCl_2][Cl'] = 0·6$ ; $[SnCl_4'']f''/[SnCl_3'][Cl']f'^2=0·3$ ; $[SnBr`]/a_{Sn``}\cdot[Br']=13$; $[SnBr_2]/[SnBr`][Br']f'^2=5$; $[SnBr_3'][SnBr_2][Br']=0·44$. From these figures the molar percentages of the various stannous complexes present in solutions containing halogen ions at increasing concentrations have been calculated. The concentration of the complex ions $SnCl_3'$ and $SnBr_3'$ increases over a certain concentration range at a rate roughly proportional to the halogen-ion concentration ; Goldschmidt's conclusion, viz., that these complex ions are the true reducing agents in acid solutions, is therefore supported. The results of the measurements are not incompatible with Young's figures for the conductivities of similar solutions. H. F. Gillbe.

Relation between the hydrolysis equilibrium constant of esters and the strengths of the corresponding acids. R. J. Williams, A. Gabriel, and R. C. Andrews (J. Amer. Chem. Soc., 1928, **50**, 1267—1271).—The equilibrium constants for the hydrolysis of some methyl and ethyl esters were determined by the direct method. For esters which are not too dissimilar, those of the stronger acids appear to be more completely hydrolysed under like conditions than those of the weaker acids. The constants, however, vary with the conditions, and their relation with the acid strength seems to be very complex. S. K. Tweedy.

Activity coefficients of ions in aqueous solutions of non-electrolytes. J. N. Brönsted and J. W. Williams (J. Amer. Chem. Soc., 1928, **50**, 1338—1343).—The effect of variation in the dielectric constant of the solvent on activity coefficients has been studied by measuring the solubilities of croceo- and luteo-tetranitrodiamminocobaltates in sodium chloride solutions containing ether or varying quantities of sugar. The requirements of the Debye–Hückel theory are confirmed, even when the solvent is a mixed one. S. K. Tweedy.

Activity coefficients of hydrogen chloride in ethyl alcohol. J. W. WOOLCOCK and (SIR) H. HARTLEY (Phil. Mag., 1928, [vii], 5, 1133—1144).—The activity coefficients of hydrogen chloride in ethyl alcohol have been determined from measurements of the $E.M.F.$ of the cell $H_2|HCl|AgCl|Ag$ at 25° over the concentration range 0·0003—1·2M. The values of the $E.M.F.$ obtained are in good agreement with those of Danner (A., 1924, ii, 117) and are lower than those of Harned and Fleysher (A., 1925, ii, 538). The activity coefficient over the range 0·0003—0·004M is given by $-\log f = 3·40C^{1/2}$, the value being greater than that required by the Debye theory. The discrepancies are attributed to the incomplete ionisation of the hydrogen chloride.
A. E. MITCHELL.

Activity of cadmium iodide in aqueous solution. F. H. GETMAN (J. Physical Chem., 1928, 32, 940—946; cf. this vol., 241).—The activity coefficients of cadmium iodide at concentrations down to 0·005M have been calculated from measurements at 25° of the $E.M.F.$ of the cells $Cd|CdI_2(M)|AgI|Ag$, $Cd|CdI_2(M)|PbI_2|Pb$–Hg, and Pt–H_2(1 atm.)$|HI(M)|PbI_2|Pb$–Hg. The values derived from the first two cells show good agreement. The variation of the activity coefficient with concentration is similar for cadmium chloride, bromide, and iodide. The coefficients for aqueous solutions form a progressive series in which the values are in the order given above, and they differ from each other more widely than do the corresponding values for the alkali halides. The divergence of the curve obtained by plotting the activity coefficient against the logarithm of concentration from the corresponding conductivity ratio curve is greatest in the case of cadmium iodide.
L. S. THEOBALD.

Entropy of dilute solutions. A. LANDÉ (Z. anorg. Chem., 1928, 171, 143—145).—Planck's expression for the entropy of a dilute solution has been derived by a method in which, instead of supposing that the temperature is raised and the pressure lowered until the solution is in the state of an ideal gas, these variables are kept constant, and the validity of the gas laws for the solutes is utilised. R. CUTHILL.

Application of the third law of thermodynamics to some organic reactions. G. S. PARKS and K. K. KELLEY (J. Physical Chem., 1928, 32, 734—750).—Previous investigations (Gibson, Latimer, and Parks, A., 1920, ii, 586) have only approximately confirmed the validity of the third law of thermodynamics for organic reactions. The law has now been tested using the reaction $CHMe_2·OH_{liquid} = COMe_{2 liquid} + H_{2 gas}$. The heat capacities of *iso*propyl alcohol and acetone have been measured by the method previously described (A., 1926, 232) from 70° to 293° Abs., and the heats of fusion at the m. p. found are 21·08 and 23·42 g.-cal./g. respectively. From these data $\Delta S_{298·}$ has been calculated on the assumption of the third law. From the equilibrium constants for this reaction in the gaseous phase, measured with copper as catalyst over the range 184—218°, the values of $\Delta F_{298·}$ and $\Delta H_{298·}$ have been calculated for the reaction involving the liquid alcohol and ketone, and the value of $\Delta S_{293·}$ thereby

obtained agrees well with that derived from the thermal data. The data of Lange (A., 1925, ii, 96), Conant and Fieser (A., 1923, ii, 727), and Schreiner (A., 1925, ii, 978) for the reaction $C_6H_4(OH)_2 {\rm solid} = C_6H_4O_2 {\rm solid} + H_2 {\rm gas}$ provide confirmation of the validity of the third law. L. S. THEOBALD.

Theory of fusion and of specific heat of liquid metals. A. MAGNUS (Z. anorg. Chem., 1928, 171, 73—81).—Assuming that the movements of the atoms of a liquid element are governed by the quantum laws, and that the frequency, ν, i.e., the reciprocal of the average interval between two successive impacts of an atom, is proportional to the nth power of the temperature, T, the equation $dU/dT = n(U - U_0)/T + (1-n)E(\nu,T)$ is obtained. Here U is the total energy, and $E(\nu,T)$ represents the Einstein function. Taking the value 2 for n, this equation agrees fairly well with the available data for the specific heat of mercury at higher temperatures, but below about 100° there are considerable deviations. These might appear to indicate that n is a function of T, but they can be accounted for satisfactorily by supposing that n does not vary, but that at lower temperatures the liquid is associated. It thus appears probable that when a solid melts fragments of the lattice persist in the liquid, and gradually disappear only as the temperature rises further and further above the m. p. The energy of a gas may be assumed to consist of a portion which relates to the period in which the atom is actually in collision, and is given by the above equation, and a portion, $1·5R$, which is calculated from purely kinetical considerations, and relates to the intervals between collisions. The lower the pressure the smaller is the former quantity, so that there is a continuous transition to an ideal gas.
R. CUTHILL.

Enantiotropy, monotropy, and pseudomonotropy. I. N. NAGASAKO (Bull. Chem. Soc. Japan, 1928, 3, 90—95).—Thermodynamic relationships are discussed, and pseudo-equilibria are considered.
H. F. GILLBE.

One-component system SiO_2–catalysts for the slow transformations. C. J. VAN NIEUWENBURG and C. N. J. DE NOOIJER (Rec. trav. chim., 1928, 47, 625—634).—Fenner (A., 1913, ii, 133) fixes the stability regions of the modifications of silica as quartz, up to 870°, tridymite, 870—1470°, and cristobalite from 1470° to 1710°, the true stable m. p. Since as a rule Fenner employed a very large excess (200%) of catalyst (sodium tungstate) to accelerate the rates of the changes, he investigated a part of the three-component system SiO_2–WO_3–Na_2O. An attempt has been made to obtain a more satisfactory catalyst. In all, results from 44 catalysts are given. The silica used was a pure miocene quartz sand from Lommel (Belgium), 99·9% SiO_2, the small amount of impurity consisting chiefly of rutile, hæmatite, zircon, and staurolite. The washed, ignited sand was graded (between 20 and 30 mesh per cm.), mixed with 1% of catalyst, and heated in a carbon resistance furnace up to 1300° in $1\frac{3}{4}$—2 hrs. and maintained at 1300°±15° for 1 hr. After removal from the furnace the density was determined. The original sand had d 2·64(5). On being heated

alone to 1300° the value fell to 2·62(5). The percentages converted by the catalysts are calculated on the assumption that the density of the completely converted product should be 2·30 (the mean between those of tridymite and cristobalite, 2·27 and 2·33). Fenner's catalyst (1% of sodium tungstate) causes 23% inversion, whilst the most effective examined, lithium carbonate, converts 98%. Sodium and potassium carbonates and sodium fluosilicate are also very effective catalysts. Phosphoric oxide and boron trioxide recommended by Rebuffat and Parravano were found to give poor results. The effect of grain size on the rate of transformation under otherwise comparable conditions is emphasised.

The possible technical value of using such catalysts as alkali carbonates in the manufacture of silica bricks is mentioned.   H. INGLESON.

Vapour pressures of binary systems. A. W. PORTER (Trans. Faraday Soc., 1928, 24, 343—347; cf. A., 1921, ii, 377).—It follows from the law of Duhem and Margules that equations connecting the vapour pressure with the concentration should not violate the condition that each side of the equation must be symmetrical with respect to the molar fractions (μ_1 and μ_2) of the constituents, each of which is supposed to be of the same molecular type as the substance in the vapour state. The application of Perman's data for aqueous solutions of sugar shows that Raoult's law does not hold, even in the most dilute regions, and satisfactory equations representing the data are derived for both constituents. From the data for potassium chloride solutions at 80°, general considerations relating to true, colloidal, and immiscible solutions, and to systems in which solvent is absorbed on the solute, are advanced. The equations are also applied to the determination of equilibrium constants in terms of vapour pressures instead of masses or molar fractions, and it is pointed out that the so-called activity coefficients are not constants but functions of μ_1 and μ_2 and of a term representing the mutual action between the components present. A solution may be almost " ideal " for the solvent in the presence of a small quantity of solute, but it is then by no means ideal from the point of view of the latter. The conditions are more complex for ternary systems.   J. GRANT.

Crystals of β-brass. VON GÖLER and G. SACHS (Naturwiss., 1928, 16, 412—416).—The gradual transformation of β-brass over the temperature range 300—470° is not accompanied by any change in the Laue pattern large enough to indicate a new lattice. The increase in temperature causes the weaker interferences to disappear and the stronger ones are reduced in intensity. The relation between the temperature effect and recrystallisation is discussed. The effective slip planes have been studied from tensile tests.   R. A. MORTON.

Equilibrium diagram of the copper-rich side of the copper-tin system. T. MATSUDA (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 141—161).— The existence of a transformation at 590° in copper-tin alloys containing 15—26·5% of tin has been confirmed by thermal analysis and by electrical resistance measurements. It is attributed to a eutectoid change, the eutectoid containing 26% of tin. The existence of a eutectoid transformation at 520° was also confirmed. Apart from these changes the equilibrium diagram for alloys containing 0—40% of tin agrees with that of Bauer and Vollendruck. Drop forging tests show that alloys containing 18—22% of tin become malleable above 520°. These alloys show a reduction in Brinell hardness when quenched from above 590°.   C. J. SMITHELLS.

Tin–bismuth and tin–cadmium alloys in the solid state ; assumption of stable equilibria at various temperatures. M. LE BLANC, M. NAUMANN, and D. TSCHESNO (Ber. Sächs. Ges. Wiss., math.-phys. Kl., 1927, 79, 71—106; Chem. Zentr., 1928, i, 401).—In the system tin–bismuth there is on the bismuth side a small homogeneous region extending to 1·5 at.-% Sn (micrographical observation) or 3·5 at.-% Sn (electrical observations). On the tin side at about 13 at.-% Bi a compound (? BiSn$_7$) appears, forming a homogeneous system with excess of tin. In the system tin–cadmium at 130° with 20 at.-% Cd a compound, probably CdSn$_4$, is formed, yielding a heterogeneous system with excess of cadmium. With excess of tin at 2·5 at.-% of cadmium a single homogeneous phase is formed.

     A. A. ELDRIDGE.

Thermochemical study of the system cadmium–mercury. T. W. RICHARDS, H. L. FREVERT, and C. E. TEETER, jun. (J. Amer. Chem. Soc., 1928, 50, 1293—1302).—The negative heats of dissolution in mercury of cadmium amalgams containing 16—33% Cd increase on ageing, due to the gradual disappearance of the traces of liquid phase present owing to the phenomenon of " coring." This preliminary segregation of the components may be prevented by chilling at −190°, and fresh samples so chilled give the same heats of dissolution as aged amalgams. The solidus point is defined as the point at which melting begins when the solid phase is completely homogeneous; it can be found exactly only by successive thermochemical determinations on quenched samples. The results agree with those of Bijl (A., 1903, ii, 6).   S. K. TWEEDY.

Heusler's alloys. Manganese–aluminium–copper. O. HEUSLER (Z. anorg. Chem., 1928, 171, 126—142).—The constitution of the ferromagnetic alloys of manganese, aluminium, and copper has been studied, and the m.-p. diagrams are reproduced. Since the range of composition for which the alloys are magnetic corresponds with the region of existence of ternary β mixed crystals it appears probable that these give rise to the magnetic property. In order to confirm this view, differential heating curves have been obtained with an alloy containing 14·0% of manganese and 10·5% of aluminium, and quenched from 700° and then aged at various temperatures. The results show that the thermal effect of the magnetic transformation vanishes if the β-mixed crystals are decomposed by ageing. This accords with the theory (cf. A., 1927, 502) that the ferromagnetic state results from the association of the atoms in the homogeneous solid solution to magnetic molecules. It has not been possible, how-

ever, to ascertain the composition of the magnetic substance. R. CUTHILL.

Thermal dissociation of cadmium nitrate. G. MALQUORI (Gazzetta, 1928, **58**, 217—222).—A more detailed description of results already published (this vol., 593). O. J. WALKER.

Solution equilibria between crystalline zinc hydroxide and sodium hydroxide. R. FRICKE (Z. anorg. Chem., 1928, **172**, 234—242).—The solubility of rhombic zinc hydroxide in sodium hydroxide solution is independent of the relative quantities of the substances present. For solutions containing 7—42% of sodium hydroxide, equilibrium is attained at 30° in less than 2·5 hrs., but with concentrations greater than 30% the zinc hydroxide is converted into oxide. Monosodium zincate may be prepared by saturating a hot 44% solution of sodium hydroxide with zinc oxide, filtering from residue with exclusion of carbon dioxide, and keeping the solution in a closed vessel at the ordinary temperature. After about 2 days long needles commence to separate, and by gentle shaking a thick mass of crystals is obtained. H. F. GILLBE.

Equilibrium in binary systems containing carbamide as one component. N. A. PUSCHIN and D. KONIG (Monatsh., 1928, **49**, 75—82).—The binary systems formed by carbamide (B) with trichloroacetic acid, resorcinol, quinol, phenol, guaiacol, α-naphthol, naphthalene, and diphenyl (A) have been investigated by the method of thermal analysis. In the first three cases equimolecular *compounds* of the type AB, m. p. 80°, 101°, and 130°, respectively, are formed, whilst with phenol a *compound* of the type A₂B, m. p. 59°, is formed. Guaiacol and α-naphthol yield only mechanical mixtures. With naphthalene and diphenyl two liquid layers are formed, the mutual solubilities of carbamide and the hydrocarbons being very small. The eutectic temperatures in the other cases are, respectively, 59° and 27°, 90° and 84°, 110° and 125°, 36°, 24·5°, and 65°, the corresponding mol. percentages of the component A being 37 and 75, 30 and 75, 20 and 63, 93·5, 94 and 67, respectively. J. W. BAKER.

X-Ray investigation of the decomposition of complex iron cyanides. R. BRILL and H. MARK (Z. physikal. Chem., 1928, **133**, 443—455).—When ammonium ferrocyanide is heated in a vacuum at 320°, the product appears, from its X-ray diagram, to be ferrous ferrocyanide. If this is decomposed further by heating in a current of nitrogen and hydrogen in the proportion of 1 : 3, lines which appear to correspond with α-iron soon appear in the diagram, and ultimately pure α-iron remains. At certain stages of the reduction, intermediate products, probably carbides and nitrides, can also be detected. R. CUTHILL.

Causticisation of sodium carbonate by ferric oxide. XI. Heat of dissolution of sodium carbonate. M. MATSUI, S. NAKATA, K. AKIYAMA, and K. BITO (J. Soc. Chem. Ind. Japan, 1928, **31**, 140—147).—The heat of dissolution of sodium carbonate in water was measured by means of a constant-temperature calorimeter with an electric

heating device, and found to be $Na_2CO_3[s]+aq.[1000$ mol.$]=Na_2CO_3[aq.]+5606·7\pm22·1$ g.-cal. at 25°. S. OKA.

Decomposition of orthoclase. O. K. BOTVINKIN (J. Russ. Phys. Chem. Soc., 1927, **59**, 1029—1031).—Observations on the decomposition of orthoclase by water vapour at 115°, 315°, and 318° and by water saturated with carbon dioxide at 75, 90, 95, and 120 atm. show that orthoclase is very stable towards water and aqueous solutions of carbon dioxide; the stability decreases slightly with rise of temperature and of pressure. A. RATCLIFFE.

Solubility of cadmium sulphide in hydrochloric acid. M. AUMÉRAS (Compt. rend., 1928, **186**, 1541—1543).—The application of the author's method for the study of equilibria in ionised systems (A., 1927, 1141) has shown that the solubility at 16° of cadmium sulphide in hydrochloric acid can be represented by $[HCl]=970[H_2S][CdCl_2]$ for dilute solutions. This corresponds with complete dissociation of hydrochloric acid and of cadmium chloride and with the single-stage dissociation $H_2S \rightleftharpoons HS'+H^{\cdot}$. To avoid oxidation, the experiments were performed in an atmosphere of nitrogen. J. GRANT.

Equilibria of sulphides and silicates in slags. W. JANDER and K. ROTHSCHILD (Z. anorg. Chem., 1928, **172**, 129—146).—The reversible equilibria in the systems lead silicate–ferrous sulphide, cuprous silicate–ferrous sulphide, nickelous silicate–ferrous sulphide, lead silicate–cuprous sulphide, cuprous silicate–nickelous sulphide, nickelous silicate–lead sulphide, and sodium silicate–lead sulphide have been investigated. The simple mass action law is not applicable to these systems, but by use of an approximation equation derived from the Lorenz modified mass action law the constants 1·12, 1·44, 2·25, 10·01, 1·02, and 1·64, respectively, are obtained. In the sodium silicate–lead sulphide system the experimental error is too large to admit of a satisfactory constant being obtained, since the reaction proceeds nearly to completion. From the constants for any two systems, that for a third may be calculated with considerable accuracy. The affinity relationships of the various metals towards sulphur and oxygen alter considerably at higher temperatures. H. F. GILLBE.

Quaternary system, water–sodium nitrate–sodium chloride–sodium sulphate from below 0° to above 100°. A. CHRETIEN (Caliche, 1927, **9**, 248—259).—The eutectic points and the composition of the solid and liquid phases have been determined. CHEMICAL ABSTRACTS.

Reciprocal pair: $2NaCl + Ba(ClO_3)_2 = 2NaClO_3+BaCl_2$. C. DI CAPUA and A. BERTONI (Gazzetta, 1928, **58**, 249—253).—The isotherms of the four systems $NaClO_3$–$NaCl$–H_2O, $NaCl$–$BaCl_2$–H_2O, $BaCl_2$–$Ba(ClO_3)_2$–H_2O, $Ba(ClO_3)_2$–$NaClO_3$–H_2O have been studied at 20° and the triangular diagrams constructed. The stable pair is found to be $Ba(ClO_3)_2$–$NaCl$. The composition of the solutions in equilibrium with the two stable triads $Ba(ClO_3)_2+NaCl+NaClO_3$ and $Ba(ClO_3)_2+NaCl+BaCl_2$ as solid phases has also been determined. O. J. WALKER.

Vapour pressure and heat of dilution of aqueous solutions. V. Activity. E. P. Perman (Trans. Faraday Soc., 1928, **24**, 330—336).—See this vol., 368.

Properties of metallic hydrides. A. Sieverts and A. Gotta (Z. anorg. Chem., 1928, **172**, 1—31).—The heats of formation of cerium, praseodymium, and lanthanum hydrides are 42,260, 39,520, 40,090 g.-cal./g. of hydrogen respectively, whilst the densities of the hydrides are 5·55, 5·56, and 5·83, respectively. The heats of formation differ very little from those of calcium, barium, and lithium hydrides, but whereas these substances have considerably greater densities than the corresponding metals, the reverse is true of the rare-earth hydrides investigated and of titanium, zirconium, and vanadium hydrides. In several ways, the rare-earth halides resemble those of the elements of the titanium and vanadium groups of the periodic classification, and are by their semi-metallic nature sharply differentiated from the salt-like hydrides formed by the elements of the first and second groups, and from the metallic hydrides of iron, cobalt, nickel, and platinum. H. F. Gillbe.

Accuracy of Stohmann's thermochemical data. P. E. Verkade and J. Coops, jun. (Rec. trav. chim., 1928, **47**, 606—618).—Swientoslawski's method (A., 1920, ii, 470) of correcting the older thermochemical data to the basis of the international thermochemical standard of 1922 (heat of combustion of benzoic acid 6324 g.-cal.$_{15}$/g., weighed in air) consists in comparing values A_1, A_2, A_3, etc. obtained by the earlier worker with values A_1', A_2', A_3' found later under the same conditions but using the international standard. The series of the earlier worker are regarded by Swientoslawski as homogeneous if the ratios α_1, α_2, α_3, etc. vary only within 0·1—0·15%. The mean of the values is used by him to correct the earlier data.

The heats of combustion of about 40 substances previously determined by Stohmann have been redetermined. The factors required to bring Stohmann's data to the international basis vary from 1·0031 to 0·9892, but lie mainly between the limits 0·994 and 1·002. Stohmann's results do not fall into two homogeneous groups as stated by Swientoslawski and Pillich, but constitute a very heterogeneous group. It is impossible to apply any correction to the data of Stohmann which could reduce them to the present international standard. Probably the error of Swientoslawski and Pillich arises from the use of too few comparison substances. H. Ingleson.

Absolute determination of heat of combustion of benzoic acid. W. A. Roth, O. Doepke, and H. Banse (Z. physikal. Chem., 1928, **133**, 431—442).—A redetermination of the heat of combustion of benzoic acid has given the value of 6323 g.-cal.$_{15}$/g. R. Cuthill.

Heat of formation of molecular hydrogen. F. R. Bichowsky and L. C. Copeland (J. Amer. Chem. Soc., 1928, **50**, 1315—1322).—Direct determinations give 105,000±3500 g.-cal. at constant pressure. S. K. Tweedy.

Valve oscillator for use in conductivity measurements. J. W. Woolcock and D. M. Murray-Rust (Phil. Mag., 1928, [vii], **5**, 1130—1133).—Describes the construction, from commercial standard components, of a valve oscillator of the type described by Ulich (A., 1925, ii, 671). The apparatus has been employed in the measurement of the conductivities of dilute non-aqueous solutions. A. E. Mitchell.

Conductivity measurement by means of an oscillating valve circuit. E. F. Burton and A. Pitt (Phil. Mag., 1928, [vii], **5**, 939—943).—The plate-grid coil and grid-filament coils of a valve-oscillating circuit are arranged round a tube which is to contain the specimens to be examined. The oscillations in the circuit are rectified in a second valve circuit and passed through a galvanometer. The steady current through the galvanometer is balanced by means of a contra-current from a potentiometer arrangement. If, with the circuits so arranged, a slightly conducting liquid is placed in the tube, a deflexion of the galvanometer is obtained. For example, a change in conductivity of water from 10·5 to 11·5×10⁻⁶ produced a galvanometer deflexion change of 32·2—33·7. W. E. Downey.

Voltage effect in the conductivity of electrolytes in weaker fields. M. Wien (Ann. Physik, 1928, [iv], **85**, 795—811).—In an earlier paper (A., 1927, 940) a voltage effect in the form of a deviation from Ohm's law for electrolytic resistances was recorded for moderate and strong fields. An extension of the Debye theory of electrolytic conduction has been made by Joos and Blumentritt (Physikal. Jahrb., 1927, **28**, 836) but it is restricted to weaker fields. A method of measuring the voltage effect with weak fields has now been devised and applied to a series of ferro- and ferri-cyanides and other salts in different concentrations. The voltage effect in weak fields is in accord with the expression $\Delta\lambda_v = AX^2(1-BX^2)$, A and B being constants and X the applied field in volt/cm. A is approximately proportional to the square of the product of the valencies (z) of the ions, and approximately proportional to the root of the conductivity : the expression $A = 5·5 \times z_1^2 z_2^2 (\kappa_0/\kappa)^{\frac{1}{2}} \times 10^{-13}$, in which κ_0 is the conductivity 0·001, is empirically valid. A also depends to some extent on the nature of the ions. The B term likewise increases as the product of the valencies increases, but the rate of increase of A is much greater than that of B. As the concentration decreases B increases ; on an average B is three times as great with a concentration corresponding with conductivity $\kappa = 0·000125$ as $\kappa = 0·001$.

Experiments with solutions of cobalt chloride and of potassium iodide in acetone show results of the same general type, but A is greater and B smaller than in aqueous solutions under the same conditions. R. A. Morton.

Behaviour of dilute electrolytes in high field strengths. M. Blumentritt (Ann. Physik, 1928, [iv], **85**, 812—830).—A satisfactory theoretical basis for the experimental results of Wien (cf. preceding abstract) has been evolved in terms of the Debye–Hückel theory. The equation $\Delta\lambda = AX^2(1-BX^2)$ requires A to be approximately given by $[1/(D\eta)^{\frac{1}{2}}]g(z)$, in which η is the equivalent concentration per litre, and $g(z) = z^{3·5}$ for binary electrolytes with ions having

equal viscosity constants. It is shown that the initial effect $\Delta\lambda = AX^2$ depends on concentration, dielectric constant, and the valencies of the ions, in exactly the manner found in Wien's experiments. The second term BX^2 requires B to vary as $D/\eta \cdot f(z)$, $f(z)$ being equal to z for binary electrolytes with ions showing equal viscosity constants. B varies as found by Wien. Such discrepancies as arise occur with 1—3 and 1—4 valencies in the electrolytes, and are probably due to departures from the Debye–Hückel theory. The application of Onsager's modification of the theory should clarify the position but the calculations are likely to prove more complicated.

R. A. MORTON.

Contact potentials. I. Calculation of contact potential from kinetics of diffusion. E. DENINA (Gazzetta, 1928, 58, 160—177).—The theory of electrode–electrolyte potentials is developed from the kinetics of diffusion, and it is shown that the Nernst expression $E = (RT \log P/p)/nF$ can be regarded as a special case of a more general equation. The potential at the interface of two non-miscible solutions and the Soret effect are discussed in relation to the new theory.

R. W. LUNT.

Anomalies of the *E.M.F.* relationships of palladium in hydrogen chloride solutions. F. MÜLLER (Z. Elektrochem., 1928, 34, 237—240).—The anomalous behaviour of palladium when used as an indicator electrode in oxidation–reduction reactions is connected with the presence of hydrogen chloride in the solutions. The difference in the behaviour of this metal compared with that of the others of the same group is ascribed to the existence of a sparingly soluble film of unknown nature on the surface of the electrode.

H. F. GILLBE.

Determination of the ζ-potential on cellulose. Method. D. R. BRIGGS (J. Physical Chem., 1928, 32, 641—675).—A method for the determination of the ζ-potential on cellulose materials by means of measurements of the streaming potential is described. Preliminary experiments showed that substitution of κ_s, the specific conductance of the liquid in the diaphragm, for κ_D, that of the liquid in bulk, gives values of the ratio $H\kappa_s/P$, where H is the streaming potential under a hydrostatic pressure P, which are more nearly independent of the tightness of packing of the cellulose material. κ_s can now be accurately measured by the method described and absolute values of ζ can be obtained from the streaming potential equation $\zeta = 4\pi\eta\kappa_s H/P\varepsilon$. ζ varies with the source and history of the cellulose used; approximate values for two samples of a rag pulp and for a wood pulp are 0·214, 0·016, and 0·0083 volt, respectively. The effect of ions on the ζ-potential of cellulose is studied. The literature and development of the streaming potential equation are reviewed.

L. S. THEOBALD.

Overvoltage. IV. Measurement of minimum overvoltage from the current–voltage curve. V. Relationship between minimum overvoltage and current density. T. ONODA (Z. anorg. Chem., 1928, 172, 87—108, 109—120).—IV. The hydrogen overvoltage at gold, platinum, copper, nickel, and mercury electrodes has been determined from the current–voltage curves. This method shows the influence on the overvoltage of the mode of storage of the electrodes, and also the attainment of a minimum value after anodic polarisation. The minimum values in volts obtained at 30° in 2N-sulphuric acid solution are : platinum 0·0061, gold 0·0084, nickel 0·084, copper 0·091, and mercury 0·855, in good agreement with the earlier measurements (cf. A., 1926, 941).

V. The anodic polarisation of a gold electrode at a current density greater than 0·3 coulomb/cm.² results in a certain minimum overvoltage, expressed by the equation $\pi_m = \pi_0 I^b$, where π_m is the minimum overvoltage, b is a constant dependent only on the metal employed, and π_0 is the minimum overvoltage when the current density I is 1 milliamp./cm.² The overvoltage is not influenced by a film of oxide on the electrode nor by adsorbed oxygen, but is concerned solely with the gold electrode.

H. F. GILLBE.

Electrochemical behaviour of silicate glasses. III. Cathode and anode gases. IV. Solid electrolytic deposits. M. J. MULLIGAN, J. B. FERGUSON, and J. W. REBBECK (J. Physical Chem., 1928, 32, 779—784, 843—851; cf. A., 1926, 31; this vol., 245).—III. Additional evidence of the formation and disappearance of cathode gas during the electrolysis of various glasses and of the permeability of glass to various ions is advanced. The disappearance of gas on current reversal may be due to the sodium from the hydroxide film entering the glass, and the reformation of water which is adsorbed ; in support of this, it is found that hydrogen disappears only in the presence of sodium hydroxide. Cathode gas has now been obtained with Schott glasses and with Cavalier glass. Replacement of the sodium in the soda–lime glass by silver in one case prevented the formation of cathode gas, but other experiments indicated that silver does not always uniformly replace the sodium. The movement of water into or out of glass under the influence of an electric current is also indicated. Anode gas is formed with soda–lime glass at 275° and possibly at lower temperatures. This is accompanied by the formation of a deposit insoluble in water but soluble in nitric acid ; traces of such deposits are formed at 100°. The results are in general agreement with those of Le Blanc and Kerschbaum (A., 1910, ii, 481) except for the lower temperatures now observed, a difference which may be ascribed to differences in the composition of the glasses used.

IV. Solid deposits are formed near the surface when the glasses are electrolysed with mercury first as anode and then as cathode. The deposit consists mainly of silicon, probably produced by the action of sodium on the silicates. Silver has also been deposited. The formation of these deposits appears to result from a puncturing of the anodic glass layers, and the dielectric strength of these layers depends partly on the nature of the ions which reach them.

L. S. THEOBALD.

Theory of passivity. II. Relation between passivation current density and time. W. J. MÜLLER and O. LÖWY (Monatsh., 1928, 49, 47—74). —On the basis of the theory of passivity previously enunciated (Müller and Konopicky, this vol., 247) it

is shown that the smaller the current density employed the thicker is the protective film, and a formula for the relationship between the passivation time (t_p) and the current density (i_0/F_0) is deduced. This formula $t_p=B(i_0/F_0)^{-m}$, where B is a constant and m is an exponential obtained from the experimental data, represents a straight line. $\log t_p=\log B-m \log (i_0/F_0)$ when the logarithms of time and current density are employed. The values of i_0 calculated from this equation are found to be in good agreement with the observed values in the results previously obtained for iron, nickel, zinc, and chromium, and also with fresh data for iron in various electrolytes at 20°, in N-sulphuric acid, and in sulphuric acid containing ferrous and ferric sulphates. The earlier suggestion (loc. cit.) that the protective film consists of stable hydrated sulphates is confirmed by photomicrographic investigations of the surface of the iron electrodes on which, when passivity has been produced, a crystalline layer of ferrous sulphate heptahydrate can be detected. The behaviour of protected, unprotected, and rotating electrodes has been studied and the results are those which would be expected from the theory. In electrolytes saturated with ferrous sulphate the minimum current density at which passivity can be produced has a higher value in the case of the unprotected electrode than in the case of the protected electrode, and a still higher value when a rotating electrode is used. With relatively high current densities (above 0·31 amp./cm.²) the passivation time is approximately the same with both the protected and the unprotected electrodes, but at lower current densities the time is very much longer in the latter case. With a rotating electrode the time increases rapidly with decrease in current density at values of the latter below 0·54 amp./cm.² At the same current densities the same passivation time is observed both with polished electrodes and with electrodes which have been covered with an oxide film by immersion in potassium chromate solution (Evans, A., 1927, 619). The oxide film is completely dissolved in the acid solutions used and hence any theory of passivity based on the protective oxide film is excluded.

J. W. BAKER.

Effect of superposed alternating current on the deposition of zinc–nickel alloys. H. C. COCKS (Trans. Faraday Soc., 1928, **24**, 348—358).—The variations in the average deposition potential and in the composition of the zinc–nickel alloys deposited cathodically from 0·1N-acid sulphate solutions with variations in $D.C.$ density and in the ratio $A.C : D.C.$ are recorded. In the apparatus used, although a leak of $A.C.$ into the $D.C.$ circuit and vice versa occurred, the readings of the hot wire and moving-coil ammeters in series with the cathode indicated only the $D.C.$ and $A.C.$ passing through the electrolytic cell. With rise of $D.C.$ density the reaction-resistance to nickel deposition and the hydrogen evolution increase; at the same time, the hydrogen overvoltage rises, and zinc deposition increases until it becomes the main process. As the density of the $D.C.$ component of the pulsating current is increased (the ratio $A.C : D.C.$ being constant), the composition of the deposits above the critical $D.C.$ density follows the curve for $D.C.$ alone. The phenomena attending the deposition of

zinc and nickel together and separately are outlined, and an explanation is given of the effects of superposed $A.C.$ based on its known depolarising effect on irreversible electrode processes and on the assumed net result of the periodic increases in current density above that of the $D.C.$ component (cf. Allmand and Cocks, A., 1926, 912).

J. GRANT.

Theory of electrolytic deposition of chromium from chromic acid solutions. Y. KATO and T. MURAKAMI (J. Soc. Chem. Ind. Japan, 1928, **31**, 124—128).—The current efficiency for the electrolytic deposition of chromium is very low, being less than 30% in most cases, but it increases with increasing current density. The authors assume that hydrogen overvoltage is due to accumulation of monatomic hydrogen and apply Nernst's formula to the calculation of the concentration of the monatomic hydrogen. On this assumption, the values of the concentration of the monatomic hydrogen at different densities are calculated from the overvoltage. When these concentrations and the amount of chromium deposited are plotted against the current density the resulting curves are found to be nearly parallel, and from this it is inferred that the electrolytic deposition of chromium from chromic acid solution does not result directly by the loss of electrons from CrO_4'' or Cr_2O_7'', but indirectly by the reducing action of the monatomic hydrogen on the film (consisting of chromium oxides) which is formed on the cathode. Superposition of alternating current on direct current makes the current efficiency very low, and this fact favours the above theory. The lowering of the current efficiency with rising temperature is also in accord with the theory.

K. KASHIMA.

Theory of electrodialysis. R. BRADFIELD (Naturwiss., 1928, **16**, 404—408).—Electrodialysis has the advantage of removing electrolytes from colloidal solutions more quickly than ordinary dialysis. The colloidal solution is placed between two membranes outside of which are electrodes dipping into running water. With the application of an electric field, the anions pass through the anode membrane and appear as acid, whilst the cations appear in the cathode chamber as hydroxide. With most membranes, the ions diffuse unequally and excess of one kind may seriously modify the properties of the colloid in the middle chamber. The defects of electrodialysis are minimised by using very small currents, but in so doing the advantage of rapidity is lost. If suitable negative cathode membranes and positive anode membranes could be obtained it would be possible to conserve both speed and neutrality. A stable positive membrane can be made by treating a collodion film with a 2% solution of hæmoglobin. Experiments with a parchment membrane on the cathode side and collodion, parchment, or hæmoglobin membranes on the anode side indicate that the latter is much the best, since after electrodialysis the solutions in the middle chamber show the smallest departures from neutrality with the new membrane. The efficiency of the electrodialysis ($E=[\text{acid}+\text{base}]/\text{coulombs}$) is, moreover, higher for the hæmoglobin membrane than for the other membranes; e.g., for sodium chloride it is 0·71 as against 0·41 and 0·46. For the salts of weak

acids E is considerably greater than unity, in apparent contradiction with Faraday's law. An explanation of this phenomenon is given. R. A. MORTON.

Region of existence of unimolecular reactions. L. S. KASSEL (J. Amer. Chem. Soc., 1928, 50, 1344—1352).—Previously recorded experimental data confirm the theoretical prediction (cf. this vol., 372) that unimolecular reaction rates decrease at low pressures. The typical decomposition of a polyatomic molecule will be bimolecular at high pressures (due to collision reactions), with a negligible unimolecular part (due to spontaneous decomposition of activated molecules); as the pressure is lowered the latter part gains in importance until it dominates and obscures the bimolecular part. At still lower pressures the unimolecular reaction rate decreases until it merges into a second order rate having a constant higher than that for the high-pressure bimolecular reaction. In the latter stage nearly all the activated molecules decompose, since deactivation collisions become infrequent. The decomposition of acetaldehyde represents a transition from the high-pressure bimolecular to the unimolecular stage, and the decomposition of azomethane, a transition from the unimolecular to the low-pressure bimolecular stage. Possible methods of deciding which of several types of bimolecular reaction dominates a given reaction are outlined. Unimolecular reaction rates vary over a wider range than Dushman's formula allows (A., 1921, ii, 315). S. K. TWEEDY.

Irregular mode of spherical propagation of flame. T. TERADA and K. YUMOTO (Proc. Imp. Acad. Tokyo, 1928, 4, 98—101; cf. A., 1926, 1106).—The corrugated surface of the nearly spherical flame front previously observed when mixtures of hydrogen and oxygen were ignited by a spark is attributed to shrinkage of the gas due to condensation of water vapour. The presence of anti-knock materials in the gas reduced the effect. C. J. SMITHELLS.

Effects of anti-detonants in the vapour phase. AUBERT, DUMANOIS, and PIGNOT (Compt. rend., 1928, 186, 1298—1299; cf. Moureu and Dufraisse, this vol., 180, 251).—The effect of 5% of an anti-detonant in a mixture of air and pure hexane in the wt.-ratio 17·52 : 1 is to increase the duration of combustion. In particular, with lead tetraethyl the maximum pressure is attained by a series of steps (instead of by an apparently continuous, rapid rise) which are supposed to represent successive stages of increasing complexity in the oxidation of the hydrocarbon, the complete evolution of which is ensured by the presence of the anti-detonant. J. GRANT.

Limits of inflammability of gases and vapours. H. F. COWARD and G. W. JONES.—See B., 1928, 392.

Explosions in closed vessels. Correlation of pressure development with flame movement. O. C. DE C. ELLIS and R. V. WHEELER.—See B., 1928, 392.

Flammability of mixtures of methyl and ethyl chlorides and bromides [with air]. G. W. JONES.—See B., 1928, 428.

Neutral salt action in ionic reactions. Temperature coefficients of neutral salt action. A. VON KISS and (FRL.) I. BOSSÁNYI (Rec. trav. chim., 1928, 47, 619—626; cf. A., 1927, 632, 945).—The reaction taking place between persulphate and iodine ions has been studied at seven temperatures from 0° to 75°. The temperature coefficient is unaffected by the presence of neutral salts, e.g., magnesium sulphate or potassium nitrate. The temperature coefficient has the normal value which falls with rise of temperature. H. INGLESON.

Velocity of decolorisation of potassium permanganate by oxalic acid and the influence of other substances in the solution. M. BOBTELSKY and D. KAPLAN (Z. anorg. Chem., 1928, 172, 196—212).—The occurrence and nature of induction are discussed especially in relationship to the electrical condition of the reacting system. The influence of added substances on the velocity of reduction of potassium permanganate solutions by oxalic acid has been investigated. In dilute solution the influence of ions which are unable to undergo oxidation or reduction is very small, whereas in concentrated solution the action is extremely variable, zinc, cadmium, aluminium, and chlorine ions accelerating the reaction very considerably. Other ions exert specific accelerative influences, and the suggestion is made that a method for the determination of such ions could be based on this effect. H. F. GILLBE.

Equilibrium in salt solutions. "Activity theory of reaction velocity." W. F. K. WYNNE-JONES (J.C.S., 1928, 1230—1233).—A criticism of Soper's results (cf. this vol., 24, 26). F. J. WILKINS.

Equilibrium in electrolyte solutions and the reaction-velocity equation. F. G. SOPER (J.C.S., 1928, 1233—1235).—A reply to Wynne-Jones (see preceding abstract). The evaluation of the free energy change of the medium (J. Physical Chem., 1928, 32, 67) is amended. F. J. WILKINS.

Action of nitrous acid on amino-compounds. I. Methylamine and ammonia. T. W. J. TAYLOR (J.C.S., 1928, 1099—1105).—Nitrous acid solutions stabilised according to a method previously described (A., 1927, 943) were used. They were prepared from barium nitrite and sulphuric acid, without separation of the barium sulphate. The velocity of reaction with methylamine is proportional to the product $[CH_3 \cdot NH_3^{\cdot}][NO_2'][HNO_2]$. It is suggested, therefore, that the reaction occurs between undissociated molecules of methylamine nitrite and nitrous acid. The reaction is retarded by potassium chloride and strong acids. Ammonia behaves in exactly the same way and the reaction mechanisms are therefore probably identical. F. J. WILKINS.

Kinetics of oxidation of organic compounds by bromine. I. Action of bromine on oxalic acid. E. JÓZEFOWICZ (Rocz. Chem., 1928, 8, 123—151).—The reaction between bromine and $N/80$—$N/20$ oxalic acid at 20° proceeds according to the equation $dx/dt = k_0(a-x)^2/x^2$. The hydrogen bromide produced has a retarding effect on the velocity; in the presence of excess of hydrogen bromide $dx/dt = k_0(a-x)^2/(c+x)^2$. Strong acids such as hydrochloric or nitric acid also exert an inhibiting influence, which is, however, one fifth of that for hydrogen bromide; the velocity

equation is in this case $dx/dt = k_0(a-x)^2/(0.2c+x)^2$, whilst in the presence of bromides a greater retardation takes place, dx/dt being $k_0(a-x)^2/(0.6c+x)^2$. Chlorides do not affect the reaction, which is accelerated by raising the p_H. The temperature coefficient of the reaction is 4·52. The reaction of oxidation of acid oxalates proceeds according to the same equation as for oxalic acid, but with a velocity three times as great, whilst neutral oxalates react so rapidly as to render the analysis of the reaction impossible. The above results indicate that hypobromous acid appears transiently in the reaction mixture and oxidises the oxalate anion.　　　R. TRUSZKOWSKI.

Reaction of bromine with aliphatic acids. II. Relative speeds of bromination of acetyl bromide and acetyl chloride. H. B. WATSON (J.C.S., 1928, 1137—1141).—The view that the bromination of aliphatic acids (A., 1925, i, 1232) proceeds mainly through the acid bromide, the speed of bromination of which is proportional to the concentration of the halogen, is supported by experiments on the bromination of acetyl bromide in the absence of atmospheric moisture. Small amounts of ferric chloride or sulphuric acid do not accelerate the reaction, but iodine bromide does so. Bromine reacts with acetyl chloride more slowly than with acetyl bromide. Interaction of the type $R \cdot CO_2H + R' \cdot COBr = R \cdot COBr + R' \cdot CO_2H$ between acetic acid and bromoacetyl bromide takes place to the extent of 80% in 1 hr. at 25°.　　　A. A. ELDRIDGE.

Saponification of fats in heterogeneous systems. L. LASCARAY (Rev. gén. Colloid., 1928, 6, 32—44).—The saponification reaction of fats in a heterogeneous system occurs exclusively at the interface of the phases and is explainable, together with its anomalies, by the Harkins–Langmuir theory of the structure of the interface. The rate of saponification depends on the degree of dispersion of the fat and is directly and inversely proportional to the amount of emulsifier in the system and to the proportion of unsaturated glycerides in the fat, respectively. The glyceryl radical, which tends to dissolve in water, is attached to 1, 2, or 3 fatty acid radicals in the fat layer, according as it comes from a mono-, di-, or tri-glyceride, respectively. For comparative studies of the rate of saponification in which a very stable emulsion, unaffected by outside influences, is required, the fat may be mixed well with a concentrated neutral soap solution and the emulsion warmed to 100°. Since the soap acts only as an emulsifier, reaction occurs between fat and water only, and is one of non-catalytic hydrolysis. An alcohol–water mixture exists in which the rate of saponification is minimal owing to the fact that the solubilities of fats and soaps in such mixtures decrease with an increase in the relative amount of water, whilst the emulsifying powers increase.　　　J. GRANT.

Effect of neutral salts on the velocity of saponification of ethyl acetate by sodium hydroxide. I. S. D. WILSON and (MISS) E. M. TERRY (J. Amer. Chem. Soc., 1928, 50, 1250—1254).—The influence of sodium chloride, acetate, or nitrate (0·02—0·5M) on the rate of saponification of 0·008M-ethyl acetate by 0·01M-sodium hydroxide is recorded. The equations given in the preceding paper (this vol., 718) hold in the case of sodium chloride.　　　S. K. TWEEDY.

Decomposition of diacetone alcohol by sodium hydroxide in water mixtures of organic solvents. G. ÅKERLÖF (J. Amer. Chem. Soc., 1928, 50, 1272—1275).—The decomposition velocity of diacetone alcohol with 0·1N-sodium hydroxide solution as catalyst was measured at 25° in mixtures of some alcohols with water. Contrary to Goldschmidt's rules for ester formation (A., 1927, 208), the velocity in pure primary alcohols increases with increasing mol. wt. of the solvent; it decreases as the number of hydroxyl groups increases, and, in the case of isomeric alcohols, is greatest in that alcohol with the most compact alkyl group. In some of the pure alcohols the reaction velocity is largely influenced by traces of water, this influence decreasing with decreasing mol. wt. of the alcohol or with increasing number of hydroxyl groups.　　　S. K. TWEEDY.

Velocity measurements of intramolecular changes in arylacylhalogenoamines. (MISS) C. C. J. FONTEIN (Rec. trav. chim., 1928, 47, 635—667).—An extension of the work of Blanksma (A., 1903, ii, 137) on the conversion of phenylacetylchloroamine into p-chloroacetanilide. In carrying out the velocity determinations use is made of the fact that the unchanged chloroamine reacts with potassium iodide (in the presence of hydrochloric acid), liberating iodine. The effect of changes in the acyl, halogen, and aryl groups on the reaction velocity has been studied. The following groups increased the reaction velocity in the order benzoyl>acetyl>formyl>butyryl>propionyl. The bromine atom in phenylacetylbromoamine migrates very much more readily than does the chlorine atom in the corresponding chloroamine. The introduction of the groups methyl, chlorine, and bromine into the m-position increases the reaction velocity, the effect of the halogens being approximately twice that of the methyl group. All the reactions studied are unimolecular and are catalysed by hydrochloric acid and by sunlight. For equivalent concentrations of the organic solvents used, the reaction velocity is greatest in acetic acid, intermediate in ethyl alcohol, and least in methyl alcohol. The addition of water to the solvent reduces the velocity.　　　H. INGLESON.

Influence of the alcohol group of amino-acid esters on the rate of formation of 2 : 5-diketopiperazines and on the formation of guanidino-compounds by the action of guanidine on the various amino-acid esters. E. ABDERHALDEN and S. SUZUKI (Z. physiol. Chem., 1928, 176, 101—108).—The preparation and properties of the n-propyl, isopropyl, n-butyl, isobutyl, n-amyl, and benzyl esters of glycine and their hydrochlorides are described. The rate of conversion of these esters and the methyl and ethyl esters of glycine into 2 : 5-diketopiperazines in sealed tubes at 18° and 37° has been measured; the velocity is greatest with the methyl ester and least with the benzyl ester. The same gradation occurs, the methyl ester giving the greatest velocity, when the action of guanidine on the ester hydrochlorides is measured by the amount of ammonia formed.　　　A. WORMALL.

Rate of reactions between two liquid phases. W. Fraenkel, E. Wengel, and L. Cahn (Z. anorg. Chem., 1928, **171**, 82—97).—The experiments previously carried out on the rate of dissolution in acids of metals dissolved in mercury (A., 1924, ii, 475) have been repeated and extended to amalgams of beryllium, magnesium, aluminium, cæsium, rubidium, and zinc. It now appears that if the acid concentration is not too high, the relation between the reaction velocity and the time is the same for all the amalgams. At first, hydrogen is evolved at a constant rate, but when the amount of metal falls below about 0·0005—0·001 g.-equiv./100 g. of mercury the rate becomes proportional to the concentration of the amalgam; this latter stage is not observed if the acid concentration is too high. The velocity coefficient of the second part of the reaction is directly proportional to the area of the surface at which reaction occurs, and decreases with increase in the relative amount of amalgam. The initial velocity, on the other hand, is almost independent of the volume of the amalgam, but is very nearly proportional to the acid concentration, and also increases linearly with increase in the rate of stirring; the rate of evolution of hydrogen may also be considerably influenced by the overvoltage. For the alkali metals, the constant initial velocities are in the order of the normal electrode potentials as derived from measurements with molten salts, whilst with the other metals it is the velocity coefficients of the second part of the reaction period which are in this order. The reaction between an aqueous solution of an acid and a bromoform solution of ethyl diazoacetate follows the unimolecular law at all concentrations, the velocity coefficient being independent of the hydrogen-ion concentration of the acid, but approximately proportional to the rate of stirring. R. Cuthill.

Intensive drying. R. H. Purcell (J.C.S., 1928, 1207—1215).—Intensive drying had no effect on the reduction of silver and mercury oxides by carbon monoxide, the rate of reduction of copper oxide by hydrogen, or the rate of oxidation of mercury, but the temperature required for the reduction of copper and bismuth oxides was raised by carbon monoxide to 425°. Quantitative experiments on the reduction of copper oxide by carbon monoxide showed that the rate of reaction depended on the temperature and concentration of water vapour. When little or no water vapour was present the reduction ceased to be autocatalytic. The influence of a dry third substance on the same reaction has also been studied. Alcohol, benzene, and ether catalysed the reduction somewhat less efficiently than water, whilst sulphur dioxide and bromine were without effect. F. J. Wilkins.

Velocity of formation of anhydrous calcium sulphate from gypsum. P. P. Budnikov (J. Russ. Phys. Chem. Soc., 1927, **59**, 880—889).—The velocity of formation of the insoluble anhydrous salt was determined from conductivity measurements of solutions containing finely-powdered, chemically pure synthetic gypsum that had been heated at 140°, 160°, 200°, or 220° for 2, 5, 17, 24, and 40 hrs. The results show that the amount of the insoluble anhydrous salt formed depends on the temperature and duration of heating. A. Ratcliffe.

Determination of the degree of tarnishing of a metallic surface by its reflective power. G. Ando (Mem. Coll. Sci. Kyoto, 1928, A, **11**, 85—93).—The reflective power of a metal surface is determined directly after polishing and also after keeping the polished surface for a given time in an atmosphere containing known amounts of moisture and carbon dioxide. The ratio of the two reflective powers is a measure of the degree of tarnishing. The method has been applied to several alloys. J. S. Carter.

Corrosion of metals as affected by time and by cyclic stress. D. J. McAdam, jun. (Amer. Inst. Min. Met. Eng., Tech. Pub., 1928, No. 58, 38 pp.).—Various alloys were subjected to corrosion at cyclic stresses from zero to the corrosion-fatigue limits for various times and at various cycle frequencies, and then subjected to fatigue in air. Chemical Abstracts.

Acid and salt effects in catalysed reactions. XIII. Inert salt effects in the catalytic action of acids. XIV. Influence of inert salts on the catalytic catenary for acetic acid–acetate mixtures. H. M. Dawson and A. Key (J.C.S., 1928, 1239—1248, 1248—1257).—XIII. Measurements have been made of the velocity of the iodine–acetone reaction when catalysed by hydrochloric, dichloroacetic, monochloroacetic, and acetic acids in solutions of sodium chloride (0·1—4·0M). The reaction velocity is greater than in solutions free from sodium chloride. It is not clear whether this increase in the case of hydrochloric acid solutions is due to the presence of a minute quantity of the highly active undissociated strong acid or to the stimulating action of the sodium chloride on the catalytic activity of the hydrogen ion. Both factors may be operative. The inert salt effects of weaker acids, however, seem to involve some new cause. Assuming that for hydrochloric acid the second factor only is operative, it is shown that the ionisation constant of a weak acid is first increased by the added salt and then diminished at higher salt concentrations. Similar results were obtained with lithium and potassium chlorides. The maximum values for the ionisation constants are greatest for lithium and least for potassium chloride (cf. Harned, A., 1925, ii, 538).

XIV. The influence of catalytically inert salts on the velocity of iodination of acetone when catalysed by weak acids either in the presence or absence of the corresponding salt has been investigated, and the results demonstrate that the catalytic phenomena described in the previous papers of this series are not affected to any great extent by the changes in ionic environment which are associated with the replacement of water as the solvent by solutions of catalytically inert salts. Whilst the replacement of water by 0·1—4·0M-sodium chloride solutions has a considerable effect on the catalytic activity of the hydrogen ion and the degree of ionisation of the acetic acid, it scarcely influences the catalytic activity of the acetic acid molecule and acetate ion. The v—p_H curves in all cases approximate to a true catenary. F. J. Wilkins.

Catalytic activity of hydrochloric acid and of potassium and sodium hydroxides in aqueous solution. (Miss) E. M. Terry (J. Amer. Chem. Soc., 1928, 50, 1239—1250).—On certain assumptions it is deduced that for ester hydrolysis catalysed by hydrogen or hydroxyl ions, $K_{obs.}(\gamma_{KOH}/\gamma_{HCl}) = K'd$, where K' is the coefficient of the reaction when the catalytic influence is proportional to the molality of the catalyst, and $d = \gamma_{H'}/(\gamma_{HCl}/\gamma_{KOH}) = \gamma_{OH'}/(\gamma_{KOH}/\gamma_{HCl})$. Experimental results are quoted demonstrating that $K'd$ is a constant for ester hydrolyses in acid and alkaline solution, and also in the presence of sodium and potassium chlorides, although it is not constant for sucrose inversion, in which some other, undefined, variable appears to play a part. Interpretation of the expressions is discussed.   S. K. Tweedy.

Inhibition of esterification by pyridine. K. C. Bailey (J.C.S., 1928, 1204—1206).—Experiments on the inhibition of the reaction between acetic acid and ethyl alcohol by pyridine indicate that esterification occurs partly on the walls of the containing vessel and partly in the liquid phase.   F. J. Wilkins.

Autoxidation and antioxygenic action. XXVII. Action of different catalysts on the autoxidation of furylethylene. C. Moureu, C. Dufraisse, and J. R. Johnson (Bull. Soc. chim., 1928, [iv], 43, 586—590; cf. A., 1922, i, 250; 1923, i, 91; 1925, i, 362, 363; 1927, 465).—The resinification of furylethylene, required for conversion into furylacetylene, is largely prevented by the use of an antioxygenic agent. The capacity of furylethylene for absorbing oxygen is greater than that of styrene, acraldehyde, or benzaldehyde. The course of the oxidation of furylethylene in the presence of phloroglucinol, resorcinol, quinol, α-naphthol, pyrogallol, thiophenol, iodoform, and potassium xanthate as catalysts was studied. Of the phenols, quinol showed the most intense antioxygenic action, the addition of 1 in 10^3 remarkably retarding the rapidity of oxidation.
          R. A. Pratt.

Oxidation catalytic action of iron. H. Handovsky (Z. physiol. Chem., 1928, 176, 79—88).—The following iron compounds do not effect the oxidation of leucine when the iron compound and a 0·5—1% solution of leucine are shaken with air or oxygen: ferrous sulphate, magnetic iron oxide, colloidal ferric hydroxide sols, and a mixture of metallic iron and iron oxide prepared by heating iron oxalate. Metallic iron, however, prepared by heating iron oxide in a stream of hydrogen effects the oxidation of leucine with the production of carbon dioxide, ammonia, and isovaleraldehyde (isolated as the p-nitrophenylhydrazone). Glycine, alanine, valine, tyrosine, histidine, formyl-leucine, and glycyl-leucine are similarly oxidised by the reduced iron, yielding substances which give a positive fuchsine–sulphurous acid reaction. The oxygen uptake with leucine is never more than 19% of that required for complete combustion and the oxidation is inhibited by hydrocyanic acid. When the heated reduced iron is cooled in nitrogen a black iron powder is obtained which has no oxidising action on leucine, but if the inactive iron is reheated for some time and subsequently cooled in hydrogen the oxidising power is regenerated. The conclusion is reached that it is not the iron but the hydrogen dissolved in it which effects the oxidation of amino-acids and that the "active" hydrogen reacts with oxygen to give hydrogen peroxide which is catalytically decomposed on the surface of the iron. Similarly, animal charcoal loses its power to catalyse the oxidation of leucine when heated and cooled in nitrogen but regains this power when reheated and cooled in hydrogen.   A. Wormall.

Theory of centres of activity in heterogeneous catalysis. F. H. Constable (Proc. Camb. Phil. Soc., 1928, 24, 291—306).—Previous work bearing on the theory of catalytic action is reviewed, and it is concluded that the experimental facts dealing with adsorption and catalysis can be explained quantitatively on the assumption of strong specific fields of force that emanate from special configurations of atoms on the catalyst surface.   C. J. Smithells.

Method of generalising the law of mass action for heterogeneous surface reactions. F. H. Constable (Proc. Camb. Phil. Soc., 1928, 24, 307—314).—Assuming the theory of centres of activity (see preceding abstract) the absorption of the reactants on the centres of activity is introduced as a further condition in homogeneous systems. The surface is treated as if it were homogeneous, reaction taking place as if those centres on which the heat of activation is smallest were alone responsible for chemical change. The general equation is worked out in terms of the rate of bombardment and the mean lives of the molecules on the surface. The general solution is impracticable, so the special cases of irreversible synthesis and decomposition are considered and results are obtained.   C. J. Smithells.

Theory of wall reactions. M. Pólányi (Chem. Rund. Mitteleuropa Balkan, 1927, 4, 160—161; Chem. Zentr., 1928, i, 285).—For the specific case of the catalytic acceleration of the formation of diatomic from monatomic hydrogen at glass walls Frenkel's relation $q = 15T$ g.-cal., where q is the adsorption potential, is applied. The average value of q for moist glass is 1500—4000 g.-cal., for dry glass and quartz >4500 g.-cal., and for metal 40,000 g.-cal.
          A. A. Eldridge.

Catalysis under reduced pressure. V. Grignard (Bull. Soc. chim., 1928, [iv], 43, 473—491).—A lecture.

Syntheses under high pressure. Interaction of carbon monoxide and hydrogen. G. T. Morgan, R. Taylor, and T. J. Hedley.—See B., 1928, 439.

Synthesis of alcohols higher than methyl alcohol from carbon monoxide and hydrogen. P. K. Frolich and W. K. Lewis.—See B., 1928, 397.

Reaction between atmospheric oxygen and strongly acid iodide solutions in presence and absence of arsenic acid. F. L. Hahn (Z. anal. Chem., 1928, 73, 412—413; cf. Ditz, this vol., 263; Böttger, ibid.).—The so-called "oxygen effect" is catalysed by minute quantities of metal salts, especially by those of iron. The catalytic effect of iron is repressed in presence of phosphates, arsenites, and arsenates and hence the "oxygen error" is negligible

in the iodometric determination of arsenic. The replacement of starch by benzene as an indicator is recommended in iodometric determinations involving the presence of acid. J. S. CARTER.

Synthesis of water over nickel and copper catalysts. Mixture effect and promoter action. F. E. SMITH (J. Physical Chem., 1928, **32**, 719—733; cf. Larson and Smith, A., 1925, ii, 563).—The catalytic effect in the synthesis of water between 75° and 180°, with an oxygen concentration of 2·4%, of the following catalysts, prepared by reduction of the precipitated hydroxides, has been investigated : copper, nickel, copper–nickel mixtures, a mixture of copper and alumina. A sample of copper prepared by reduction of the fused oxide was also used. The results are represented graphically and show that, in the final steady-state synthesis, the most efficient catalysts are those which form the greatest amounts of oxide during catalysis and undergo the least change in physical structure, especially shrinkage, on reduction and later heat treatment. Precipitated copper which shrinks most during its preparation is the worst catalyst. The order of decreasing catalytic efficiency is copper–alumina (19 : 1), copper from the fused oxide, nickel, nickel–copper (1 : 3), copper–nickel (1 : 7·5), and copper from the precipitated hydroxide. No mixture effect occurs in the copper–nickel series as regards catalytic efficiency, but such an effect becomes evident when the amounts of oxide formed are compared. Heating to 444° is accompanied by marked shrinkage of the catalysts, a decrease in oxide-forming capacity, and, except in the case of nickel, a corresponding decrease in catalytic efficiency. These effects were slight with the copper–alumina catalyst and large with the precipitated copper. The behaviour of the nickel may be explained by the changes in physical properties accompanying the transition temperature at 360°. The results show that the physical nature of the catalyst surface, as well as its chemical properties, is of prime importance in determining catalytic activity, and they agree with Taylor's theory of a catalytic surface (A., 1926, 365). The probable mechanism appears to consist of the interaction of hydrogen molecules and activated oxygen molecules or atoms, in the form of an oxide, at points of greatest activity on the surface of the catalyst. Contrary to the theory of Benton and Emmett (A., 1926, 482), the stable oxide formed plays little part in the synthesis. It is formed by an unavoidable side reaction which ultimately results in a partial poisoning of the catalyst. L. S. THEOBALD.

Preparation of hydrogen bromide in the presence of charcoal. V. N. BOSHOVSKI and P. DANILITSCHENKO (J. Russ. Phys. Chem. Soc., 1927, **59**, 851—858).—Hydrogen bromide is easily obtained from bromine in presence of charcoal. Experiments were first carried out at the ordinary temperature in an aqueous solution. The reaction takes place according to the equation $Br_2 + H_2O \rightleftharpoons H^{\cdot} + Br' + HBrO$. In absence of light the equilibrium is reached very slowly. The presence of activated charcoal increases the rate of the reaction. When water vapour and bromine were passed through a quartz tube containing activated and brominated charcoal at 500° all the bromine was converted into hydrogen bromide and the reaction is represented by the equation $Br_2 + H_2O \rightarrow 2HBr + O$. Oxygen combines with carbon, forming carbon monoxide or carbon dioxide, and the heat of combustion gives the 33,610 g.-cal. necessary for the above reaction. A. RATCLIFFE.

Precipitation of vanadic acid on asbestos fibre. N. N. EFREMOV and A. ROSENBERG (J. Russ. Phys. Chem. Soc., 1927, **59**, 701—714).—The catalytic action of vanadated asbestos depends on the ease with which the reaction $2V_2O_4 + O_2 \rightleftharpoons 2V_2O_5$ takes place. The asbestos fibre is soaked in a dilute sulphuric acid solution of vanadyl sulphate, $V_2O_2(SO_4)_2$, which is obtained by the reduction of a boiling solution of ammonium vanadate with ammonium hydrogen sulphite. At 40—50° the solution is made alkaline with a concentrated solution of ammonia, an excess of which must be avoided. The solution is evaporated nearly to dryness and the fibre is then spread on asbestos sheets and dried. The precipitate formed on the asbestos after drying consists chiefly of the compounds $(NH_4)_2VO_3$ and V_2O_4,H_2O. The process is repeated if necessary. To convert the quadrivalent vanadium into the quinquevalent form the asbestos is heated at 500—600°. A. RATCLIFFE.

Hydrogen electrode. S. SEKINE (Z. Elektrochem., 1928, **34**, 250—253).—The hydrogen electrode in conjunction with a lead dioxide electrode has been investigated, using N-sulphuric acid as electrolyte. On closing the circuit through a variable rheostat and milliameter, Ohm's law is valid if palladium be employed in the hydrogen electrode. With platinum, however, on decreasing the resistance the current at first increases and then decreases sharply. Quantitative measurements of this effect have been made, together with the influence of the time factor. It is suggested that the current decrease is due to the formation, at high current density, of an adsorbed film of oxygen on the platinum electrode, the escape of hydrogen being thereby inhibited. H. F. GILLBE.

Electro-deposition of thallium. O. W. BROWN and A. McGLYNN.—See B., 1928, 451.

Influence of the cathode on the electro-deposition of chromium. H. S. LUKENS.—See B., 1928, 414.

Behaviour of plating baths and anodes during electro-deposition of chromium. R. SCHNEIDEWIND and S. F. URBAN.—See B., 1928, 450.

Effect of tervalent chromium and iron on chromic acid chromium plating baths. R. SCHNEIDEWIND, S. F. URBAN, and R. C. ADAMS, jun.—See B., 1928, 450.

Electrochemical oxidation of solutions of cerous salts. I. A. ATANASIU (Bul. Soc. Romane Stiin., 1928, **30**, 61—67).—Both cerous sulphate and cerous nitrate may be completely oxidised by electrolysis of the acid solution with an anode of sheet platinum, the cathode being immersed in a 20% solution of sulphuric acid or nitric acid, as the case may be, contained in a porous pot. The current yield for the nitrate is about four times as great as it is for the

sulphate, and for either salt decreases with increase in the current density at the anode. Dilute acid solutions of ceric nitrate or ceric sulphate may be kept for 30 days without undergoing any change.

R. CUTHILL.

Decomposition of carbon monoxide in the corona due to alternating electric fields. E. OTT (J.C.S., 1928, 1378).—A reference to previous work (A., 1925, ii 579; cf. Lunt and Venkateswaran, A., 1927, 531).

F. J. WILKINS.

Electrocatalytic reduction of carbon monoxide. G. FESTER and M. SCHIVAZAPPA (Z. anorg. Chem., 1928, **171**, 163—167).—By cathodic reduction of carbon monoxide, using as electrode copper gauze coated with powdered nickel, and a sulphuric acid solution of vanadic acid as electrolyte, small amounts of formaldehyde may be obtained.

R. CUTHILL.

Periodic electrolytic oxidation of formic acid. E. MÜLLER and S. TANAKA (Z. Elektrochem., 1928, **34**, 256—264).—The electrolytic oxidation of formic acid takes place in two stages, an intermediate compound being formed on, and remaining attached to, the anode. The velocity of the second stage is dependent on the rate at which this compound breaks up into adsorbed hydrogen and carbon dioxide. The periodic phenomena are probably due to the existence of a metastable limiting concentration of the intermediate substance.

H. F. GILLBE.

Photochemical ozonisation and its relation to the polymerisation of oxygen. O. R. WULF (Proc. Nat. Acad. Sci., 1928, **14**, 356—358).—The fact that in gaseous oxygen at high pressure ozone is formed at wave-lengths 2090 and 2530 Å., whilst the molecule O_2 does not absorb in this region, can be explained by assuming that there exists in oxygen a molecular form of the element other than the molecule O_2. Evidence is put forward to show that this is the polymeride O_4. The new absorption cannot be due to the influence of molecular impacts on the absorption of the molecule O_2, as has been supposed, for reasons concerning the position of the absorption, its behaviour on alteration of temperature and pressure, and the characteristics of the ultra-violet absorption of oxygen.

A. J. MEE.

" After-effect " in certain photochemical reactions. II. B. K. MUKERJI and N. R. DHAR (J. Indian Chem. Soc., 1928, **5**, 203—208; cf. A., 1926, 366).—A continuation of previous work. If the following photochemical reactions are allowed to proceed, first in the light and then in the dark, the velocity coefficient is larger, for a short time after the removal of the light, than when there has been no exposure to light : oxidation of ferrous sulphate, oxalic acid, sodium nitrite, sodium malate, and sodium lactate, respectively, by iodine; the bleaching of dicyanin; the decomposition of Fehling's solution in presence of ferric chloride; the decomposition of potassium manganioxalate, and the reduction of copper sulphate by ammonium oxalate in the presence of ferric chloride. The last reaction does not take place at all in the dark unless the reactants have been previously exposed to light. The phenomenon of " after-effect " may be explained by supposing that the life-period of the activated molecules is considerably prolonged by the action of light, and these molecules revert only slowly to the inactive state in the dark.

M. S. BURR.

Photolysis of benzaldehyde. M. DE HEMPTINNE (Compt. rend., 1928, **186**, 1295—1297).—The suggestion of Henri and Wurmser (A., 1927, 946) that the photolysis of benzaldehyde into benzene and carbon monoxide is due to the total absorption portion of the spectrum of its vapour, whilst the other portions are responsible only for molecular excitation, is confirmed by the fact that only rays of wave-lengths less than 2600 Å. produce photolysis at the ordinary temperature. At 0·2 mm. and 208°, the absorption spectrum of the vapour is greatly modified, the fine bands between 2966 and 2610 Å. becoming continuous, whilst rays of wave-lengths greater than 2700 Å. will produce photolysis. In the absence of illumination, benzaldehyde vapour is decomposed into benzene only above 400°. These phenomena have passed unnoticed when benzaldehyde has been used in solution.

J. GRANT.

Mechanism of formation of the latent photographic image. F. C. TOY (Nature, 1928, **121**, 865).—For very thin layers of silver bromide the three curves representing, respectively, the relative photoconductivity effects, the relative photographic effects, and the relative light absorptions, each plotted against the wave-length for equal incident intensity, are closely similar ; hence the primary stage of the photographic mechanism is probably intimately connected with that producing conductivity changes on illumination.

A. A. ELDRIDGE.

Additivity of photographic densities. G. TICHOV (Bull. Acad. Sci. Leningrad, 1927, 511—532; Chem. Zentr., 1928, i, 464).—A study of the intensity of blackening of a photographic plate in relation to the additivity of the light sources.

A. A. ELDRIDGE.

Activation of hydrogen by the catalytic action of metals. M. U. POLJAKOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 847—849).—See this vol., 459.

A. RATCLIFFE.

Formation of crystalline gold. G. I. COSTEANU (Bul. Soc. Romane Stiin. 1928, **30**, 35—37).—Minute hexagonal plates of metallic gold have been obtained by the slow evaporation of a mixed solution of stannic bromide and auric bromide.

R. CUTHILL.

Experiments on transmutation. J. A. N. FRIEND (J.C.S., 1928, 1321—1324).—Specimens of gold, silver, and barium sulphate exposed to radium emanation gave no spectroscopic evidence of transmutation. The coloration of quartz glass by emanation is discussed.

F. J. WILKINS.

Bleaching powder. VIII. Decomposition of calcium hypochlorite by carbon dioxide. S. URANO (J. Soc. Chem. Ind. Japan, 1928, **31**, 53—60).—Carbon dioxide decomposes calcium hypochlorite in presence of water : $3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2$; it also decomposes aqueous calcium hypochlorite and chloride : $Ca(OCl)_2 + CaCl_2 + 2CO_2 = 2CaCO_3 + 2Cl_2$. Although the formation of chlorate or the evolution of chlorine, respectively, is caused by heat only, carbon

dioxide accelerates these reactions, since the liberated hypochlorous acid exerts an oxidising action. As carbon dioxide expels almost all the chlorine from bleaching powder, Lunge assumed the chemical constitution of bleaching powder to be Ca(OCl)Cl; a mixture of hypochlorite and chloride, however, also loses all its chlorine by the action of carbon dioxide. Even calcium chloride itself is decomposed by carbon dioxide in presence of oxidising agent, e.g., potassium permanganate. The chemical constitution of bleaching powder cannot therefore be deduced from the action of carbon dioxide. K. KASHIMA.

Hydrates of cadmium, zinc, and magnesium nitrates. G. MALQUORI (Gazzetta, 1928, 58, 209—216).—Results already published (this vol., 480) are given in more detail. Of the nitrates mentioned above, cadmium nitrate is the only one which can be completely dehydrated by nitric acid at the ordinary temperature. The heat of hydration of anhydrous cadmium nitrate is $+11\cdot52$ kg.-cal. The structure of the hydrated nitrates of bivalent metals is discussed and the views of Lembert (A., 1923, ii, 313) are supported. O. J. WALKER.

Formation and properties of mercuric ammonium chloride. F. G. GERMUTH (Amer. J. Pharm., 1928, 100, 285—293).—In the determination of magnesium the addition of ammonium chloride to a solution of magnesium chloride in which freshly-precipitated mercuric oxide is suspended greatly accelerates the rate of formation of magnesium oxide. When a mixture of magnesium chloride and mercuric oxide with an excess of ammonium chloride is gently heated in a vacuum the sublimate formed contains mercuric ammonium chloride, $HgCl_2,2NH_4Cl,2H_2O$, m. p. 210—212°, subl. 220—223°/755 mm. The compound, which appears to crystallise in the same system as the hydrate $CuCl_2,2NH_4Cl,2H_2O$, is also produced from an aqueous mixture of the two chlorides. It seems probable that the accelerating effect of the ammonium chloride in the determination of magnesium is due to the formation of the salt. H. INGLESON.

Samarium subhalides. W. PRANDTL and H. KÖGL (Z. anorg. Chem., 1928, 172, 265—272).—The so-called samarium subchloride has been prepared in a pure state, and free from oxychloride, as follows: the hexahydrated trichloride is precipitated by passing hydrogen chloride into a solution of the samarium oxide in hydrochloric acid solution, dehydrating this substance by melting in a current of dry oxygen-free hydrogen chloride, and reducing by pure hydrogen. The product is of a deep brownish-red colour, and is transparent only in thin layers. Samarium subbromide, prepared, although with greater difficulty, in a precisely analogous manner, is opaque and almost black. On heating the sub-salt at about 1000° in an atmosphere of hydrogen in a gold vessel, the corresponding trihalide volatilises and the surface becomes coated with a gold–samarium alloy. The subhalides thus behave as molecular compounds or solid solutions of samarium and samarium trihalide.

H. F. GILLBE.

Substances analogous to graphite. II. R. CIUSA (Gazzetta, 1928, 58, 222—223; cf. A., 1925, i, 1083).—A graphite, $(C_6)_n$, has been obtained from hexaiodobenzene by heating it first in a closed tube and then in an open tube in a current of nitrogen. The graphite obtained at 770° has a resistivity of $0\cdot11$ and d 2·25. These values are very nearly equal to those obtained for Ceylon graphite.

O. J. WALKER.

Influence of the "conversion" yield and the temperature of condensation on the purity of the product and on the "condensation yield" in the synthesis of carbonyl chloride. F. GIORDANI.—See B., 1928, 446.

Influence of iron oxide on the properties of glass. S. ENGLISH, H. W. HOWES, W. E. S. TURNER, and F. WINKS.—See B., 1928, 404.

Liquid silicate immiscibility. J. W. GREIG (Amer. J. Sci., 1928, [v], 15, 375—402).—Polemical against Tanton (ibid., 66; cf. Greig, B., 1927, 440; this vol., 132). F. J. WILKINS.

Occurrence of titanium tetrachloride in commercial disilicon hexachloride. F. S. KIPPING and R. A. THOMPSON (J.C.S., 1928, 1377).—Evidence of the presence of titanium tetrachloride in commercial disilicon hexachloride was indicated by reactions with hydrogen peroxide and with thymol and sulphuric acid. Addition of ether caused the separation of a yellow compound, probably $TiCl_4,Et_2O$. Complete removal of the tetrachloride was effected only by five or six fractional distillations.

F. J. WILKINS.

Hydrogenation of tin salts at high temperatures and pressures. V. N. IPATIEV and V. I. NIKOLAEV (J. Russ. Phys. Chem. Soc., 1928, 60, 331—338).—The reduction of aqueous solutions of stannic hydroxide and sulphate and stannic chloride was studied at various temperatures and pressures. Stannic hydroxide is the most readily reduced to the metallic state and the presence of anions such as sulphate and chloride ions has an inhibiting influence. A. RATCLIFFE.

Oxidation of the mixture of stannous hydroxide and sodium sulphite in sodium carbonate solution with air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1928, 3, 95—98).—A mixture of stannous hydroxide and sodium sulphite in sodium carbonate solution is oxidised very slowly by air, since the oxidation of stannous hydroxide inhibits that of sodium sulphite. H. F. GILLBE.

Action of phenylhydrazine on metallic oxides and salts. II. **[Preparation of] lead suboxide.** E. PUXEDDU (Gazzetta, 1928, 58, 224—231; cf. A., 1916, i, 292).—Phenylhydrazine reduces lead monoxide and dioxide and triplumbic tetroxide to lead suboxide, which is obtained as a brown or black powder of composition satisfying the formula Pb_2O (which is not the case with preparations from lead oxalate). The reaction temperature is maintained at 80—150°; above this, metallic lead is also formed. For the reduction of lead dioxide the phenylhydrazine is employed in ethereal solution, as otherwise the reaction is violent.

Mercuric or mercurous chloride is reduced by phenylhydrazine to mercury. This is used for the determination of the latter. The test-tube containing the

reagents is warmed at first gently and then at 80°; the mercury is washed with acidified water and with alcohol, and is dried in a potassium hydroxide desiccator containing mercury. E. W. WIGNALL.

Monobasic, polybasic, and polymonobasic acids and their differentiation. E. WEITZ and H. STAMM (Ber., 1928, 61, [B], 1144—1155; cf. A., 1925, ii, 1147).—The solubility of ammonium and alkali salts of polybasic acids is generally diminished by addition of ammonia, frequently in a very marked manner, whereas that of the salts of monobasic acids is either increased or only slightly diminished. The observed effect may be regarded as the algebraic sum of two distinct tendencies, the competition of ammonia and the salt for water and the effort to form ammines. Exceptions are encountered with hydrofluoric and periodic acids, which are known to exhibit marked tendency towards polymerisation, and persulphuric and dithionic acids. The two last-named acids differ structurally from most inorganic polybasic acids in that their molecules contain two distinct monobasic acid groups, and for such compounds the term "polymonobasic" is suggested. The ions may be arranged in order of increasing tendency towards the formation of ammines in the sequence PO_4''', IO_5''', SO_4'', F', S_2O_6'', Cl', NO_3'', Br', ClO_3', S_2O_8'', I', CNS', ClO_4'. The relationships with organic acids are less obvious. The monocarboxylic compounds mainly resemble the monobasic inorganic acids. The polycarboxylic acids of the fatty series, although containing two separated carboxyl groups, behave as polybasic. Phthalic and terephthalic acids are definitely polybasic, whereas *iso*phthalic, trimesic, and benzene-*m*-disulphonic acids are polymonobasic. Hofmeister's lyotropic sequence for the ions is arranged in the opposite order to that given above, so that the tendency of anions towards union with ammonia is the reverse of their tendency towards combination with water. Further regularities are observed with regard to solubility, since the barium compounds of monobasic acids are soluble in water, whereas those of polybasic acids are insoluble or sparingly soluble; this rule is maintained intact only by regarding iodic, hydrofluoric, and periodic acids as polybasic and persulphuric, dithionic, and the polythionic acids as monobasic. The rule holds generally for organic acids; barium *iso*phthalate and *m*-benzenedisulphonate are soluble in water, whereas barium phthalate and terephthalate are sparingly soluble. A less trustworthy criterion is the solubility in aqueous or anhydrous alcohol; the ammonium and alkali salts of monobasic inorganic acids are usually appreciably more soluble than those of polybasic acid. In this instance, the polymonobasic acids behave as monobasic acids. Great caution must be observed in reaching conclusions as to the basicity of acids from the solubility of their ammonium or alkali salts in water alone. The influence of the ions on the coagulation of dialysed ferric chloride solution has been examined. The unique position of the polymonobasic acids and their inclination towards the monobasic acids is clearly displayed in their colloid-chemical action. Whereas, however, a fairly sharp differentiation of inorganic acids into mono- and poly-basic compounds is possible on the basis of the effects of ammonia and solubility of the barium salts, this is not possible on colloid-chemical grounds. An intermediate group appears to exist comprising polymonobasic acids, acids apparently polybasic on account of polymerism, and the majority of organic acids.

The inability of polymonobasic acids to yield hydrogen salts is due to the independence of the two acidic groups and the consequent absence of a marked difference in the first, second, etc. dissociation constants; a step-wise neutralisation appears therefore improbable. H. WREN.

Fluoride of bivalent uranium. A. SIEVERTS (Z. anorg. Chem., 1928, 170, 191—192).—The statement, which appears in some of the literature, that a fluoride of bivalent uranium was isolated by Giolitti and Agamennone is erroneous, the formula $UF_2,2H_2O$ in the original paper (Atti R. Accad. Lincei, 1904, [v], 14, i, 165) clearly being a misprint for $UOF_2,2H_2O$. R. CUTHILL.

Univalent manganese. II. W. MANCHOT and H. GALL (Ber., 1928, 61, [B], 1135—1140; cf. A., 1927, 220; Grube and Brause, this vol., 29).—The *salt*, $Na_5Mn(CN)_6$ is obtained as a colourless, microcrystalline powder, very sensitive to oxidising agents when a solution of sodium manganocyanide is reduced by aluminium and sodium hydroxide; the resulting solution is filtered into a solution of sodium hydroxide and sodium cyanide saturated with sodium acetate. The precipitated compound is centrifuged and the residue treated similarly with concentrated sodium hydroxide solution, saturated sodium acetate, and finally with alcohol. If sodium cyanide is omitted in the above preparation, salts similar to the compound $Na_5Mn(CN)_6$ are obtained which contain a much smaller proportion of sodium. The *potassium* salt, $K_5Mn(CN)_6$, may be prepared similarly from potassium manganocyanide, but a preferable method consists in reducing the sodium compound (as above) and adding the filtered solution to a solution of potassium hydroxide and potassium cyanide saturated with potassium chloride. Variations in the procedure afford similar salts containing a smaller proportion of potassium, and the existence of a compound, $K_2Mn(CN)_3$, is highly probable. If, however, potassium cyanide is used in the final washing of the precipitates, the salt $K_5Mn(CN)_6$ is invariably obtained. Grube and Brause's claim of the isolation of a salt, $K_3Mn(CN)_4$, appears arbitrary; repetition of their experiments yields the pentapotassium compound. H. WREN.

Ruthenium chlorides. H. REMY and A. LÜHRS (Ber., 1928, 61, [B], 917—925).—Ruthenium chloride soluble in water (cf. Remy and Wagner, A., 1927, 328) does not differ in composition from the variety insoluble in water. Analyses show that it is free from hydrogen and hence undoubtedly contains tervalent ruthenium. When titrated by the amalgam method (Remy, A., 1921, ii, 209) it requires exactly one equivalent of hydrogen to yield a solution of maximal blue intensity. This amount is also required by the so-called "aquopentachlororuthenate" of Howe (A., 1904, ii, 490), the composition of which, therefore, corresponds with the formula $2K_2RuCl_5,3H_2O$ advanced by Briggs (A.,

1926, 926). The compound obtained by the action of hydrochloric acid on ruthenium tetroxide contains quadrivalent but not tervalent metal as previously assumed, since when titrated to a blue solution it requires two equivalents of hydrogen as maximum. The double salt, $K_4[Ru_2OCl_{10}]$, obtained as a well-defined compound by various other methods, is readily prepared from its solutions; this compound, which likewise contains quadrivalent ruthenium, replaces the previous so-called "brown or α-pentachlororuthenates." The blue solutions obtained by the complete reduction of ruthenium salts by sodium amalgam contain the bivalent metal. The green coloration, formed intermediately during the reduction exclusively of quadrivalent ruthenium salts in solution strongly acidified with hydrochloric acid, is due to compounds of tervalent ruthenium.　　H. WREN.

Action of concentrated sulphuric acid on metallic rhodium. S. F. SHEMTSCHUSHNI (Ann. inst. platine, 1927, **5**, 361).—With mechanical stirring, rhodium dissolves in hot concentrated sulphuric acid.　　CHEMICAL ABSTRACTS.

Osmium. III. E. FRITZMANN (Z. anorg. Chem., 1928, **172**, 213—233).—A summary of the work of Tschugaev.　　H. F. GILLBE.

Spectrum analysis of minerals. F. LÖWE (Fortschr. Min. Kryst. Pet., 1927, **12**, 220—227; Chem. Zentr., 1928, i, 825).

Centrifugal separation of solid phases. F. VON WOLFF (Fortschr. Min. Kryst. Pet., 1927, **12**, 93—95; Chem. Zentr., 1928, i, 825).—Purification and quantitative separation of minerals are effected with a centrifuge; the tube contains a short pipette with the heavy liquid in which the powdered mineral is placed. An electrically heated centrifuge for use with fusible salts is described.　　A. A. ELDRIDGE.

Quantitative analysis of cations without the use of hydrogen sulphide. D. STROHAL (Arh. Hemiju, 1928, **2**, 77—85).—A system for the quantitative analysis of cations which does not involve the use of hydrogen sulphide is described.
　　R. TRUSZKOWSKI.

Smooth platinum wire for electrometric titrations in neutralisation reactions. S. POPOFF and M. J. McHENRY (Ind. Eng. Chem., 1928, **20**, 534—538).—Using a smooth platinum wire as an air electrode, acidities and basicities can be determined with considerable precision even in presence of oxidising agents, e.g., permanganate. Acidities can be determined with accuracy in presence of phenol, cresols, or varnishes. The method is particularly adapted to the determination of alkaloids and yields results which are more trustworthy than those obtained using the hydrogen or quinhydrone electrodes. The procedure is identical with that customarily followed in making hydrogen electrode measurements, except that the hydrogen stream is replaced by a stream of air free from carbon dioxide. An electrode of tungsten wire may be used, but the change in $E.M.F.$ at the end-point is not so pronounced as with platinum.
　　J. S. CARTER.

Quinhydrone electrode in amyl alcohol solutions. Determination of neutralisation

numbers of petroleum products. H. SELTZ and D. S. McKINNEY (Ind. Eng. Chem., 1928, **20**, 542—544).—The neutralisation numbers of petroleum products can be determined potentiometrically with considerable precision, using as solvent amyl alcohol saturated with lithium chloride and containing 0·04% of quinhydrone. The alkali used for titration is a solution of potassium or lithium hydroxide in amyl alcohol. The titration vessel is a wide-mouthed bottle closed by a stopper containing holes for an electrode, the burette jet, nitrogen inlet, and outlet tubes, and the reference electrode. The reference electrode is a test-tube having a small hole near the closed end. The lower portion of the test-tube is occupied by an agar-agar–lithium chloride gel, which functions as a bridge. Above this are the amyl alcohol solvent and an electrode. The electrodes are bright platinum. Using this arrangement, the $E.M.F.$ passes through zero during the titration and the leads to the potentiometer must be reversed. This may be avoided by adding benzoic acid to the reference electrode, but this is not recommended. In the determination of neutralisation numbers of mineral oils, 10 g. of oil are dissolved in about 125 c.c. of solvent. A larger amount of oil is not advisable since the conductivity, and hence the sensitivity, of the cell is considerably reduced.　　J. S. CARTER.

Adjustment of the reaction of indicator solutions and its importance in determining the hydrogen-ion concentration of slightly buffered solutions. W. H. PIERRE and J. F. FUDGE (J. Amer. Chem. Soc., 1928, **50**, 1254—1262).—A critical study of the various methods of preparing and adjusting certain indicator solutions is described. A simple method of adjustment is given, although the quinhydrone electrode is satisfactory for this purpose. Indicator solutions should be adjusted to a p_H value midway between the extreme values for which they are used, and not to neutrality.　　S. K. TWEEDY.

Ionocolorimeter; its use in the determination of ionic acidity of solutions. CAILLE (Bull. Soc. Chim. biol., 1928, **10**, 590—601).—A modified colorimeter is described in which the light travels through a fixed length of the liquid under examination, containing a known amount of an indicator such as methyl-red or bromothymol-blue which has different colours at different p_H values, by one optical path and through two baths, containing solutions of the indicator at the same concentration and at the p_H values which completely liberate the two differently coloured isomerides, by the other. A device controlling the movement of the two dipping glasses in the latter path ensures that the liquid path in that case is always equal to the length of the liquid under examination. Compensating absorption glasses equalise the intensities of the two components of the light. The calibration curves for most indicators follow the straight-line law.
　　G. A. C. GOUGH.

Determination of chlorine ions. U. N. SLAVIANOV (J. Russ. Phys. Chem. Soc., **60**, 355—359).—The errors arising in the gravimetric and volumetric determination of chlorine ions are discussed and a method based on that of Volhard, but with elimination of most of the errors, is described.　　A. RATCLIFFE.

Determination of chlorine, bromine, and iodine in organic compounds. H. ter Meulen (Rec. trav. chim., 1928, 47, 698—700; cf. A., 1924, ii, 55).—The method of determination of these halogens by hydrogenation of the organic compound in the presence of gaseous ammonia is satisfactory only when precautions are taken to prevent the loss of the ammonium halide which is produced. In the new procedure the exit gases pass over strongly-heated barium carbonate and thus any halogen present in them is retained as the barium salt. In certain cases the use of a hydrogenating catalyst is necessary. For this purpose a roll of heated nickel foil is recommended. Results obtained by this method agree well with the theoretical.   H. Ingleson.

Determination of very small quantities of iodides. J. T. Dunn.—See B., 1928, 402.

Micro-determination of iodine in potable waters. III. Oxidation method. M. Settimj.—See B., 1928, 466.

Rapid determination of gases in metals, especially oxygen in steel. W. Hessenbruch and P. Oberhoffer.—See B., 1928, 409.

Sulphur dioxide and its aqueous solutions. I. Analytical methods, vapour density, and vapour pressure of sulphur dioxide. Vapour pressure and concentrations of the solutions. C. E. Maass and O. Maass (J. Amer. Chem. Soc., 1928, 50, 1352—1368).—If commercially pure sulphur dioxide is passed over phosphorus pentoxide and condensed, and the liquid repeatedly distilled in a vacuum, a very pure gas is obtained. Sulphurous acid may be accurately determined by rendering the solution strongly alkaline and titrating with acidified iodine solution in presence of a little sugar. Iodine solution may be standardised against gaseous sulphur dioxide, weighed directly, by this method. The vapour densities of sulphur dioxide were measured from −6° to 30° and an equation is deduced, involving the apparent mol. wt., which enables the weight of gas removed from a known volume to be calculated from the initial and final pressures. The following vapour pressures are recorded: pure sulphur dioxide (1—27°), aqueous solutions (10—27°), two-phase water–sulphur dioxide system (10—27°). In the latter system the saturated water phase has a constant pressure, which can be read off from the graph, and its composition (solubility of sulphur dioxide) determined by extrapolating the vapour-pressure curve for aqueous solutions. The concentration of water in the sulphur dioxide phase may be calculated by Raoult's law, but a method is given whereby its partial pressure may be measured directly. A method of separating a portion of a liquid phase from a liquid–liquid–gas phase without disturbing the equilibrium is described.
S. K. Tweedy.

Micro-determination of nitrogen in cellulose nitrate. D. Krüger.—See B., 1928, 400.

Electrometric titration of the nitrite ion with potassium permanganate. I. A. Atanasiu (Bul. Soc. Romane Stiin., 1928, 30, 69—71).—Permanganate may be titrated electrometrically at 45° with 0·1M-potassium nitrite, using a platinum electrode, but the titration as a method of determining nitrite is subject to the same errors as Lunge's method.
R. Cuthill.

Ceric salts as oxidising agents in electrometric titration. I. A. Atanasiu (Bul. Soc. Romane Stiin., 1928, 30, 73—76).—If an acid solution of ceric sulphate is titrated electrometrically with 0·1M-potassium nitrite, using a platinum electrode, there is a point of inflexion on the titration curve corresponding with the reaction of 2 mols. of sulphate with 1 mol. of nitrite. The presence of an alkali metal persulphate interferes.   R. Cuthill.

Modification of Ridsdale's method for determining phosphoric acid. A. S. Dodd.—See B., 1928, 445.

Protein reactions of various metaphosphates. D. Balarev (Z. anal. Chem., 1928, 73, 411—412).—The relative minimal concentrations of Tammann's tri- and tetra-metaphosphates, and the metaphosphates obtained by heating sodium ammonium hydrogen phosphate and by dissolution of phosphorus pentoxide in water required to cause coagulation of a solution of protein are 1, 0·083, 0·016, and 0·0071, respectively. The protein reaction may be used as a means for the identification of metaphosphates.
J. S. Carter.

Zinc spot in the Marsh test. H. B. Arbuckle and O. J. Thies, jun. (J. Elisha Mitchell Sci. Soc., 1927, 43, 50—54).—The reaction $Zn + 2HCl = ZnCl_2 + H_2$ is reversible. Deposition of zinc may take place when hydrochloric but not sulphuric acid is used in the Marsh test.   Chemical Abstracts.

Test for borates. A. Gabriel and H. G. Tanner (J. Amer. Chem. Soc., 1928, 50, 1385).—The alkaline solution is evaporated nearly to dryness, the residue treated with 1 c.c. of concentrated sulphuric acid and then, after cooling, with 2 c.c. of methyl alcohol. The vapours are blown through a long capillary tube into a Bunsen flame, which is coloured green by methyl borate.   S. K. Tweedy.

Application of Desgrez's apparatus for the determination of total carbon to alkalimetric microanalysis. L. Lescœur and T. Turobinski (Bull. Soc. Chim. biol., 1928, 10, 606—616).—The solution under examination is oxidised under the conditions described by Nicloux (A., 1927, 436) at the ordinary pressure in a stream of air free from carbon dioxide, and the gaseous products, after removal of traces of chlorine by passage over dry potassium ferrocyanide, are absorbed in barium hydroxide. Since the gases contain other acidic substances besides carbon dioxide, the barium carbonate is removed and determined gravimetrically or preferably volumetrically.   G. A. C. Gough.

Volumetric determination of carbon dioxide. L. Lescœur and (Mlle.) S. Manjean (Bull. Soc. Chim. biol., 1928, 10, 523—536).—The gas containing carbon dioxide is circulated through 0·02N-barium hydroxide (containing 5% of barium chloride) and the loss of alkalinity determined by slow titration with 0·02N-hydrochloric acid. Correction is made for the carbon dioxide present in the air in the apparatus.   G. A. C. Gough.

Determination of potassium. S. MORGULIS and A. PERLEY (J. Biol. Chem., 1928, 77, 647—649).—The factor 0·071 given by Kramer and Tisdall (A., 1921, ii, 412) for calculation of the amount of potassium from the result of the final titration is not constant for different reagents and different amounts of potassium; each new reagent should therefore be standardised against known different amounts of potassium. Phosphorus does not interfere with the determination of potassium by this method. C. R. HARINGTON.

Effect of silica dishes in the determination of potassium. L. D. HAIGH (J. Assoc. Off. Agric. Chem., 1928, 11, 219—220).—In the determination of potassium by the official method, the evaporation and ignition of the potassium residues in silica dishes tend to render part of the potassium insoluble when phosphates are present. T. M. A. TUDHOPE.

Ceric sulphate as a volumetric oxidising agent. I. Determination of calcium. II. Determination of iron. III. Titration of iodide. IV. Determination of arsenic. V. Determination of antimony. VI. Volumetric determination of cerium. H. H. WILLARD and P. YOUNG (J. Amer. Chem. Soc., 1928, 50, 1322—1334, 1334—1338, 1368—1371, 1372—1376, 1376—1378, 1379—1385).—I. Ceric sulphate solution, conveniently prepared by dissolving impure cerium dioxide in sulphuric acid (d 1·5), may be standardised against sodium oxalate in presence of hot sulphuric, perchloric, or hydrochloric acid. The end-point may be determined electrometrically or visually (colourless to yellow), although in the latter case the burette reading must be corrected slightly. The reverse titration proceeds quantitatively in hot solutions in presence of sulphuric, perchloric, or nitric acid. Exactly the same conditions hold for the determination of ferrous iron (Someya, this vol., 146). The oxalate titration with ceric sulphate proceeds quantitatively at the ordinary temperature in the presence of a little iodine chloride (catalyst); methylene-blue may then be used as an internal indicator, provided the conditions are suitable for a rapid end-point equilibrium being attained. Calcium may be determined by precipitating it from solution as oxalate and titrating the solution of the latter in hydrochloric acid with ceric sulphate.

II. Iron may be accurately titrated with ceric sulphate after reduction with stannous chloride in hydrochloric acid (followed by addition of mercuric chloride) or with zinc or aluminium in sulphuric acid. Neither arsenious acid nor manganese interferes with the titration. The end-point may be determined electrometrically or by using less than 0·8 c.c. of 1% diphenylamine or diphenylbenzidine solution as internal indicator. The former is preferable in the analysis of iron ores. The oxidation of ferrous iron due to atmospheric oxygen introduces a constant error which may be eliminated either by applying a small correction factor or by standardising the ceric sulphate against iron of known purity (cf. Furman, this vol., 499).

III. Alkali iodide in sulphuric acid solution may be electrometrically titrated by ceric sulphate solution; moderate amounts of bromide may be present. In hydrochloric acid solution, the results are about 0·5% too low owing to loss of iodine. The former titration may be reversed and may then be used for determining cerous cerium after a bismuthate oxidation (Metzger, A., 1909, ii, 620).

IV. Arsenious acid in hydrochloric acid solution may be titrated electrometrically at 80° with ceric sulphate solution. Potassium bromide may be used as a catalyst, less salt being required the higher are the temperature and the acid concentration. The titration may be carried out at the ordinary temperature in presence of iodine chloride; methylene-blue is a suitable indicator. When determining arsenic the ceric sulphate solution should be standardised against arsenious oxide of known purity, or else the normality factor obtained by oxalate titration should be multiplied by 1·003.

V. Antimonious chloride may be titrated electrometrically at the ordinary temperature in presence of iodine chloride. No correction factor is required.

VI. Cerium, in presence of other rare earths, is oxidised with ammonium persulphate in presence of silver nitrate (catalyst) and then titrated with either potassium iodide (a blank correction is necessary), sodium nitrite (the end-point equilibrium is attained slowly), or ferrous sulphate. Sodium nitrite solution may be standardised by oxidation in acid solution with silver bromate, the precipitated silver bromide being collected and weighed, or else by electrometric titration with potassium permanganate solution.
S. K. TWEEDY.

Titrimetric determination of calcium and magnesium carbonates in limestone. J. S. PIERCE, W. C. SETZER, and A. M. PETER.—See B., 1928, 402.

Micro-determination of metallic elements. I. Micro-chemistry of potassium ferrocyanide. [Micro-determination of zinc.] R. NAKASEKO (Mem. Coll. Sci. Kyoto, 1928, A, 11, 95—112).—The minimum quantity of iron detectable with potassium ferrocyanide is 1 in 3×10^6 of solution, the optimum acidity being about 0·1N (strong acid). When solutions of ferric chloride are added to dilute solutions of ferrocyanides the presence of neutral salts or of acidity retards the development of the blue colour.

A method for the micro-determination of zinc is outlined. The solution, which should be free from iron and manganese, is evaporated and the residue ignited. The residue is treated with 2 c.c. of water, 1 c.c. of 6N-hydrochloric acid, and 1 c.c. of 5N-ammonium chloride, and 0·02N-potassium ferrocyanide added dropwise from a burette until the granular precipitate becomes colloidal (formation of $Zn_3K_2[Fe(CN)_6]_2$). The whole is diluted to 10 c.c., inserted in a water-bath at 60—70°, and kept in the dark for 30 min., when it is centrifuged. The excess of ferrocyanide in the supernatant liquor is determined with the aid of a reference table by observing the time required for the development of the blue colour when 0·05 mg. of iron (1 drop of a standard solution) is added to 5 c.c. The amount of zinc in the sample analysed is $(a - 500b) \times 0.47$ mg., where a is the number of c.c. of 0·02N-ferrocyanide added and b the normality of the excess of ferrocyanide.

3 A

Acid solutions of potassium ferrocyanide undergo rather rapid decomposition when exposed to daylight and deposit Prussian blue. On long keeping, dilute neutral solutions are slowly hydrolysed with deposition of ferrous cyanide. J. S. CARTER.

Solubility influences and quantitative analysis. I. E. WENDEHORST (Z. angew. Chem., 1928, **41**, 567—568).—The fact that the normally negligible solubilities of certain substances are often not inconsiderable in presence of neutral salts is responsible for a number of errors in gravimetric determinations. Experiments in which known quantities of zinc and cadmium were precipitated by sodium carbonate and ammonium carbonate, respectively, from media containing varying amounts of sodium, potassium, or ammonium salts show that under these conditions the amount of oxide finally weighed may be slightly greater, or considerably less, than the theoretical amount. In presence of considerable amounts of ammonium chloride no zinc was precipitated.

J. S. CARTER.

Colorimetric determination of lead. A. D. PETROV (J. Russ. Phys. Chem. Soc., **60**, 1928, 311—316).—The reaction whereby lead peroxide gives with p-tetramethyldiaminodiphenylmethane in presence of acetic acid an intense blue colour has been applied to the detection and determination of lead. The analysis is easily carried out and gives sufficiently accurate results. Iron and other impurities reduce the accuracy of the method. A. RATCLIFFE.

Deposition of metals on copper from cyanide solutions. I. Separation and determination of small amounts of lead. B. S. EVANS.—See B., 1928, 449.

Volumetric determination of small quantities of thallium. J. PROSZT (Z. anal. Chem., 1928, **73**, 401—404).—To the solution of thallous salt are added 3—4 drops of hydrochloric acid (d 1·19) for each mg. of thallium present. Saturated bromine water is then added dropwise until a yellow colour persists. The excess of bromine is removed by treating with a few c.c. of a 5% solution of phenol and a little potassium iodide. The liberated iodine is titrated with 0·01 or 0·02N-thiosulphate solution, using a microburette. The small variation of the thallium factor of the thiosulphate solution with the quantity of thallium involved must first be determined by trial measurements, using known small amounts of thallium.

J. S. CARTER.

Electrolytic deposition of traces of metals and their characterisation by spectrum analysis. E. BAYLE and L. AMY (Bull. Soc. chim., 1928, [iv], **43**, 604—624; cf. A., 1912, ii. 821; 1925, ii. 1208).—The authors claim to have increased the sensitiveness of the methods of Hartley and Moss, and of Jolibois and Bonnet. A detailed account of their electrolytic deposition apparatus is given. A glass electrolytic cell is used, having the anode of platinum, which need not necessarily be pure, and the cathode of copper, or of copper-free zinc for copper determinations. The nature of the electrolytic bath varies according to the metal to be deposited. Several media exist for each metal, and by appropriate choice, two metals could be deposited simultaneously or separately.

Details are given for the deposition of gold, silver, copper, lead, antimony, chromium, manganese, cobalt, and nickel. By spectrum analysis, the authors detect 10^{-3} to 10^{-7} mg. of substance dissolved in any volume. The sensitiveness of the deposition method varies with the electrode used and the metal under investigation. The following limits (g.) are given : (a) with a copper electrode : gold 10^{-6}, silver 10^{-8}, lead 10^{-10}, antimony 10^{-4}, cobalt 10^{-5}, nickel 5×10^{-7}, iron 10^{-7}, copper 10^{-8}, manganese 10^{-10}, and zinc 10^{-8} : (b) with a zinc electrode : silver 10^{-6}, copper 10^{-7}. The presence of marked amounts of the salts of alkali or alkaline-earth metals, and of ammonium salts does not alter the sensitiveness. The number of lines on the spectrogram allows a partial evaluation of the amount of metal present if it alone is deposited. The sensitiveness of the results obtained with the ten elements already referred to is compared with the sensitiveness of some of their respective characteristic chemical reactions. R. A. PRATT.

Determination of minute amounts of mercury. A. STOCK and W. ZIMMERMANN (Z. angew. Chem., 1928, **41**, 546—548).—A method for the determination of quantities of mercury of the order 10^{-3}—5×10^{-5} mg. and for the detection of amounts of the order 7×10^{-6} mg. is described. The initial stages are similar to those already described (A., 1926, 703, 814), save that deposition on a copper wire is effected in evacuated apparatus and at 50—60°. The sublimate obtained on distillation is dissolved in 0·25 c.c. of chlorine water and excess of chlorine expelled by air. The solution is treated with a drop of a cold, saturated solution of carbamide and diluted to 0·5 c.c. in the cell of a microcolorimeter. The blue colour produced on addition of a drop of a saturated, alcoholic solution of diphenylcarbazone is observed in a darkened room by yellow light. Comparative tests are made with solutions of pure mercuric chloride under identical conditions.

J. S. CARTER.

Systematic detection of the rare elements. T. KATO (J. Soc. Chem. Ind. Japan, 1927, **30**, 658—670).—A systematic method of separation and detection of all rare-earth metals except germanium and radium is worked out, and is described in a tabular form. S. OKA.

Electrometric titration of lanthanum, cerium, and thorium as ferrocyanides. I. A. ATANASIU (Bul. Soc. Romane Stiin., 1928, **30**, 51—59).—A 0·005—0·007M-solution of lanthanum nitrate in 30% alcohol may be titrated electrometrically with 0·1M-potassium ferrocyanide, using a platinum electrode, the point of inflexion on the titration curve corresponding with the formation of the salt $KLaFe(CN)_6$. The end-point is less definite if about 10% of alkali metal salts is present. The titration of thorium nitrate must be carried out at about 70°, but the presence of alcohol is not necessary ; the end-point is reached when an equimolecular amount of ferrocyanide has been added. In presence of 10% of ammonium or potassium chloride this titration is impossible. R. CUTHILL.

Potentiometric determination of iron with permanganate by a new method. T. HECZKO (Z. anal. Chem., 1928, **73**, 404—411).—The electrodes

are two platinum wires. The free end of one is in contact with the bulk of the solution of ferrous salt, whilst the free end of the other is wrapped round the upper portion of a short rod of pumice. Connexions are made to a galvanometer. Before commencing a titration the pumice is completely immersed in the solution and then partly withdrawn. The well-stirred solution is now titrated with permanganate, the throw of the galvanometer being observed after each addition. The end-point is reached when the ratio throw/c.c. of permanganate is maximal. The pumice should be immersed for a short period when the end-point is approached. The method depends on the establishment of an $E.M.F.$ as a result of the difference between the ferrous-ion concentrations in the pumice and the bulk of the solution. J. S. CARTER.

Gravimetric separation of iron and mercury. G. SPACU (Bul. Soc. Stiinte Cluj, 1927, **3**, 394—397; Chem. Zentr., 1928, i, 825).—Pyridine is added dropwise to the solution of the metals, containing ammonium thiocyanate, until the dark red colour becomes yellowish-brown. The precipitate is washed with hot water and ignited to ferric oxide, whilst the mercury is determined in the filtrate as sulphide.

A. A. ELDRIDGE.

Micro-determination of metallic elements. II. Micro-detection of iron with dimethylglyoxime. R. NAKASEKO (Mem. Coll. Sci. Kyoto, 1928, A, **11**, 113—117).—The tint and depth of colour produced on mixing solutions of iron, hydrogen sulphide, ammonia, and dimethylglyoxime vary with the order of mixing, but are constant under constant conditions. For the colorimetric determination of iron the test solution is first treated with a freshly-prepared, saturated solution of hydrogen sulphide to reduce ferric salts. The mixture is then treated with dimethylglyoxime (1% alcoholic solution) and finally with ammonia. The foregoing and the thiocyanate method are about equally sensitive. J. S. CARTER.

Determination of ferrous oxide in rocks. E. SALVATORE and A. SQUEO (Z. Krist., 1927, **66**, 162—166; Chem. Zentr., 1928, i, 825).—An electrically heated platinum dish containing the rock with hydrofluoric acid is covered by a greased cover-glass; a stream of dry carbon dioxide and a platinum wire stirrer are provided. A. A. ELDRIDGE.

Determination of iron in iridium sponge. O. E. ZVJAGINTSEV (Ann. inst. platine, 1927, **5**, 361).—The material is fused with sodium carbonate, the mass is extracted with water, and most of the ferric oxide removed from the iridium oxide by means of hydrochloric acid. CHEMICAL ABSTRACTS.

Determination of iron in red lead. H. HEINRICHS.—See B., 1928, 456.

Determination of iron and aluminium in the presence of calcium, magnesium, and phosphoric acid. A. J. PATTEN and O. B. WINTER (J. Assoc. Off. Agric. Chem., 1928, **11**, 202—208).—The method described by Patten (ibid., 1923, **6**, 418) has been investigated and found trustworthy. The method is specially applicable to the analysis of plants. The ferric iron and the aluminium are precipitated as phosphates by the addition of an excess of ammonium

acetate to the solution, which is slightly acid to thymol-blue. The ammonium acetate, acting as a buffer, maintains the solution below p_H 5·4. Iron and aluminium phosphates are precipitated at p_H 5·0—5·4, whereas calcium phosphate is not precipitated below p_H 6·5. A micro-method for the determination of the iron and aluminium is described. After the separation of the iron and aluminium as phosphates, they are determined colorimetrically, the iron by means of thiocyanate, and the aluminium by means of the ammonium salt of aurintricarboxylic acid (aluminon). T. M. A. TUDHOPE.

Determinative mineralogy. III. [Microchemical tests.] P. C. PUTNAM, E. J. ROBERTS, and D. H. SELCHOW (Amer. J. Sci., 1928, [v], **15**, 423—430; cf. this vol., 267).—A study has been made of the sensitivity of, and the effect of the presence of other metals on, the microchemical tests for iron, gallium, indium, and palladium. A new test for palladium, which is dependent on the formation of palladium dimethylglyoxime, is described.

F. J. WILKINS.

Detection of cobalt by means of diphenylthiocarbazone. H. FISCHER (Wiss. Veröff. Siemens-Konzern, 1928, **6**, [2], 147—149).—The addition of a solution of diphenylthiocarbazone in 10% ammonia containing a little hydrazine sulphate as stabiliser to a feebly ammoniacal solution of a cobalt salt produces a violet coloration when more than 1 μg. of cobalt per c.c. is present. The reaction will detect 0·1% Co in nickel if the solution is kept until the green nickel compound has flocculated. Zinc under the same conditions gives a purplish-red colour. To detect cobalt in presence of zinc the reaction is carried out in N-sodium hydroxide solution and the colour of the test compared with that produced by a zinc solution free from cobalt; under these conditions, the cobalt colour rapidly disappears and a grey precipitate of cobalt sulphide and sulphur separates.

A. R. POWELL.

Electrometric titration of uranyl ion with potassium ferrocyanide. I. A. ATANASIU (Bul. Soc. Romane Stiin., 1928, **30**, 77—81).—In order to titrate uranyl acetate electrometrically with 0·1M-potassium ferrocyanide using a platinum electrode, the acetate solution must contain 35% of alcohol and be at 70°. There is then an abrupt change in potential corresponding with the formation of uranyl ferrocyanide. Uranyl nitrate cannot be titrated in this way. R. CUTHILL.

Potentiometric stannometry. E. MÜLLER and J. GÖRNE (Z. anal. Chem., 1928, **73**, 385—400).—Potentiometric measurements involving stannous chloride should be carried out in an atmosphere of nitrogen. In presence of sufficient hydrochloric acid the following reactions may be followed potentiometrically : $Sn^{..}+I_2 \longrightarrow Sn^{....}+2I'$; $2Fe^{...}+Sn^{..} \longrightarrow 2Fe^{..}+Sn^{....}$ (75°); $2HCrO_4'+14H^{.}+3Sn^{..} \longrightarrow 2Cr^{...}+8H_2O+3Sn^{....}$; $2Fe(CN)_6'''+Sn^{..} \longrightarrow 2Fe(CN)_6''''+Sn^{....}$; $2Au^{...}+3Sn^{..} \longrightarrow 2Au+3Sn^{....}$; $Pt^{....}+2Sn^{..} \longrightarrow Pt+2Sn^{....}$ (75°). Where no desirable temperature is indicated the reactions may be followed at the ordinary temperature. With solutions of gold and platinum it is advisable to add chlorine

water and potassium bromate, respectively, to ensure that the metals are in their highest state of oxidation before titration with stannous chloride. The titration curve will then show two breaks. The first break corresponds with the removal of the excess of oxidising agent and the commencement of the reaction indicated above. It is perhaps advisable to replace the usual platinum electrode by a graphite rod during the first stage of the platinum titration. When solutions of stannous sulphate containing sulphuric acid are titrated at 75° with a solution of mercuric perchlorate the first break in the curve corresponds with the completion of the reaction $Hg^{..}+Sn^{..} \longrightarrow Hg+Sn^{....}$, and the third break with $Hg+Hg^{..} \longrightarrow 2Hg^{.}$. The intermediate break is probably a result of the reaction $2Sn^{....}+Hg^{..}+Hg \longrightarrow Hg_2^{..}Sn_2^{....}$. The presence of antimony $(Sb^{...})$ does not interfere. The reaction between permanganate and stannous sulphate, $2MnO_4'+5Sn^{..}+16H^{.} \longrightarrow 2Mn^{..}+5Sn^{....}+8H_2O$, can be followed at the ordinary temperature in presence of sulphuric acid. J. S. CARTER.

Iodometric determination of vanadium in special steels and in ferrovanadium. K. ROESCH and W. WERZ.—See B., 1928, 409.

Analysis of platinum ores by fusion with lead. S. F. SHEMTSCHUSHNI (Ann. inst. platine, 1927, 5, 364).—The ore (1 g.) is fused with lead (25 g.) at 1250—1300° in a graphite crucible for 2·5 hrs., the metal is dissolved in nitric acid, the lead being precipitated as sulphate and the excess of sulphuric acid removed with barium chloride. The insoluble residue is dissolved in aqua regia (only iridium remains undissolved) and the mixed solutions are analysed in the usual way. CHEMICAL ABSTRACTS.

Separation of rhodium from iridium by potassium iodide. V. V. LEBEDINSKI (Ann. inst. platine, 1927, 5, 364).—A boiling aqueous solution of potassium iodide is added to a boiling neutral solution of the chlorides, ebullition being continued for 3—4 min. The rhodium iodide is collected and washed with dilute aqueous potassium iodide, and the separation repeated after dissolution in aqua regia and evaporation to dryness. The iodide is reduced by heating in hydrogen, and the residual metal washed with hot water. The iridium in the filtrate is determined by reduction with zinc. CHEMICAL ABSTRACTS.

Analysis of iridium. O. E. ZVJAGINTSEV (Ann. inst. platine, 1927, 5, 189—192).—The metal (1—2 g.) is fused under borax with silver (10—20 g.) and the mass digested with nitric acid; the process is repeated and the platinum and palladium are determined in the solutions. The ignited residue of iridium with some rhodium is weighed, and the difference regarded as base metals. To test for iron and ruthenium, 2—3 g. are fused with sodium carbonate, and the mass is extracted with water; ruthenium is precipitated from the extract with nitric acid, whilst the insoluble residue contains iron. For the final analysis, the sample (7—10 g.) is heated in hydrogen and cooled in carbon dioxide, the loss representing oxygen and volatile compounds; the metal is heated with barium dioxide (3 pts.) in a nickel crucible for 2 hrs., the product extracted with hot water and dissolved in

aqua regia, the treatment being repeated until all the iridium is dissolved. The excess of nitric acid is removed by evaporation and the solution diluted to 1 litre; the barium is removed with the correct quantity of sulphuric acid, and sodium nitrate added to the hot solution, with stirring, until it becomes yellow. A slight excess of sodium carbonate is then added, and iron, nickel, etc. are precipitated as hydroxides by boiling. The filtrate is acidified with hydrochloric acid, and platinum, rhodium, ruthenium, etc. are precipitated as sulphides by addition of sodium sulphide to the hot solution. After evaporation of the filtrate with hydrochloric acid most of the iridium is precipitated as potassium or ammonium chloroiridate, and the remainder with magnesium. CHEMICAL ABSTRACTS.

Physical methods in chemical laboratories. I. Introduction. F. PANETH (Z. angew. Chem., 1928, 41, 507—508).—An introductory discussion. J. S. CARTER.

Physical methods in chemical laboratories. IV. Significance of spectroscopy in chemical investigations. I. E. RABINOWITSCH (Z. angew. Chem., 1928, 41, 555—561).—Energy-levels and term-systems are briefly explained, and the methods whereby heats of ionisation and dissociation are deduced from spectroscopic evidence are indicated. J. S. CARTER.

Physical methods in chemical laboratories. II. Vacuum technique. K. PETERS (Z. angew. Chem., 1928, 41, 509—515).—Modern methods of evacuation, measurement of pressure, and investigation of in-leaking are reviewed and the scope of the application of vacuum methods to analytical, photochemical, preparative, and other problems is briefly outlined. A number of diagrams and references are given. J. S. CARTER.

Manometer for vacuum distillation. F. FRIEDRICHS.—See B., 1928, 429.

Design of fractionating columns. D. B. KEYES, R. SOUKUP, and W. A. NICHOLS, jun.—See B., 1928, 429.

Extraction apparatus especially suitable for liquids. P. H. PRAUSNITZ (Chem. Fabr., 1928, 324—325).—A continuous extractor can be used equally as well as a Soxhlet even when of considerable cross-section if the condensed extracting liquid is prevented from falling in one place. This is effected by widening the lower end of the condenser and drawing it out into a large number of points. Extraction is more rapid than with a Soxhlet apparatus. The same device is applied to Wagenaar's apparatus for extracting a solute from a lighter liquid with a heavier one. A glass filter is of no use as a distributor in these two cases, but is serviceable in the extraction of a heavier liquid with a lighter one. C. IRWIN.

Apparatus for carrying out filtrations, precipitations, etc., in absence of air. P. DICKENS (Chem. Fabr., 1928, 323—324).—A conical flask with side tube closed by a glass tap and narrowed at the top is united by a funnel to a similar but inverted flask. Suitable ground-glass joints are provided for the funnel. C. IRWIN.

Adiabatic calorimeter for high temperatures. W. KANGRO (Z. Elektrochem., 1928, **34**, 253—256).— A new adiabatic calorimeter for use at 800—900° is described. An electric oven containing a pure silver block and platinum resistance thermometer is surrounded by a similarly equipped cylindrical oven; the two thermometers are connected in a bridge in such a manner that a change of temperature in the inner oven results in an equal and almost simultaneous change of that of the outer oven. H. F. GILLBE.

Electrical methods in hygrometry. P. W. BURBIDGE and N. S. ALEXANDER (Proc. Physical Soc., 1928, **40**, 149—155).—The possibility of applying electrical methods to the measurement of humidity is investigated. The two methods considered depend on (1) the change in resistance of organic materials when exposed to water vapour and (2) the change in mobility of ions due to water vapour. In neither case is the method suitable for general use, although each could be applied in special cases. C. J. SMITHELLS.

Optics of the total radiation pyrometer. H. MIETHING (Wiss. Veröff. Siemens-Konz., 1928, **6**, (2), 135—146).—The absorption of heat radiations by the glass and quartz lenses of the ardometer (a total radiation pyrometer) has been determined graphically for black-body conditions between 700° and 2000° and the calculations have been confirmed by experiment. It is shown to be impossible to measure the radiation energy of selectively radiating bodies by means of an ardometer with glass lenses, as high results are obtained with bodies (e.g., metals) the emissive power of which decreases, and low results with bodies the emissive power of which increases in the infra-red with rise of temperature.
A. R. POWELL.

Photographic examination of moving flames. A. G. WHITE (J.C.S., 1928, 1159—1161).—A new method is described for the examination of moving flames which is independent of their luminosity, and takes advantage of the fact that the progress of the flame causes an abrupt change in the optical properties of the medium through which it passes. It gives better definition and better resolution than the ordinary direct photographic method.
F. J. WILKINS.

Relationship between chemical composition and the resistance of glasses to the action of chemical reagents. II. Glasses containing iron oxides. V. DIMBLEBY and W. E. S. TURNER.— See B., 1928, 404.

Instrument to record the carbon dioxide content of a gaseous mixture. R. GORDON and J. F. LEHMANN.—See B., 1928, 391.

Simple, automatic control of vacuum. S. P. MILLER and P. V. McKINNEY (Ind. Eng. Chem., 1928, **20**, 552).—The vacuum is controlled by a valve to the atmosphere. The valve is a fine, capillary opening in contact with a rubber stopper mounted on the arm of an electro-magnet. The latter is operated by platinum contacts in the mercury of the manometer. A vacuum reduced to 5 mm. is controlled within 0·3 mm. J. S. CARTER.

Vacuum resistance vessel for conductivity measurements and conductometric analyses. I. A. REMEZOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 925—931).—A vessel for conductivity measurements has been devised in which owing to its complete isolation from the influence of the surroundings it is possible to maintain a constant temperature for 18— 20 min. after switching on the current. Measurements with an accuracy of ± 0.05—0.01% have been made with this instrument. When used for conductometric analyses a micro-burette is ground into the lid of the vessel. Good results were obtained for the neutralisation of a series of acids and alkalis by this method. A. RATCLIFFE.

Method of determination of m. p. with electrical signal. G. WICK and G. BARCHFELD (Chem. Fabr., 1928, 281).—The substance is packed in the bottom of a glass tube and above it rests a narrow glass rod on which rests a contact arm. The tube is placed in a heated block and when liquefaction occurs the rod and arm fall, closing an electric circuit.
C. IRWIN.

New microcolorimeter and its use. H. KLEINMANN (Chem. Fabr., 1928, 263—264, 278—279).—The colorimeter is similar in principle to the Duboscq instrument and consists of a pair of vessels of 1 c.c. capacity, dipping rods, lamps, scales, and eyepiece. For accurate results careful filtration of the solutions is necessary and air bubbles must not be allowed. Errors then should not exceed 1%. The instrument is suitable in conjunction with a micro-Kjeldahl apparatus for the determination of nitrogen by Nessler reagent. Quantities as small as 5×10^{-6} mg. can be determined, the principal difficulty being, not of manipulation, but in obtaining reagents sufficiently free from ammonia. C. IRWIN.

High-frequency vacuum furnace for laboratory use. E. W. FELL (Arch. Eisenhüttenw., 1927—1928, **1**, 659—661; Stahl u. Eisen, 1928, **48**, 661—662).— A 3·6-kw. high-frequency induction furnace working in a large evacuated glass bell-jar is described and figured. The bell-jar rests on a ground-glass plate, from which it is separated by a soft rubber washer. In the centre of the plate on a thick insulating slab of asbestos is the induction coil of water-cooled copper tube surrounding a refractory crucible which is surmounted by a refractory radiation shield. The connexions to the vacuum pump are made through an opening in the top of the bell-jar which also carries a small periscope in which the behaviour of the mass may be observed. The tubes for cooling water and the electrical connexions are passed through holes in the glass plate which are then rendered gas tight with a suitable plastic cement. Means are also provided for dropping small quantities of metal or flux on to molten charge during an experiment.
A. R. POWELL.

Report on metallography. H. C. BOYNTON and others (Proc. Amer. Soc. Testing Materials, 1928, **27**, i, 597—599).—Nickel-silver is best etched with boiling ferric ammonium sulphate solution. Etching reagents for identifying carbides etc. in alloy steels are discussed. CHEMICAL ABSTRACTS

Geochemistry.

Electrical conductivity and refractive index of peat-bog waters. I. A. SMORODINCEV and A. N. ADOVA (J. Russ. Phys. Chem. Soc., 1928, **60**, 497—505).—Changes in the mineral content of peat-bog water may be followed by electrical conductivity measurements. Where the content of organic matter is high, as in sphagnum waters, no strict parallelism exists between the solid content and the electrical conductivity. Sedge-grass waters, which have low refractive indices, possess an electrical conductivity four to five times as great as that of sphagnum waters. The refractive index varies, up to a certain point, proportionally to the organic content.

      R. TRUSZKOWSKI.

Spectrochemistry of Portuguese mineral waters; that of Gerez. A. P. FORJAZ (Compt. rend., 1928, **186**, 1366—1367).—A water from a porphyroid granitic formation in the north of Portugal was examined spectrographically after concentration and removal of the alkaline-earth metals. In addition to the elements already detected in these structures (*ibid.*, 1921, **173**, 1170) germanium, cæsium, silver, and lead were found. The rôle of germanium as an indicator of geological age and origin is mentioned.

      J. GRANT.

Base exchange and the formation of petroleum. M. STUART (Nature, 1928, **121**, 940; cf. Taylor, this vol., 612).—It is questioned whether in Nature solid fats could be a sedimentary deposit in water and accumulate as such together with sand; further, a study of the effect of the bacterial decomposition in sea water under anaërobic conditions by *Microspira aestuarii* (van Delden) of protoplasm and of vegetable oils incorporated as sediments in clay is suggested.

      A. A. ELDRIDGE.

Helium and the genesis of petroleum. C. C. FARR and M. N. ROGERS (Nature, 1928, **121**, 938).—The formation of higher hydrocarbons from methane by α-particles observed by Lind and Bardwell (A., 1926, 769, 1077) may account for the genesis of petroleum, in view of the fact that in the mid-United States of America the regions in close proximity to oil-fields are also regions in which the natural gases have a high helium content. Tentative calculations suggest that the formation of 1 cu. ft. of helium would produce nearly 2 tons of liquid hydrocarbon.   A. A. ELDRIDGE.

Thermal instability of the earth's crust. H. H. POOLE and J. H. J. POOLE (Phil. Mag., 1928, [vii], **5**, 662—667).—The published physical data on solid and liquid basalts lead to the result that the adiabatic temperature gradient of the earth's crust is 0·75° per kilometre at the surface and decreases with increasing depth. On similar grounds, the m.-p. gradient is 3° per kilometre at a depth of 40 kilometres. The two gradients should be equal at a depth of about 200 kilometres. At depths less than 200 kilometres, it is improbable that the adiabatic could be steeper than the m.-p. gradient. These results lead to the conclusion that, in the absence of infusible continental masses, a deep layer of magma the radioactivity of which is at all comparable with that of surface specimens of basic or ultra-basic rocks would undergo periodic changes of state possibly accompanied by corresponding changes in the temperature gradient in the crust. In the presence of continental masses, however, resolidification of the underlying basaltic magma would be prevented, and the present solidity of the magma underlying the continents is best explained by Joly's assumption that tidal effects in the liquid magma produce lateral displacements of the continents and thus allow the escape of accumulated heat.   A. E. MITCHELL.

Geochemical inertia of the elements of the triads. P. VINASSA DE REGNY (Atti R. Accad. Lincei, 1928, [vi], **7**, 23—25; cf. this vol., 267).—Further consideration leads to the conclusion that, as a rule, simple or compound substances, whether natural or artificial, organic or inorganic, have even molecular numbers. Almost the whole of the earth's mass is composed of substances with atomic numbers up to 28, *i.e.*, lying within the first triad. The geochemical inertia of the elements of the triads is to be attributed to the number and arrangement of the electrons corresponding with a condition of equilibrium.   T. H. POPE.

Quantitative mineralogical and chemical classification of igneous rocks. E. T. HODGE (Univ. Oregon Pub. [Geol. Series], 1927, **1**, 133—200).—Rocks are classified mineralogically in four classes, based on the content of felspars and felspathoids; the classes are subdivided into 19 orders, based on the ratio of orthoclase (and orthoclase equivalents) to the other felspars. The classes and orders are divided into seven ranges, based on the law of saturation, the ranges passing through every class and order. The arrangement is such that the mineralogical composition gives the chemical composition.

      CHEMICAL ABSTRACTS.

Allochromy, morphotropy, and formation of minerals, particularly gem stones. R. KLEMM (Fortschr. Min. Kryst. Petr., 1927, **12**, 47—48; Chem. Zentr., 1928, i, 894).—Change in habit on entry of colouring elements is considered; formation of mixed crystals is postulated.   A. A. ELDRIDGE.

Synthetic spinel. F. RINNE (Fortschr. Min. Kryst. Petr., 1927, **12**, 68—69; Chem. Zentr., 1928, i, 894).

Rock-forming alkali hornblendes. W. KUNITZ (Fortschr. Min. Kryst. Petr., 1927, **12**, 49—50; Chem. Zentr., 1928, i, 896).—The end components of the series syntagmatite–arfedsonite correspond with the formulæ $HCa_3Al_3Fe_5Si_6O_{25}$ and $HNa_3Fe_5Si_9O_{25}$. Becke's series gastaldite–riebeckite was confirmed, the first and last formulæ being $H_2(NaAl)_2Mg_4Si_9O_{27}$ and $H_2(NaFe)_2Mg_4Si_9O_{27}$. It is believed that the whole of the iron was originally ferrous.   A. A. ELDRIDGE.

Change of the green colour of beryl into blue. J. KURBATOV and W. KARGIN (Zentr. Min. Geol., 1927, *A*, 361—362; Chem. Zentr., 1928, i, 481).—When ordinary beryl is heated at 450—500° for 30

min., it becomes bluish; the change is apparently due to the presence of iron. A. A. ELDRIDGE.

Rosterite and other beryls. F. ZAMBONINI and V. CAGLIOTI (Gazzetta, 1928, 58, 131—152).—Following a description of the chemical and crystallographic analysis of the beryl rosterite the composition of this substance is discussed with reference to that of other beryls. It is suggested that all beryls consist of mixed crystals of the general formula $R_2SiO_3, R_2Al_2Si_2O_8$, where R_2 may denote one or more of : Li_2, Na_2, K_2, Cs_2, Rb_2, Be, Ca, or Mg. R. W. LUNT.

Thomsonite from the basalt of Disko, Greenland. H. R. VON GAERTNER and F. MACHATSCHKI (Zentr. Min. Geol., 1927, A, 365—366; Chem. Zentr., 1928, i, 482).—The crystals of thomsonite contained SiO_2 41·64, Al_2O_3 29·96, CaO 11·24, Na_2O 3·50, K_2O 0·49, H_2O 13·14%. A. A. ELDRIDGE.

Rare-earth elements. N. A. ORLOV (J. Russ. Phys. Chem. Soc., 1928, 60, 515—544).—A number of rare-earth minerals are discussed, and in certain cases analysed, the results obtained confirming those of other authors. The methods used for the separation of the individual elements from each other are reviewed in detail, and a combination of fractional crystallisation and precipitation methods is proposed for the separation of yttrium from erbium and ytterbium. R. TRUSZKOWSKI.

Occurrence and detection of the platinum metals in Norwegian rocks. II. G. LUNDE and M. JOHNSON (Z. anorg. Chem., 1928, 172, 167—195).—The amounts of platinum metals, gold, and silver in a number of Norwegian rocks have been determined by methods similar to those described in the previous paper (A., 1927, 439). Results are given also for the quantities of these metals present in the ordinary analytical reagents. H. F. GILLBE.

Chlorite-schists from the Tatra Mts. S. JASKÓLSKI (Bull. Acad. Polonaise, 1928 for 1927, A, 703—717).—The chlorite-schists of the Tatra Mts. grade into and have been derived from amphibolites and amphibolite-biotite-schists. Analyses of these rocks show a similarity in composition to diorites, from which the amphibolites were no doubt derived. Two analyses are also given of the chlorite isolated from these rocks, and their composition is compared with that of celadonite. L. J. SPENCER.

Nature of clay, and its significance in the weathering cycle. G. W. ROBINSON (Nature, 1928, 121, 903—904).—Evidence is adduced in support of the view that the primary residual product of the chemical weathering of silicates is a mixture of kaolinite and nontronite, or of hydrated silicates having the same silica/sesquioxide ratio (2·0). A. A. ELDRIDGE.

Variation of the refractive indices of sphalerites and their iron contents. S. NISHIO (J. Fac. Eng. Tokyo, 1928, 17, 183—189).—By the immersion method in fused mixtures of sulphur and selenium, determinations for different wave-lengths were made of the refractive indices of blende from several Japanese localities, and the results are plotted on curves. The extreme values for sodium light are 2·370 (with 1·16% Fe) and 2·428 (with 10·35% Fe). L. J. SPENCER.

Constituents and genesis of a few minerals produced from hot springs and their vicinities in Japan. III. **Calcium carbonate minerals deposited from effervescent springs.** I. SUGANUMA (Bull. Chem. Soc. Japan, 1928, 3, 87—89).—A high temperature is not necessary for the production of aragonite, in contradiction to Meigen's views. H. F. GILLBE.

Organic Chemistry.

Oleic, palmitic, and stearic acids as parents of petroleum. N. D. ZELINSKI and K. P. LAVROVSKI (Ber., 1928, 61, [B], 1054—1057; cf. B., 1927, 865).—Decomposition of oleic acid in the presence of 30% of aluminium chloride commences at the ordinary temperature and is very vigorous at 150°, giving carbon dioxide, inflammable gases which decolorise permanganate solution, and liquid products. The hydrocarbons of lowest b. p. are somewhat similar to analogous fractions obtained by the condensation of ethylene. The fractions of intermediate and highest b. p. do not contain hexahydroaromatic derivatives, but are rich in paraffin and *cyclo*paraffin hydrocarbons which have not been fully elucidated but probably contain derivatives of *cyclo*pentane. It is remarkable that aluminium chloride transforms oleic acid into liquid paraffin hydrocarbons but not into *cyclo*hexane hydrocarbons or solid paraffins. Stearic and palmitic acids decompose more readily than oleic acid in the presence of aluminium chloride, giving carbon dioxide and reducing gases. Palmitic acid yields a small liquid distillate, b. p. 70—130°, and a solid paraffin,

(?)$C_{30}H_{62}$, m. p. 79·5°, mean mol. wt. 412. Stearic acid gives small liquid fractions, b. p. 130—190° and 100—140°/15 mm., respectively, and 60% of a solid paraffin hydrocarbon, (?)$C_{34}H_{70}$, m. p. 80·5°, mol. wt. 511.

It is not improbable that palmitic and stearic acids are the parents of petroleums rich in solid paraffins. H. WREN.

Oxidation of *n*-hexane. M. BRUNNER and E. K. RIDEAL (J.C.S., 1928, 1162—1170).—The oxidation of hexane is shown to be very similar to the auto-oxidation of benzaldehyde, there being a period of induction during which peroxide molecules are formed which can react with hexane. When the concentration of the peroxide rises to a certain value there is probably a chain mechanism of excitation of peroxide molecules and rapid combustion sets in. The temperature of initial combustion is not characteristic of the hydro-carbon (cf. Lewis, A., 1927, 851). The induction period can be shortened by a rise in temperature or an increase of oxygen pressure. Aniline exerts a marked inhibiting effect on the oxidation and pumice causes

slow combustion accompanied by a slight decrease in pressure due to the formation of aldehydes and polymerised products from the decomposition of peroxide molecules. B. W. ANDERSON.

Synthesis of Δ^α-butene. H. J. LUCAS and R. T. DILLON (J. Amer. Chem. Soc., 1928, 50, 1460—1464). —The methods of obtaining Δ^α-butene are reviewed. Its preparation in 43 g. lots from allyl bromide and magnesium methyl bromide at 70° (cf. Kirrmann, A., 1926, 934) and purification by washing and fractional distillation are detailed. H. E. F. NOTTON.

Preparation and physical properties of α-, β-, and iso-butylenes and n- and iso-butanes. C. C. COFFIN and O. MAASS (J. Amer. Chem. Soc., 1928, 50, 1427—1437).—α-Butylene (a) is prepared from butyl iodide and alcoholic potassium hydroxide, β-butylene (b) from butyl alcohol in presence of phosphoric acid at 250—280° (King, J.C.S., 1919, 115, 1404), iso-butylene (c) from isobutyl alcohol (cf. A., 1927, 851), and n- (d) and iso- (e) butanes from the appropriate butylene and hydrogen using a nickel catalyst at 150—200°. All were purified by repeated fractionation. A large number of measurements of physical properties are recorded over the following temperature ranges. Vapour pressure : (a) −3·7° to −77·5° (e.g., 811·4 mm., −4·4° ; 83·3 mm., −52·3°) ; (b) 20·4° to −66·8° (707·4 mm., −1·0° ; 79·6 mm., −47·1°). Density : (a) 9·8° to −46·0° ($d^{-0.5}$ 0·6170 ; $d^{-30.9}$ 0·6528) ; (b) 17·8° to −42·4° ($d^{9.9}$ 0·6303, $d^{-30.4}$ 0·6638) ; (d) 32·5° to −34·4° ($d^{18.9}$ 0·5805, $d^{-30.2}$ 0·6318) ; (e) 25·3° to −27·8° ($d^{20.2}$ 0·5591, $d^{-27.8}$ 0·6131). Surface tension : (a) 20° to −55° (13·85 at 10°) ; (b) 20° to −50° (14·82 at 10°) ; (d) 29·7° to −36·1° (13·64 at 10·1°) ; (e) 23·3° to −36·3° (11·61 at 9·8°). The following constants are tabulated and compared with those obtained (A., 1921, i, 489) with the corresponding lower homologues ; m. p. ; b. p. (a) −6·1°, (b) 1·0°, (c) −6·6°, (d) −0·5°, (e) −10·2° ; critical temperature ; Ramsay and Shields' constant ; Trouton's constant ; surface tension at the b. p. (a) 15·95, (b) 16·78, (c) 15·72, (d) 14·90, (e) 14·10 ; total surface energy ; mol. vol. at the b. p., and mol. vol. at the m. p. H. E. F. NOTTON.

Polymerisation. XI. Polymerisation and depolymerisation of amylenes under the influence of silicates. S. V. LEBEDEV and I. A. VINOGRADOV-VOLZYNSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 441—452).—A mixture of amylenes, consisting of trimethylethylene and methylethylethylene, yielded when heated with floridin (a silicate activated by heating at 300—350°) diamylene, b. p. 37—39°. This product when heated at 150—160° with floridin yielded gaseous and liquid products. The former consist of 8·25% of methane and 91·4% of a mixture of iso- and ψ-butylenes, with possibly traces of propylene. The liquid products consisted of isopropylethylene, isopentane, trimethylethylene, γ-methyl-Δ^β-pentene, b. p. 67—69°, heptylene, octylene, and nonylene. R. TRUSZKOWSKI.

Polymerisation of acetylene. I. C. FUJIO (J. Soc. Chem. Ind. Japan, 1928, 31, 77—86).—When purified acetylene is passed through a glass tube filled with a catalyst and heated at 400—700°, the yield and nature of the tar produced depend on the temperature,

rate of passing acetylene, and the nature of the catalyst ; the maximum yield was about 82% by passing 5 litres of the gas per hour over clay heated at 650°. The tar fraction b. p. below 175° consisted of benzene and other aromatic hydrocarbons and the fraction b. p. 175—250° mostly of naphthalene. The yield of the " gas oil " fraction of the tar was greatest with charcoal as catalyst. When a metal tube was used instead of glass, the decomposition of acetylene into carbon, hydrogen, and other gaseous substances took place more abundantly than the polymerisation. The tar thus produced differed from that obtained by using a glass tube ; the fraction of b. p. 100—250° was large and that of b. p. 175—250° contained only a trace of naphthalene. A porcelain tube, however, behaves like glass in the polymerisation of acetylene. K. KASHIMA.

Activity of halogen derivatives of the propyl series. B. V. TRONOV and A. J. GERSEVIC (J. Russ. Phys. Chem. Soc., 1927, 59, 727—739).—The connexion between the number and position of halogen atoms in the molecule and their reactivity was investigated from the viewpoint of Lowry's theory of alternate polarity and the electronic conception of double linkings for compounds of the ethyl series, both saturated and unsaturated.

The activity, both " ionic " and " molecular," of the halogen atoms was estimated by the rate of reaction with pyridine and sodium methoxide, respectively. A second halogen atom if in the α-position to the first decreases the ionic activity, but increases it if in the β-position, in accordance with the theory of alternate polarity, whereas in both cases the activity towards sodium methoxide is increased. In monosubstituted α-derivatives, the halogen atom is much more active in ionic and slightly more active in molecular reactions than in β-derivatives. An adjacent double linking always greatly enhances the activity, whilst a hydroxyl group has the same effect as a second halogen atom. M. ZVEGINTZOV.

Reaction of the Grignard reagent with γ-chloropropyl p-toluenesulphonate ; a method of lengthening carbon chains by three carbon atoms. S. S. ROSSANDER and C. S. MARVEL (J. Amer. Chem. Soc., 1928, 50, 1491—1496).—In equimolecular proportions Grignard reagents and γ-chloropropyl p-toluenesulphonate give only small yields of the desired product (cf. Gilman and Beaber, A., 1923, i, 453). Thus, magnesium butyl halides give only the corresponding γ-chloropropyl halides ; magnesium n-heptyl bromide gives n-decyl chloride (11·4%) ; magnesium n-hexyl bromide, n-nonyl chloride (14%) ; magnesium benzyl chloride, δ-phenyl-butyl chloride (42%), and magnesium δ-phenylbutyl chloride, η-phenylheptyl chloride (25%). Volatile sulphur compounds and substances of high b. p. are also formed. An improved yield of the derivative with three additional carbon atoms is obtained from 1 mol. of a Grignard reagent containing six or more carbon atoms and 2 mols. of γ-chloropropyl p-toluenesulphonate. In this way γ-phenylbutyl chloride (50% of the theoretical yield), γ-phenylpropyl chloride (62%), n-amyl chloride (23%), n-nonyl chloride (52%), n-pentadecyl chloride (30%), γ-cyclohexylpropyl

chloride (62%), η-phenylheptyl chloride (44%), and n-decyl chloride (50%) were formed together with considerable quantities of the corresponding γ-chloropropyl halide. Magnesium benzyl chloride (1 mol.) yields with 1 mol. of n-butyl p-toluenesulphonate, mainly amylbenzene with butyl chloride and toluene, and with 2 mols. an increased yield of the first two.

H. E. F. NOTTON.

Oxonium compounds. D. McIntosh (Proc. Nova Scotian Inst. Sci., 1927, 16, 96—103).—See A., 1926, 144.

Colour reactions of some alcohols. L. Ekkert (Pharm. Zentr., 1928, 69, 289—296).—The colour reactions obtained by treating very dilute solutions of the aliphatic alcohols (propyl to octyl) in ethyl alcohol (96%) containing small amounts of furfuraldehyde, various aromatic aldehydes, or sucrose with concentrated sulphuric acid are recorded. These reactions, which are to a great extent specific, may be used to distinguish between small amounts of isomeric alcohols. G. A. C. GOUGH.

Rate of oxidation of alcohols by chromic and nitric acids in aqueous solution. B. V. Tronov, B. F. Udodov, and M. J. Tschishova (J. Russ. Phys. Chem. Soc., 1927, 59, 1149—1156).—The rate of oxidation by chromic acid ($0.3N$) and nitric acid (39% and 67%) of methyl, ethyl, n- and iso-propyl, iso- and $tert.$-butyl, γ-methylbutyl, propylenyl, and benzyl alcohols, $cyclo$hexanol, methyl glycol, and glycerol was measured at 17—19° in equimolecular solution, by determining from time to time the amount of acid used. Owing to the complex nature of the products, esterification and partial insolubility of some of the alcohols, only the first few values were used for comparison. The rate of oxidation of the saturated monohydric primary alcohols increased with the length of the carbon chain. Secondary alcohols are more easily oxidised by nitric acid, but less easily by chromic acid, whilst $tert.$-butyl alcohol is not effected. The unsaturated alcohols are more reactive than the saturated. M. ZVEGINTZOV.

Rate of oxidation of alcohols, ethers, and esters by potassium permanganate and chromic anhydride under various conditions. B. V. Tronov and A. A. Lukanin (J. Russ. Phys. Chem. Soc., 1927, 59, 1157—1172; cf. preceding abstract).—The behaviour of ethyl alcohol, ether, and acetate, n- and iso-propyl alcohols, propaldehyde, and propyl acetate towards both acid and alkaline potassium permanganate and chromic anhydride (both with and without an excess of sulphuric acid) was investigated, in order to elucidate certain difficulties encountered in previous investigations. The bimolecular velocity coefficient for the oxidation reaction was determined at 19—21°, the compound to be oxidised being present in equimolecular proportions, or in excess. The primary alcohols with permanganate and all the alcohols and ethers with chromic anhydride give satisfactory coefficients. isoPropyl alcohol does not, whilst the esters are hydrolysed by chromic anhydride. The rate of oxidation is always greatly increased by excess of acid or alkali, and the alcohols are much more readily oxidised than the other compounds. All the earlier observations (cf. loc. cit.) are confirmed. M. ZVEGINTZOV.

Rate of oxidation of alcohols by potassium permanganate. B. V. Tronov, A. A. Lukanin, and J. J. Pavlinov (J. Russ. Phys. Chem. Soc., 1927, 59, 1173—1197; cf. preceding abstracts).—The rate of oxidation by $0.03N$-potassium permanganate in equimolecular proportions in neutral solution at 16°, 18°, 21°, and 24° of the following alcohols was investigated : Methyl, n-propyl, isopropyl, trimethylcarbinol, ethyl, n-butyl, isobutyl, isoamyl, heptyl, cetyl, $sec.$-butyl, $cyclo$hexanol, $tert.$-amyl, pinacol, ethylene glycol, propylene glycol, glycerol, erythritol, adonitol, mannitol, allyl, and benzyl. The first four were also oxidised in alkaline solution. In neutral solution the primary alcohols and ethylene glycol only give a satisfactory bimolecular velocity coefficient.

All the monohydric alcohols (except allyl alcohol) reduce neutral potassium permanganate as far as quadrivalent manganese, whilst with the others the reduction is more complete. In alkaline solution (in which oxidation is always many times more rapid than in neutral) the velocity coefficient falls rapidly up to 10—20% of available oxygen, and is then steady up to 40—50%.

The saturated polyhydric alcohols are the more readily oxidised the greater is their number of hydroxyl groups. Of the monohydric alcohols the secondary are slightly more active than the primary, whilst the tertiary are almost inactive. Activity increases with the length of the chain. The benzene nucleus, and especially unsaturated linkings, very greatly increase the rate of oxidation. M. ZVEGINTZOV.

Catalytic oxidation with air of ethyl, isopropyl, and n-butyl alcohols. R. M. Simington and H. Adkins (J. Amer. Chem. Soc., 1928, 50, 1449—1456). —The catalysts used include copper, silver, platinum, nickel, alloys of copper with silver, zinc,* bismuth, cadmium, palladium, platinum, nickel, manganese, and silicon, and of silver with gold, zinc, bismuth, and palladium, also mixtures of copper oxide with oxides of molybdenum,* uranium, iron, vanadium,* and tungsten * (* with all except these, the reaction proceeded without external application of heat). Gauze, pellets, strip, and wire catalysts were equally efficient. The yields of carbon monoxide and dioxide, saturated and unsaturated hydrocarbons, aldehyde or ketone, and acid are tabulated for some 12 catalysts. The maximum yields of aldehyde and ketone were : ethyl alcohol 76.0% (using an alloy of Cu 90%, Ag 10%), isopropyl alcohol 76.1% (silver pellets), n-butyl alcohol 72.5% (Cu 80%, Zn 20%) and 72.0% (silver). The yield of hydrogen was small except with catalysts containing zinc. Alloys containing 99% of silver or copper did not differ catalytically from the pure metals, so that probably a large proportion of the surface is active. Plated catalysts are ineffective on account of the rapid dissolution of the plating in the underlying metal. With any self-heating catalyst the mol. ratio of the carbon dioxide formed from equal mols. of alcohol is ethyl, 3 : isopropyl, 2 : n-butyl, 1.

H. E. F. NOTTON.

isoPropylacetylenylcarbinol and two stereoisomeric forms of diisopropylbutinenediol. V. Krestinski and V. Marjin (J. Russ. Phys. Chem. Soc., 1927, 59, 1135—1140).—See A., 1927, 1052.

Alkali compounds of polyhydric alcohols and carbohydrates. L. SCHMID, A. WASCHKAU, and E. LUDWIG (Monatsh., 1928, 49, 107—110).—Carefully-purified ethylene glycol, glycerol, dextrose, lævulose, glycogen, and chitin form definite *monosodium compounds* when treated with sodium in pure, anhydrous liquid ammonia solution (cf. Schmid and Becker, A., 1925, i, 1386), the compound in each case being isolated and analysed. In the case of the inulin compound the inulin was recovered unchanged in rotation by decomposition with water.

J. W. BAKER.

Configuration of α-glycols formed by oxidation of ethylene derivatives. J. BÖESEKEN (Rec. trav. chim., 1928, 47, 683—693).—The evidence for the configuration of the diols obtained by the oxidation of various open-chain and cyclic olefine derivatives by alkaline potassium permanganate or peracids is summarised and an attempt at correlation is made. In the case of open-chain derivatives the evidence is not conclusive, the only proved case being the oxidation of maleic acid (*cis*) exclusively to meso-tartaric acid, and of fumaric acid (*trans*) to racemic acid. In the cyclic series *cyclo*pentene, 1-methyl- and 1-phenyl-*cyclo*pentene, indene, *cyclo*hexene, 1-methyl-*cyclo*hexene, and tetrahydronaphthalene-1 : 2-diol when oxidised with potassium permanganate yield exclusively, or almost exclusively, the *cis*-1 : 2-diols. Evidence for the configuration of the diols is based (1) on the possibility of optical resolution of the *trans*-isomeride, (2) the formation of complexes with boric acid and borates, with resulting increase in electrical conductivity, and (3) the formation of cyclic condensation products with acetone. Thus oxidation by permanganate takes the expected course and it is suggested that intermediate products of the type

$$\begin{array}{c} -\text{C}-\text{O} \\ -\text{C}-\text{O} \end{array}\!\!\!>\!\text{Mn}<$$

are formed which, by hydrolysis, yield the *cis*-diols. On the other hand, oxidation by means of peracids usually takes the opposite course. Perbenzoic acid yields the ethylene oxide, whilst peracetic acid yields the monoacetate of the diol, each product being smoothly hydrolysed to the same diol. Thus *cyclo*pentene, 1-methyl*cyclo*pentene, *cyclo*hexene, and 1-methyl*cyclo*hexene yield exclusively the *trans*-diol, whilst indene and 1-phenyl*cyclo*hexene yield a mixture of *cis*- and *trans*-diols. In the former case the proportion of the two forms depends largely on the acidity or alkalinity of the medium and on the temperature, the *cis*-form preponderating in acid media. In the latter case in 0·05N-sulphuric acid at low temperatures the *cis*- and *trans*-diols are formed in approximately equimolecular proportions. Thus the presence of a phenyl group on the ethylenic carbon atom causes the formation of a large quantity of the *cis*-form. Confirmation of this is found in the oxidation of stilbene and *allo*-stilbene with peracetic acid. Decomposition of butan-β-ol with phosphoric acid at 200° yields mainly *cis*-Δβ-butene, since the latter on oxidation with peracetic acid yields racemic butane-βγ-diol.

J. W. BAKER.

Preparation of οδ-dihydroxy-*n*-butane (tetra-methyleneglycol) and αδ-dibromo-*n*-butane. A. MÜLLER (Monatsh., 1928, 49, 27—30).—αδ-Di-hydroxy-*n*-butane [phenylurethane, m. p. 183—183·5° (corr.), 163—164° on remelting; Hamonet, A., 1905, i, 403, gives 180—181°] is readily prepared in 54% yield by reduction of ethyl succinate with sodium and absolute alcohol, followed, after removal of the alcohol by steam distillation in the usual manner, by distillation of the product with superheated steam. The aqueous distillate is distilled in a vacuum and an aqueous distillate passes over, leaving behind almost pure tetramethylene glycol, which is again distilled in a vacuum. When the glycol is treated with a current of dry hydrogen bromide at 80° for 5 hrs. a 70% yield of αδ-dibromo-*n*-butane is obtained.

J. W. BAKER.

Pinacolin transformation of a βγ-butylene glycol. T. TAIRA (Bull. Agric. Chem. Soc. Japan, 1927, 3, 46—48).—When βγ-butylene glycol is distilled with 25% sulphuric acid, some methyl ethyl ketone is produced.   CHEMICAL ABSTRACTS.

Dimethyl peroxide. A. RIECHE [with W. BRUMSHAGEN] (Ber., 1928, 61, [*B*], 951—956).—*Di-methyl peroxide*, b. p. 13·5°/740 mm., d 0·8—0·85, is prepared by the action of potassium hydroxide on a mixture of hydrogen peroxide and methyl sulphate in an indifferent atmosphere. The gaseous substance is very freely soluble in alcohol and ether, freely soluble in water. Its constitution is established by its reduction to methyl alcohol. Its oxidising action is not profound; iodine is liberated slowly from acidified potassium iodide solution, whereas quinol and hydrazobenzene are not oxidised. Almost quantitative reaction ensues when its ethereal solution is shaken with aqueous titanium trichloride. It is extremely explosive, particularly when in the gaseous state, being unusually sensitive to shock; light appears to have little effect on it. Formaldehyde is produced by its explosive decomposition.   H. WREN.

Synthesis of partly acylated glycerides. II. B. HELFERICH and H. SIEBER (Z. physiol. Chem., 1928, 175, 311—315; cf. this vol., 44).—By the action of *p*-nitrobenzoyl chloride on glycerol αγ-ditrityl ether in dry pyridine at 0° is obtained the β-*p*-nitro-benzoate, m. p. 188° (corr.), which by hydrolysis with hydrogen bromide in acetic acid yields *glycerol-β-p-nitrobenzoate*, m. p. 120—121° (corr.). The structure of this is proved by its ready conversion by the action of benzoyl chloride in pyridine into glyceryl αγ-dibenzoate β-*p*-nitrobenzoate (Bergmann, Brand, and Dreyer, A., 1921, i, 444). *Glyceryl αγ-ditrityl ether β-palmitate*, m. p. 70—72° (corr.), is similarly obtained from the αγ-ditrityl ether and palmityl chloride.   J. W. BAKER.

Polymerisation and condensation. II. Products of interaction of potassium acetate and epichlorohydrin. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1928, 77, 685—696).—Epichloro-hydrin was heated with anhydrous potassium acetate (*a*) for 24 hrs. at 120° rising to 150°, (*b*) for 48 hrs. at 125° rising to 155°. By fractional distillation of the product there was obtained in the first case unchanged epichlorohydrin, glycidol acetate, diacetin, and *diacetylglycerylglycidol*, b. p. 110—114°/0·1 mm., m. p. 125°, and in the second case the above compounds together with impure *triacetyldiglycerol*, b. p.

155—168°/0·05 mm.; the distillation residue appeared to consist of polymerides of glycerol of high mol. wt.

C. R. HARINGTON.

Chloromethyl sulphate. V. GRIGNARD, C. TOUSSAINT, and J. CAZIN (Bull. Soc. chim., 1928, [iv], 43, 537—542).—An account of work carried out prior to the investigation of Fuchs and Katscher (this vol., 43). Chloromethyl ether (1 mol.) and fuming sulphuric acid (60%; 1 mol.) in the cold afford a fraction, b. p. 82—83°/22 mm., of the approximate composition $3SO_3,2(CH_2Cl)_2O$, probably a mixture of maximum b. p., and identical with the liquid obtained by Houben and Arnold (A., 1907, i, 1000). If the temperature is allowed to rise to 160° until 4 mols. of sulphur trioxide are taken up, the products are a little chloromethyl sulphate, fractions of the approximate composition $2SO_3,(CH_2Cl)_2O$ and $3SO_3,(CH_2Cl)_2O$, and a solid residue, m. p. about 150°, probably methylene sulphate. With 1 mol. of sulphur trioxide after several hrs. at 160° a little chloromethyl sulphate is formed accompanied by chloromethyl pyrosulphate, $2SO_3,(CH_2Cl)_2O$. Chloromethyl sulphate, b. p. 100—103°/12—13 mm., d_D^{12} 1·634, n_D^{12} 1·453, is obtained in 26% of the theoretical yield by distilling sulphur trioxide (1 mol.) into 1 mol. of chloromethyl ether, at 105°, raising the temperature to 200°, adding 0·5 mol. of chloromethyl ether, and heating for ½ hr. at 200°; at 180° the yield is only 14·3%. Equimolecular quantities heated in a sealed tube at 180—200° for 50 min. give a 31% yield of chloromethyl sulphate. Hydrolysis with dilute sodium hydroxide affords sulphuric and hydrochloric acids, formaldehyde, and formic acid, the last-named being formed by the action of the alkali on the formaldehyde. Attempts to chloromethylate aniline, phenol, and benzene with this reagent were unsuccessful.

R. BRIGHTMAN.

Preparation and properties of ββ′-dicyanodiethyl sulphide. V. V. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1927, 59, 921—924).—Ethylenecyanohydrin, prepared by the action of potassium cyanide on the chlorohydrin, when treated at 0° with thionyl chloride in chloroform solution, yields β-chloropropionitrile, which reacts vigorously with anhydrous sodium sulphide in the presence of methyl alcohol to give ββ′-*dicyanodiethyl sulphide*, m. p. 24—25°, possessing none of the toxic properties of "mustard gas." On warming with acids and alkalis, thiodipropionic acid is obtained quantitatively.

M. ZVEGINTZOV.

Spectrochemical investigation of esters of selenious and selenic acid. W. STRECKER and W. DANIEL (Annalen, 1928, 462, 186—194).—An investigation to discover the existence or otherwise of the selenium analogues of the unsymmetrical "sulphites," $R·SO_2·OR$. Whilst, however, symmetrical ethyl sulphite and the isomeric unsymmetrical ester are respectively converted by magnesium phenyl bromide into diphenyl sulphoxide and phenyl ethyl sulphone (cf. A., 1910, i, 532), the products of the interaction of alkyloxides and selenyl chloride on the one hand and of silver selenite and alkyl halides on the other give rise to selenium when similarly treated. Optical examination of the selenious esters prepared by the two different methods fails to reveal any difference between them.

Methyl selenite, prepared by adding selenyl chloride to a well-cooled ethereal suspension of sodium methoxide, has b. p. 69°/15 mm., $d_4^{20·1}$ 1·7890, $n_a^{18·3}$ 1·48078. When prepared at a low temperature from methyl iodide and silver selenite in ethereal suspension, it has d_4^{20} 1·761, $n_a^{16·3}$ 1·48058. Ethyl selenite from selenyl chloride has b. p. 82—83°/14·5 mm., d_4^{21} 1·500, $n_a^{23·1}$ 1·46247, that from silver selenite having b. p. 83—84°/15 mm., d_4^{20} 1·492, $n_a^{16·3}$ 1·46125. n-*Propyl selenite* from selenyl chloride has b. p. 109°/15 mm., d_4^{20} 1·349, $n_a^{14·6}$ 1·46166, whilst that from the silver salt has b. p. 111°/16·5 mm., d_4^{21} 1·343, $n_a^{16·6}$ 1·46086.

The difficulties encountered by Meyer and Wagner (A., 1922, i, 620) when purifying selenic esters have been overcome and pure specimens of three esters have now been examined: methyl selenate, b. p. 68—68·5°/3 mm., d_4^{20} 1·750, $n_a^{19·3}$ 1·44103; *ethyl selenate*, b. p. 76°/3 mm., d_4^{20} 1·498, $n_a^{19·3}$ 1·43942; n-*propyl selenate*, b. p. 83—84°/3 mm., d_4^{20} 1·335, $n_a^{19·3}$ 1·45308. Details are given for the preparation of these esters from silver selenate. The esters can be kept indefinitely in sealed vessels.

When sodium methylsulphonate is heated with phosphorus selenide, P_2Se_5, a 30% yield of dimethyl selenide and a 38% yield of dimethyl diselenide (calculated on the phosphorus selenide) result (cf. Jackson, 1875). Hochwalt's directions (cf. B., 1926, 513) for diminishing the production of the diselenide were found unsatisfactory. Dimethyl selenide has b. p. 54—55°/753 mm., d_4^{19} 1·401, $n_a^{14·6}$ 1·47990, whilst the b. p. (hitherto unrecorded) of the diselenide is 150—151°/745 mm. Attempts to prepare dimethyl selenoxide by oxidation of the selenide proved abortive. The densities at other temperatures and refractive indices for other wave-lengths are recorded.

E. E. TURNER.

Reaction of bromine with aliphatic acids. II. Relative speeds of bromination of acetyl bromide and acetyl chloride. H. B. WATSON.—See this vol., 716.

Periodic electrolytic oxidation of formic acid. E. MÜLLER and S. TANAKA.—See this vol., 720.

Steric series. IX. Configuration of the monosubstituted propionic and succinic acids. K. FREUDENBERG and A. LUX (Ber., 1928, 61, [B], 1083—1089; cf. this vol., 153).—Comparison of the optical properties of derivatives of l-bromosuccinic acid with those of l(−)-malic and l(−)-bromopropionic acid shows the adherence of lævorotatory bromosuccinic acid to the l-series. If the work of Kuhn and Wagner-Jauregg (this vol., 506) is also taken into account, the following series may be regarded as established, natural l(+)-lactic, l(−)-halogenopropionic acids, l(+)-alanine, l(−)-malic, l(−)-monohalogenosuccinic, and l(+)-aspartic acids. Review of the results afforded by optical and chemical methods of determining the configuration of active compounds shows that α-hydroxy-, amino-, and halogeno-fatty acids of the same configuration almost universally suffer similar change in rotation under the influence of the same substituents provided that the use of solvents is avoided and all dipolar and associ-

ating groups (carboxyl, hydroxyl, amino-) are masked. Clough's method appears to give trustworthy results within the individual groups, but it is not suitable for comparison of substances belonging to different groups. In the subjoined table the abbreviations "opt." and "chem." denote the determination of configuration by optical and chemical methods :
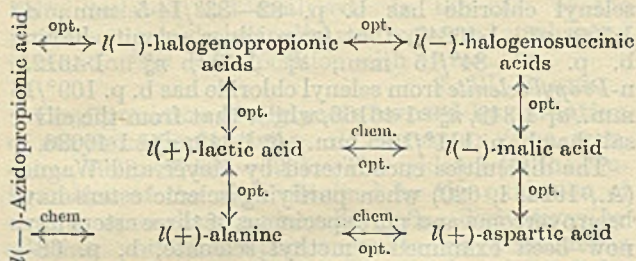
The following data are recorded : $l(-)$-bromosuccinic acid, m. p. 179°, $[\alpha]_D^{20}$ −70·2° ; $l(-)$-*bromosuccinyl chloride*, b. p. 56°/1 mm., d^{22} 1·796, $[\alpha]_D^{22}$ −58·4° ; methyl *l*-bromosuccinate, b. p. 79°/1 mm., d^{19} 1·513, $[\alpha]_D^{19}$ −65·3° ; *propyl* l-*bromosuccinate*, m. p. 108°/1 mm., d^{23} 1·279, $[\alpha]_D^{23}$ −41·5° ; dl-*bromosuccinbisdimethylamide*, m. p. 79° (obtained also from the active chloride) ; methyl $l(-)$-chlorosuccinate, $[\alpha]_D$ −42·3° ; ethyl $l(-)$-chlorosuccinate, $[\alpha]_D^{20}$ −32·7° ; $l(-)$-methoxysuccinyl chloride, d^{22} 1·341, $[\alpha]_D^{22}$ −44·6° ; l(−)-*acetylmalyl chloride*, b. p. 118°/14 mm., d^{22} 1·377, $[\alpha]_D^{22}$ −13·1°.　　　　　H. WREN.

Esters of α-bromobutyric acid. V. DEULOFEU (Bull. Soc. chim., 1928, [iv], **43**, 549—551).—The *propyl*, b. p. 190·5—194° (50%), iso*propyl*, b. p. 179—182° (30%), and *allyl*, b. p. 189—193° (25%), esters of α-bromobutyric acid have been prepared in the yield indicated, using sulphuric acid as catalyst (cf. Michael, A., 1902, i, 69).　　　　　R. BRIGHTMAN.

Components of unsaturated acids of chrysalis oil. W. KIMURA (J. Soc. Chem. Ind. Japan, 1927, **30**, 858—865).—The unsaturated acids were separated from the saturated acids by means of the lead salt–alcohol method and brominated. They were found to consist of oleic, linoleic, and linolenic acids as formerly reported by other investigators, but the content of linoleic acid was not so small as formerly reported. The same conclusion was reached from the identification of the products of the oxidation of the mixed acids by potassium permanganate. The oxidation products were found to be dihydroxystearic acid, α- and β-sativic acid, and linusic acid.　　　　　S. OKA.

Soya-bean oil. I. **Component fatty acids.** II. **Isolation of dipalmitolein.** K. HASHI (J. Soc. Chem. Ind. Japan, 1927, **30**, 849—855, 856—858).—I. The fatty acids of soya-bean oil were separated into a solid (10·6%) and a liquid (85·4%) part by means of Twitchell's lead salt–alcohol method. The solid fatty acids were esterified with methyl alcohol and the esters fractionated. They were found to consist of much palmitic acid, an appreciable amount of stearic acid, and a little arachidic acid. Bromination of the liquid fatty acids shows the presence of linolenic acid, 2·9% ; linoleic

acid, 51·5% ; oleic acids, 35·6% ; and solid fatty acids, 11·1%.

II. The dipalmitolein was extracted with acetone from soya-bean oil and purified by ten recrystallisations from the same solvents.　　　S. OKA.

Reduction of α-elæostearic acid. ($\Delta^{\iota\lambda}$-Linoleic acid and Δ^{κ}-oleic acid.) J. BÖESEKEN and J. VAN KRIMPEN (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 238—240).—By an improvement in the hydrogenation method previously employed (A., 1927, 1169), the first reduction product of ethyl α-elæostearate has been obtained pure and octodecadienic acid, m. p. 28·5°, n_D^{70} 1·4639, has been separated from it and shown by ozonisation to have double linkings at ι and λ. For the ethyl ester n_D^{70} is 1·4746, mol. refraction 96·87 (calc. 95·28), and iodine value 109 (calc. 180). These facts point to the existence of a conjugated system. If this ester is hydrogenated with two thirds of the calculated amount of hydrogen, the product hydrolysed, and the acid recrystallised, the largest fraction has m. p. 38·5°, n_D^{70} 1·4432, yields hexoic and sebacic acids on ozonisation, and gives no lowering of m. p. when mixed with Bertram's vaccenic acid (Chem. Weekblad, 1927, **24**, 226).　M. S. BURR.

Separation of glycerides. IV. **Oil of silkworm pupa.** B. SUZUKI and Y. YOKOYAMA. V. **Cod-liver oil.** B. SUZUKI and Y. MASUDA (Proc. Imp. Acad. Tokyo, 1928, **4**, 161—164, 165—168).—IV. Bromination of oil of silkworm pupa by the method previously described (this vol., 152) gives *dioleo-linolenin bromide*, m. p. 86°, yielding, on hydrolysis with hydrochloric acid, hexabromo- and dibromo-stearic acids, two iso*linoleo-dilinolenin bromides*, m. p. 133° and 154° (hydrolytic products, hexabromostearic acid and *iso*linoleic acid tetrabromide), trilinolenin bromide, m. p. 172° (cf. *loc. cit.*), *triolein bromide* (hydrolytic product, dibromostearic acid), *palmito-oleo-linolenin bromide* (hydrolytic products, hexabromostearic, dibromostearic, and palmitic acids), and *palmito-diolein bromide* (hydrolytic products, dibromostearic and palmitic acids).

V. From cod-liver oil, there were obtained *stearidono-diclupanodonin bromide*, m. p. 125°, hydrolysed by hydrochloric acid to *octabromostearic acid* (I), m. p. 200° (decomp.), and decabromobehenic acid, *diarachidono-clupanodonin bromide*, m. p. 112° (hydrolytic products, decabromobehenic and octabromoarachidic acids), *diclupanodono-linolenin bromide*, m. p. 118° (hydrolytic products, hexabromostearic and decabromobehenic acids), *clupanodono-stearidono-zoomarin bromide*, m. p. 220° [hydrolytic products, (I), dibromopalmitic and decabromobehenic acids], *clupanodono-arachidono-zoomarin bromide*, m. p. 105° (hydrolytic products, decabromobehenic, octabromoarachidic, and dibromopalmitic acids), *clupanodono-stearidono-arachidonin bromide*, m. p. 240° (decomp.) ; [hydrolytic products, (I), decabromobehenic and octabromoarachidic acids], two *linoleno-dizoomarin bromides* (hydrolytic products, hexabromostearic and dibromopalmitic acids), and *linoleo-diazoomarin bromide* (hydrolytic products, tetrabromostearic and dibromopalmitic acids).

[With Y. YOKOYAMA.]—Debromination of (I), followed by catalytic reduction of the unsaturated acid,

$C_{18}H_{28}O_2$ (stearidonic acid), produced, gives stearic acid. H. BURTON.

Influence of the ring oxygen atom on the rate of reaction of certain lactones. E. HOLLO (Ber., 1928, **61**, [*B*], 895—906).—Measurements are recorded of the rates of hydrolysis and lactonisation of ethylene glycollate, α-hydroxypropionate, α-hydroxy-*n*-butyrate, α-hydroxy*iso*butyrate, δ-valerolactone, and α-methyl-δ-valerolactone in 50 vol.-% aqueous acetone at 25° (±0·1°) in the presence of hydrogen chloride as catalyst, the course of the change being followed by titration with barium hydroxide at 0° in presence of phenolphthalein. Alkyl groups in the α-position retard hydrolysis and lactonisation, their effect being more pronounced in the first process; their sequence of activity is Me<Et<Me$_2$. With the ether-lactones investigated, the presence of a cyclic oxygen atom depresses the rate of hydrolysis to about 56—57% and that of lactonisation to about 39—41% of that of the usual δ-lactones.

Ethylene glycollate, m. p. 31°, b. p. 213—214°/747·6 mm., d_4^{35} 1·2521, is prepared in 70—80% yield by the action of chloroacetic acid on the monosodium compound of ethylene glycol in the presence of ethylene glycol. Excess of solvent is removed at as low a temperature as possible or by means of acetone and the sodium β-hydroxyethoxyacetate is decomposed with hydrochloric or phosphoric acid; the liberated acid is distilled, whereby anhydrisation occurs for the main part. Slowly when preserved, immediately under the influence of hydrogen ions, the monomeric form passes into a *polymeride*, m. p. 66—68°, b. p. 216—220°, from which it is regenerated by distillation. Analogous methods are used in the preparation of *ethylene α-hydroxypropionate*, b. p. 100—101°/17 mm., *ethylene α-hydroxy-n-butyrate*, b. p. 104·5—105°/20 mm., and *ethylene α-hydroxyiso-butyrate*, b. p. 120—128°/20 mm., which could not be caused to solidify and are found by analysis to contain a small proportion of the corresponding hydroxy-acids. δ-Valerolactone, b. p. 116—118°/25 mm., is obtained in 60—70% yield by heating sodium δ-iodovalerate in a vacuum; it slowly passes into a colourless polymeride. *α-Methyl-δ-valero-lactone* has b. p. 116—117°/16 mm. H. WREN.
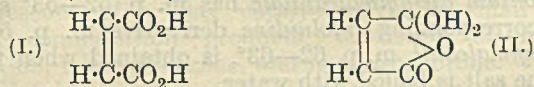
Configurational relationships of α-hydroxy-valeric and lactic acids. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1928, **77**, 555—562).—*d*-α-Hydroxy-*n*-valeric acid, $[\alpha]_D^{20}$ +1·5° (*barium* salt, $[\alpha]_D^{20}$ −4·9°), was converted into *ethyl α-hydroxy-n-valerate*, b. p. 81°/20 mm., $[\alpha]_D^{20}$ −5·05°, which gave, on reduction, l-*pentane*-αβ-*diol*, b. p. 78—81°/1 mm., $[\alpha]_D^{20}$ −9·8° in alcohol (*diphenylcarbamate*, m. p. 110—113°, $[\alpha]_D^{20}$ −12·2° in alcohol). α-*Chloropentan*-β-*ol*, b. p. 59—62°/14 mm., obtained by the action of chloroacetaldehyde on magnesium propyl bromide, was oxidised to *chloromethyl propyl ketone*, b. p. 55—57°/15 mm.; this was converted into *hydroxymethyl propyl ketone*, b. p. 62—64°/18 mm., which, on treatment with actively fermenting yeast, gave d-*pentane*-αβ-*diol*, b. p. 97—99°/13 mm., $[\alpha]_D^{20}$ +16·62° in alcohol (*diphenylcarbamate*, m. p. 107—110°, $[\alpha]_D^{20}$ +16·5° in alcohol); this, with hydrogen bromide, gave d-α-*bromopentan*-β-*ol*, b. p. 72—74°/18 mm.,

$[\alpha]_D^{20}$ +10·5°, which, on reduction, gave d-*methyl-propylcarbinol*, $[\alpha]_D^{20}$ +14·3° in alcohol (α-*naphthyl-carbamate*, m. p. 94—96°, $[\alpha]_D^{20}$ +17·7°). It follows that *d*-α-hydroxyvaleric acid is configuratively related to *d*-γ-hydroxyvaleric acid (since the latter gives *d*-pentane-αβ-diol on reduction) and hence to *d*-lactic acid (A., 1926, 1024). C. R. HARINGTON.

**Synthesis of trimethyl*cyclo*homotetronic acid.** R. ANSCHÜTZ and H. QUITMANN (Annalen, 1928, **462**, 97—104).—β-Acetoxy-αα-dimethylbutyric acid is converted by thionyl chloride into β-acetoxy-αα-dimethyl-butyryl chloride, b. p. 101°, which reacts with methyl sodiocyanoacetate to give *methyl β-acetoxy-αα-dimethyl-butyrylcyanoacetate*,

OAc·CHMe·CMe$_2$·CO·CH(CN)·CO$_2$Me, b. p. 108°/0·5—1 mm. (*ammonium* salt, hygroscopic; *silver* salt). The corresponding *ethyl* ester has b. p. 110—112°/0·5—1 mm. (*silver* salt) . Either ester is converted by concentrated hydrochloric acid into *trimethyl*cyclo-*homotetronic acid*, $\begin{matrix} \text{CMe}_2\text{·CO·CH}_2 \\ \text{CHMe·O·CO} \end{matrix}$ (also +1 or 2H$_2$O), m. p. 106·5°, b. p. 116—117°/0·5—1 mm. (*silver* salt described), also obtained by the action of sodium hydroxide at 50° on *methyl trimethyl*cyclo*homotetronic acid carboxylate*, $\begin{matrix} \text{CMe}_2\text{·CO·CH·CO}_2\text{Me} \\ \text{CHMe·O·CO} \end{matrix}$, b. p. 112—114°/0·5—1 mm., which is formed when methyl sodiomalonate reacts with β-acetoxy-αα-dimethylbutyryl chloride. The tetronic acid condenses with formaldehyde in aqueous solution to give the *methylenebis-*derivative, $\begin{bmatrix} \text{CMe}_2\text{·CO·CH·} \\ \text{CHMe·O·CO} \end{bmatrix}_2 \text{CH}_2$, m. p. 191°, with chloral similarly to give the *trichloroethylidenebis-*derivative, m. p. 143° (decomp.), and with paraldehyde in dilute aqueous acid solution to give the *ethylidenebis* compound, m. p. 154° (decomp.). E. E. TURNER.

History of the isomerism of fumaric and maleic acids. R. ANSCHÜTZ [with O. SCHARFENBERG, P. TRUMMEL, A. VON VOLBORTH, and O. NEUHAUS] (Annalen, 1928, **461**, 155—191).—Partly historical, partly polemical against Kuhn and Ebel (A., 1925, i, 780), and for the rest mainly a publication of results recorded in Bonn theses since 1888. The object of the present paper is to decide between the two possible formulæ (I and II) for maleic acid and its derivatives :

$$\text{(I.)} \quad \begin{matrix} \text{H·C·CO}_2\text{H} \\ \| \\ \text{H·C·CO}_2\text{H} \end{matrix} \qquad \begin{matrix} \text{H·C—C(OH)}_2 \\ \| \quad\quad >\text{O} \\ \text{H·C—CO} \end{matrix} \quad \text{(II.)}$$

It is concluded that there are two main tendencies at work : that for the formation of symmetrical molecules (as I) and that for the formation of five-membered rings (as II). The results obtained appear to show that the salts, esters, and amic acid are of type (I) for maleic acid itself, whilst alkyl- and phenyl-maleic acids give derivatives of type (II). When more than one alkyl group is present, the ammonium salts of the amic acids closely resemble ammonium carbamate, a fact which is put forward as evidence in favour of the above contention. A number of new substances are described, as below.

Citraconamic acid, $\begin{matrix} \text{CH—C(NH}_2)\text{·OH} \\ \| \quad\quad >\text{O} \\ \text{CMe·CO} \end{matrix}$, has m. p.
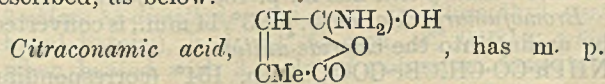
124—125° (*silver* salt; *methyl* ester, m. p. 84—85°). The *ammonium* and *silver* salts and the *methyl* (m. p. 126—127°) and *ethyl* (m. p. 158°) esters of citraconanilic acid (as I or II) are described. *Citracon-p-toluidic acid*, from *p*-toluidine and citraconic anhydride in ether, has m. p. 170—171° (*methyl* and *ethyl* esters, m. p. 105° and 168—169°, respectively; *ammonium* and *silver* salts). *Citracon-p-tolil*, m. p. 114—115°, is formed from the last-named acid or esters by boiling with water. *Citraconsemiphenylhydrazide* has m. p. 108·5°.

Ethyl hydrogen ethylfumarate, $CO_2H \cdot CH \colon CEt \cdot CO_2Et$, has m. p. 88°, whilst its isomeride, $CO_2Et \cdot CH \colon CEt \cdot CO_2H$, has m. p. 53°. *Ammonium ethylmaleamate* is described, as are also *ethylmaleimide*, m. p. 141°, and *ethylmaleanilic acid*, m. p. 106—107°. The last-named is converted by boiling water or by acetyl chloride into the *anil*, m. p. 129—130°, which is steam-volatile. The *methyl* ester, m. p. 118—119°, and *ammonium* salt of ethylmaleamic acid are described.

Dimethylmaleic acid, prepared from the *cyanohydrin*, b. p. 127—128°/13 mm., d_4^{25} 1·0549 (*acetyl* derivative, b. p. 148—149°/18 mm.), of ethyl acetoacetate by Michael's method, was converted through the anhydride into *ammonium dimethylmaleamate* (corresponding *silver* salt and *methyl* ester, m. p. 57—58°, described). Both ammonium ethyl- and dimethyl-maleamates behave like ammonium carbamate towards hydrochloric acid. The free amic acids are incapable of existence, the acid therefore producing ammonium chloride and the corresponding anhydride. Evaporation of a solution of ammonium dimethylmaleate gives the imide, m. p. 113°. Addition of ethereal ethylamine to an ethereal solution of dimethylmaleic anhydride gives *ethylammonium dimethylmaleamate*, converted by hydrochloric acid into dimethylmaleic anhydride. *Ammonium dimethylmaleanilate* and the corresponding *silver* salt and *methyl* ester, m. p. 69—70°, are described. *Dimethylmale-p-toluidic acid* has m. p. 74—77° (*ammonium* and *silver* salts; the *methyl* ester, from the silver salt and methyl iodide, passes on recrystallisation into the p-*tolil*, m. p. 110°).

Ammonium diethylmaleamate, m. p. 136—137°, and the corresponding *silver* salt are described. *Phenylammonium diethylmaleanilate* has m. p. 52—53° and the corresponding p-*toluidine* derivative m. p. 57°. *Diethylmaleanil*, m. p. 62—63°, is obtained when the aniline salt is boiled with water.

Ammonium diphenylmaleamate has m. p. 147—148° (*silver* salt). p-*Methylphenylammonium diphenylmale-p-toluidate*, m. p. 119—120°, is convertible into *diphenylmale-p-tolil*, m. p. 194°.

Ammonium and *silver bromocitraconamate* are described. *Phenylammonium bromocitraconanilate*, m. p. 127—128°, is convertible into bromocitraconanil, m. p. 144°. The *ammonium* and *silver* salts of bromocitraconanilic acid are described. p-*Methylphenylammonium bromocitracon-p-toluidate* and the corresponding *ammonium* and *silver* salts are described. *Bromocitracon-p-tolil* has m. p. 135·9—136°.

Bromofumaryl chloride, b. p. 93°/14 mm., is converted by aniline into the *chloride-anilide*, $NHPh \cdot CO \cdot CH \colon CBr \cdot COCl$, m. p. 154° (corresponding

methyl ester-anilide, m. p. 126°; the *dianilide*, m. p. 162°). *Anilidofumardianilide* has m. p. 194° and *anilidomaledianilide*, m. p. 175°. *Bromofumaryl chloride-p-toluidide* has m. p. 159°, the *di-p-toluidide*, m. p. 184°, and *bromofumar-p-toluidic acid*, m. p. 169° (*methyl* ester, m. p. 105—106°). *Bromofumar-β-naphthylamide chloride* has m. p. 160° and the *di-β-naphthylamide* m. p. 234°. *Bromofumar-β-naphthylamic acid* has m. p. 176—177° (indef.) (*methyl* ester, decomp. 116—117°). The *silver* salt and *methyl* ester, m. p. 122°, of bromomaleanilic acid are described. *Bromomale-p-toluidic acid* has m. p. 162°, the *methyl* ester, m. p. 92°, and the p-*tolil*, m. p. 144—145°. *Bromomale-β-naphthylamic acid*, m. p. 173°, *methyl* ester, m. p. 112°, and the corresponding *β-naphthylimide*, m. p. 208°, are described.

Fumaryl bromide has b. p. 113—115°/32 mm., *fumaryl chloride methyl ester* b. p. 83°/17 mm., *fumaryl chloride ethyl* ester b. p. 84°/17 mm., *benzyl fumarate* m. p. 60—61°, and *benzyl hydrogen fumarate* m. p. 98°. *Benzyl hydrogen citraconate*, m. p. 86°, gives benzyl alcohol and citraconic anhydride when distilled at 13 mm. *Benzyl mesaconate* has b. p. 160—165°/0·5 mm. and *benzyl hydrogen mesaconate* (α compound) m. p. 71·5°. E. E. TURNER.

Cleavage of ethyl αα'-dibromoadipate by diethylamine. R. C. FUSON (J. Amer. Chem. Soc., 1928, 50, 1444—1449).—It is suggested that ethyl 1-diethylamino*cyclo*butane-1 : 2-dicarboxylate is first formed and then decomposes into (*a*) ethyl acrylate, which gives with diethylamine ethyl β-diethylaminopropionate, and (*b*) ethyl α-diethylaminoacrylate, which is hydrolysed by dilute acid to ethyl pyruvate. This mechanism is confirmed by the observation that the product regarded by von Braun (A., 1926, 1128) as ethyl α-diethylaminopropionate is actually the β-diethylamino-derivative (Flürscheim, A., 1904, i, 19), and that in absence of water or acid, the reaction product contains, in addition to the β-diethylaminoester, a second ester of the same b. p. which is converted by acid into ethyl pyruvate.

H. E. F. NOTTON.

Reduction of polybasic α-hydroxy-acids under the simultaneous influence of catalysts. V. N. IPATIEV and G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1927, 59, 1083—1086).—See A., 1927, 1054.

Effect of hydrogen at high pressures and temperatures on solutions of substituted hydroxysuccinic acids in the presence of alumina and nickel oxide as catalysts. G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1927, 59, 1071—1076; cf. A., 1926, 1124).—The behaviour of the sodium salts of α-hydroxy-α'-methylsuccinic, α-hydroxy-αα'-dimethylsuccinic, and α-hydroxy-α-methyl-α'-ethylsuccinic acids at 250° and 60—80 atm. in the presence of hydrogen, with alumina and nickel oxide as catalysts, was investigated, in order to verify the mechanism suggested (*loc. cit.*) for the condensation of sodium lactate into sodium succinate, under the same conditions, by way of the formation and decomposition of α-hydroxy-αα'-dimethylsuccinic acid. In all cases, a yield of 25—30% of methylsuccinic acid was obtained, together with quantities varying from 18 to 45% of formic and acetic acids, as well as traces

of the higher fatty acids. In the case of α-hydroxy-α-methyl-α'-ethylsuccinic acid, 30% of butyric acid was formed. M. ZVEGINTOV.

Condensation of α-hydroxy- and α-keto-acids under the simultaneous influence of catalysts. V. N. IPATIEV and G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1927, **59**, 1077—1081).—See A., 1927, 1053.

Lactone formation of cellobionic and glucoarabonic acids, and its bearing on the structure of cellobiose. P. A. LEVENE and M. L. WOLFROM (J. Biol. Chem., 1928, **77**, 671—683).—Cellobionic acid forms one lactone with a 5-membered ring, whilst glucoarabonic acid forms two lactones with 4- and 5-membered rings, from which it follows that in cellobiose the reducing sugar is substituted in the δ-position (cf. Zemplén, A., 1926, 822; Haworth and others, this vol., 47). *Cellobiose oxime,* m. p. 122—123°, has been obtained crystalline; other modifications of the work of Zemplén (*loc. cit.*) are described.
C. R. HARINGTON.

α-Chloro- and α-bromo-α-sulphopropionic acids and their resolution. H. J. BACKER and H. W. MOOK (Bull. Soc. chim., 1928, [iv], **43**, 542—549).—*α-Chloro-α-sulphopropionic acid* (+H₂O), m. p. 93—94° [*potassium, thallium,* and *barium* (+3H₂O) salts], is obtained in 50% yield by the action of 1 mol. of sulphuric anhydride on 1 mol. of α-chloropropionic acid at 120—170°, or in 70% yield by heating barium α-sulphopropionate with 100% excess of barium chlorate and hydrochloric acid in a sealed tube at 100°. *α-Bromo-α-sulphopropionic acid* (+H₂O), m. p. 105—110° [*potassium, thallium,* and *barium* (+3H₂O) salts], is similarly prepared. With barium α-sulphopropionate a temperature of 140—175° is required for bromination. Both acids have been resolved by decomposition of their sodium salt with strychnine acetate. l-*α-Chloro-α-sulphopropionic acid* (*strychnine* salt; *sodium* salt, [α]$_D$ —0·73°) has [α]$_D$ —0·20°, l-*α-bromo-α-sulphopropionic acid* (*strychnine* salt, sodium salt, [α]$_D$ —0·33°), [α]$_D$ —0·03°. Both the active acids and their salts are stable at temperatures up to 100°, and the presence of alkali effects hydrolysis and not racemisation (cf. A., 1925, i, 359, 632). R. BRIGHTMAN.

Silver xanthate. A. REYCHLER (Bull. Soc. chim. Belg., 1928, **37**, 165—167).—Silver xanthate is prepared by the action of potassium xanthate on silver nitrate, chloride, bromide, or iodide. It is a yellow, crystalline substance, unaffected by boiling dilute hydrochloric and sulphuric acids, but is decomposed by a mixture of nitric and hydrochloric acids forming silver chloride. It is not acted on by dilute alkalis, but is decomposed by concentrated alkalis. It is soluble in alkali cyanide solutions, from which it is reprecipitated by acidification, but it does not dissolve in sodium thiosulphate solution. If potassium xanthate is added to a sodium thiosulphate solution of a silver salt, silver xanthate is precipitated.
H. BURTON.

Action of zinc on mixtures of polyhalogenated hydrocarbons with ketones and aldehydes. I. CUCULESCU (Bul. Soc. Romane Stiin., 1928, **30**, 39—41).—When metallic zinc acts on a mixture of a polyhalogenated paraffin hydrocarbon with an aldehyde or ketone, the metal combines with the halogen, and the resulting halide may form a molecular compound with the aldehyde or ketone, and at the same time hydrocarbons are evolved; in no case is an organo-metallic compound produced. The mixtures containing an aldehyde react more readily than those containing a ketone. R. CUTHILL.

Application of the Merling reaction to aldehydes. Synthesis of isopropylacetylenylcarbinol. V. KRESTINSKI and F. SOLODKI (J. Russ. Phys. Chem. Soc., 1927, **59**, 1141—1147).—See A., 1927, 1052.

Synthesis with diazomethane. IV. Reaction between aldehydes and diazomethane. F. ARNDT and B. EISTERT (Ber., 1928, **61**, [*B*], 1118—1122).—Chloral in ethereal solution is slowly converted by diazomethane into *ααα-trichloropropylene βγ-oxide,* b. p. 44—45°/13 mm. (together with a small proportion of methyl dichloroacetate), and not trichloroacetone as stated by Schlotterbeck (A., 1907, i, 185, 478; 1909, i, 553). The constitution of the compound follows from its indifference towards o-nitrophenylhydrazine and semicarbazide and its conversion by concentrated hydrochloric acid into β-*hydroxy-αααγ-tetrachloropropane,* b. p. 95—96°/17 mm. (noncrystalline *benzoyl* derivative), and by acetic anhydride and ferric chloride into βγ-*diacetoxy-ααα-trichloropropane,* b. p. 126—128°/16 mm.

m-Nitrobenzaldehyde and diazomethane afford exclusively m-nitroacetophenone, whereas p-nitrobenzaldehyde gives a mixture of p-nitroacetophenone and p-nitrophenylethylene oxide. It appears that the production of substituted ethylene oxides is to be expected, particularly from those aldehydes which have a pronounced tendency towards the formation of hydrates. H. WREN.

Nierenstein reaction. M. NIERENSTEIN (Nature, 1928, **121**, 940).—Polemical concerning the reaction between diazomethane and acyl chlorides.
A. A. ELDRIDGE.

Catalytic condensation of methyl ethyl ketone. A. PETROV (J. Russ. Phys. Chem. Soc., 1928, **60**, 485—489).—Methyl ethyl ketone when heated to 380—400° under 80—100 atm. pressure in the presence of a clay catalyst gives a small yield of condensation products, consisting of mesityl oxide, triethylbenzene, and homoisophorone. Where sodamide is used as the catalyst, the yield of condensation products is considerably higher; these consist of a mixture of isomeric homoisophorones, which on hydrogenation yield a mixture of cyclic hydrocarbons, $C_{12}H_{24}$. R. TRUSZKOWSKI.

Action of phosphorus pentachloride on ethyl tert.-butyl ketone. Transformation of β-hydroxy-δδ-dimethylpentan-γ-one (trimethylacetylmethylcarbinol) into acetyl-tert.-butylcarbinol. V. VASSILIEV (Bull. Soc. chim., 1928, [iv], **43**, 563—567).—Ethyl tert.-butyl ketone with 1 mol. of phosphorus pentachloride (slight excess) at 70° affords β-*chloro-δδ-dimethylpentan-γ-one* (α-chloroethyl tert.-butyl ketone), b. p. 84°/53 mm., d_0^{20} 0·9814, which when heated with 3 mols. of potassium formate in

methyl alcohol at 150° for 10 hrs. gives mainly *acetyl*-tert.-*butylcarbinol*, b. p. 108—111°/100 mm., d_4^{20} 0·9352 (*semicarbazone*, m. p. 188°), together with a little δδ-*dimethylpentane*-βγ-*diol*, m. p. 54°, the formation of the glycol being due to the reducing action of the potassium formate. Under these conditions the trimethylacetylmethylcarbinol (β-hydroxy-δδ-dimethylpentan-γ-one, first formed (cf. Favorsky and Achmarine, A., 1913, i, 12), b. p. 103—108°/100 mm. (semicarbazone, m. p. 133—134°), is almost entirely converted into the isomeric acetyl-*tert.*-butylcarbinol, the conversion not being, however, quite complete, since with magnesium phenyl bromide the product affords, in addition to β-*phenyl*-δδ-*dimethylpentane*-βγ-*diol*, m. p. 82·5°, traces of γ-*phenyl*-δδ-*dimethylpentane*-βγ-*diol*, m. p. 94°. The keto-alcohol prepared from β-bromo-δδ-dimethylpentan-γ-one is also a mixture, and in either case complete conversion into acetyl-*tert.*-butylcarbinol is obtained by heating in a sealed tube at 120° for 5—6 hrs. with a little sulphuric acid. With magnesium methyl bromide acetyl-*tert.*-butylcarbinol gives βδδ-*trimethylpentane*-βγ-*diol*, m. p. 64·5—65° (crystallographic measurements for the two forms are given), oxidised by 4% potassium permanganate to β-hydroxy-αα-dimethyl-β-*tert.*-butylethylene oxide, and identical with the glycol obtained by Prileschaeff (A., 1904, i, 795).

R. BRIGHTMAN.

Transformation of oxoctenol into acetylmethyl-*tert.*-butylcarbinol. (MLLE.) A. I. OUMNOV (Bull. Soc. chim., 1928, [iv], **43**, 571—573).—When heated in a sealed tube for 8 hrs. at 120° with alcoholic sulphuric acid β-hydroxy-αα-dimethyl-β-*tert.*-butylethylene oxide (oxoctenol) is converted into *acetylmethyl*-tert.-*butylcarbinol*, b. p. 176—178°/746 mm., d_0^{20} (*semicarbazone*, m. p. 190—190·5°), oxidised by chromic acid and potassium hydrogen sulphate to pinacolin and acetic acid, together with some trimethylacetic acid (by oxidation of pinacolin).

R. BRIGHTMAN.

Transformation of *iso*butyryldimethylcarbinol into acetylmethyl*iso*propylcarbinol. (MLLE.) A. I. OUMNOV (Bull. Soc. chim., 1928, [iv], **43**, 568—571).—*iso*Propyl α-bromo*iso*propyl ketone with 20% potassium carbonate gives a ketone alcohol, b. p. 161—162°, d_0^{20} 0·9132 (*semicarbazone*, m. p. 178—179°), isomeric with that obtained when the corresponding chloro-ketone is used (A., 1913, i, 12). With magnesium phenyl bromide the new product affords γ-*phenyl*-βδ-*dimethylpentane*-βγ-*diol*, m. p. 75—76°, oxidised by chromic anhydride and potassium hydrogen sulphate to acetone and phenyl *iso*propyl ketone. The new ketone alcohol is thus iso*butyryl*-*dimethylcarbinol*, and when warmed with alcoholic sulphuric acid for 8 hrs. at 120° is converted into the isomeride previously prepared (*loc. cit.*). With magnesium phenyl bromide this isomeride affords β-*phenyl*-γδδ-*trimethylpentane*-βγ-*diol*, b. p. 153—155°/14 mm., oxidised to acetophenone and methyl *iso*propyl ketone, the latter being further oxidised to acetic acid and acetone. The isomeride is thus *acetylmethyl*-iso*propylcarbinol* and not *iso*butyryldimethylcarbinol, as originally stated (*loc. cit.*), the latter undergoing transformation under the experimental conditions, probably with intermediate formation of

an oxide alcohol. The presence of traces of such an intermediate compound may explain the low yields (up to 70%) obtained in preparation of the semicarbazones, and of variations in density and b. p. of the ketone alcohol prepared from the chloroketone and by transposition. R. BRIGHTMAN.

Carbohydrates and polysaccharides. XIII. Properties of γδ-dihydroxycarbonyl derivatives and their bearing on the polymerisation of polysaccharides. H. HIBBERT and C. P. BURT (J. Amer. Chem. Soc., 1928, **50**, 1411—1416).—Δ^β-*Hepten*-ζ-*one*, b. p. 150—152°, synthesised from crotonaldehyde by way of Δ^β-buten-α-ol, α-bromo-Δ^β-butene, and *ethyl* Δ^β-*butenylacetoacetate*, b. p. 135—139°/46 mm., is oxidised by barium permanganate to *methyl* γδ-*dihydroxyamyl ketone*, b. p. 139—143°/10 mm. In presence of a trace of sulphuric acid at 90° this loses 1 mol. of water, giving a resinous polymeric *anhydride*, mol. wt. 553—590 in benzene. The corresponding product from methyl γδ-dihydroxybutyl ketone (cf. A., 1924, i, 16) has mol. wt. 395—445 in phenol and 3706 in camphor. The nature of these anhydrides and their relation to cellulose are discussed. When the next higher homologue, βγ-dihydroxy-β-methylheptan-ζ-one (Harries, A., 1902, i, 345), is heated with or without traces of sulphuric acid, β-methyl-Δ^β-heptenone βγ-oxide is formed without notable polymerisation. H. E. F. NOTTON.

Ring structure and optical relationships in the mannose–rhamnose–lyxose series of sugars. Isolation of a new form of lyxose. W. N. HAWORTH and E. L. HIRST (J.C.S., 1928, 1221—1230).—The additive principle of optical superposition as used by Hudson (cf. A., 1926, 714) in ascribing a 1 : 4 ring structure to α-methylglucoside and 1 : 5 and 1 : 4 ring structures to α- and β-mannose, respectively, is adversely criticised. Crystalline β-*lyxose*, m. p. 117—118°, [α]$_D$ —70°, was prepared by treatment of calcium galactonate with hydrogen peroxide and ferric acetate. The new sugar shows rapid mutarotation to [α]$_D$ +14°, the equilibrium value for α-lyxose, to which it bears the same relation as does β-mannose to α-mannose. The connexion between the *cis*- and *trans*-nature of the hydroxyl groups and the relative solubilities of the α- and β-forms of the sugars is discussed. B. W. ANDERSON.

Decomposition of sugars by the action of very dilute alkalis. F. FISCHLER and A. F. LINDER (Z. physiol. Chem., 1928, **175**, 237—247).—In extension of the work on dextrose (A., 1927, 449) the decomposition of various monoses (lævulose and galactose) and bioses (lactose and maltose) by very dilute alkali has been studied, similar results being obtained in each case. The yield of methylglyoxal is diminished when no sodium sulphite is added, and reaches its maximum when the distillation is carried out in a current of carbon dioxide, with 0·04—0·02N-sodium carbonate and with the addition of sodium sulphite. With varying concentration of alkali the yield reaches a maximum value with 0·1N-potassium hydroxide or 0·1—0·01N-sodium carbonate solutions, and decreases when larger or smaller concentrations are employed. The rotation of the sugar is reduced almost to zero after heating for 1—2 hrs. under these

conditions. Diminution in the reducing power of the sugar or of dihydroxyacetone is the greater the stronger is the alkali concentration, the values obtained with all hexoses being of the same order, and those with bioses forming a second series similar amongst themselves, but differing somewhat from the monose values. The production of acidity by the action of various concentrations of alkali has also been studied. The maximum quantity of acid (1·35—2 equiv./mol. of hexose) is produced by the action of $0\cdot1N$-potassium hydroxide, smaller, and approximately equal amounts being produced by the action of $0\cdot5N$- and $0\cdot01N$-alkali solutions; the same values are obtained either in the presence or absence of oxygen. Similar results are obtained with dihydroxyacetone. These results, therefore, confirm the authors' view (*loc. cit.*) that the primary degradation product of all hexoses is dihydroxyacetone (2 mols.) (bioses being first converted into hexoses), the production of acid products being due to the action of oxygen liberated from the sugar molecules themselves. J. W. BAKER.

Sugars. VIII. H. KILIANI (Ber., 1928, **61**, [*B*], 1155—1169; cf. A., 1926, **51**, 940).—The double lactone of *l*-mannosaccharic acid appears to differ from all analogously-constituted compounds of the sugar group by its pronounced ability to reduce Fehling's solution. Similar properties have been attributed by Peirce (A., 1916, i, 18) to the double lactone of *d*-$\alpha\alpha$-manno-octaric acid; this compound is identical with the α-galaoctanehexol-di-acid of Kiliani and Wingler (A., 1922, i, 321), which has no reducing properties. The action of Peirce's compound is probably due to the presence of traces of aldehydic or ketonic acids frequently left after oxidation of carbohydrates with nitric acid. It is emphasised, however, that Fehling's solution frequently shows abnormal reactions with acids or lactones unless they have previously been neutralised by alkali. The sensitiveness of the dilactone to Fehling's solution must therefore be ascribed to the production of an aldehydic or a ketonic group. The formation of the former is improbable, since it involves a terminal carboxyl group. Fission of the dilactone by potassium hydroxide can occur in only two ways, between either the $\alpha\beta$ or the $\beta\beta'$ carbon atoms; if potassium cyanide is added to the mixture and the resulting nitrile is hydrolysed, the enantiomorphous form of the acid obtained by Düll (cf. A., 1926, 940) by the oxidation of lævulosecarboxylic acid must result in the former case, whereas the production of two previously unknown tricarboxylic acids is possible in the latter case. Actually, the *calcium* salt, $(C_7H_7O_{10})_2Ca_3,9H_2O$, and the corresponding basic *copper* salt, $(C_7H_7O_{10})_2Cu_3,Cu(OH)_2,18H_2O$, differ completely from the corresponding compounds of Düll's $\alpha\beta\gamma\delta$-tetrahydroxybutane-$\alpha\alpha\delta$-tricarboxylic acid; fission therefore occurs between the $\beta\beta'$ carbon atoms. The fate of the two hydrogen atoms lost by the mannosaccharic acid molecule during ketonisation remains undecided; the production of methylamine during the change could not be detected.

Precautions necessary for the successful oxidation of *l*-mannonolactone are described and a new, rapid method for the preparation of the double lactone of *l*-mannosaccharic acid is described in detail.

Pure lævulose is readily converted into the crystalline cyanohydrin, which is extraordinarily unstable (the presence of impurities in crude lævulose appears to render the product more stable), so that a process is described whereby the sugar is transformed into "lævulosecarboxylic" acid without isolation of the cyanohydrin. The acid is isolated as the crystalline *brucine* salt (*tetrahydrate*; anhydrous, m. p. 162°), from which it is prepared by the successive use of barium hydroxide and oxalic acid; it is oxidised by nitric acid to $\alpha\beta\gamma\delta$-tetrahydroxybutane-$\alpha\alpha\delta$-tricarboxylic acid (*tetrahydrated potassium* salt).

The use of oxalic in place of sulphuric acid is recommended for the determination and precipitation of barium in salts of organic acids. H. WREN.

Effect of borate on oxidation of dextrose and other sugars. M. LEVY and E. A. DOISY (J. Biol. Chem., 1928, **77**, 733—751).—The oxidation of dextrose, lævulose, galactose, lactose, and maltose by any alkaline copper reagent is more or less inhibited by the presence of borate, probably owing to formation of a boric ester of the sugar; acid oxidising agents such as Barfoed's reagent are not affected in this way. The oxidation of the aldehydic group of aldoses by hypoiodite is also decreased by borate except in the case of lactose. Boric acid should therefore not be used as a preservative for biological specimens required for investigation of carbohydrate metabolism. C. R. HARINGTON.

Carbohydrate oxidation. VIII. Action of potassium hydroxide on lævulose. W. L. EVANS and J. E. HUTCHMAN (J. Amer. Chem. Soc., 1928, **50**, 1496—1503).—The action of various concentrations of aqueous potassium hydroxide on lævulose at 25°, 50°, and 75° has been studied. The amounts of lactic acid, pyruvaldehyde, and acetic and formic acids obtained are shown graphically. The results are, in general, the same as those obtained both with dextrose and with glyceraldehyde (cf. this vol., 397; A., 1926, 1228), which indicates that both sugars are in equilibrium (although the equilibrium mixtures are not quantitatively identical) with a large proportion of $\gamma\delta$-"enediol," which is subsequently degraded to glyceraldehyde. The curves for formic acid indicate the formation of some $\alpha\beta$-"enediol." Although the quantities are different in each case, the maximum yield of pyruvaldehyde is obtained at the same alkali concentration from both lævulose and glyceraldehyde, and the same is true of the yield of formic and acetic acids from dextrose and lævulose.
H. E. F. NOTTON.

Synthesis of sucrose. A. PICTET and H. VOGEL (Helv. Chim. Acta, 1928, **11**, 436—442).—A more detailed account of work already published (see this vol., 510).

Action of trimethylamine on acetobromocellobiose and acetobromomaltose. G. ZEMPLÉN, Z. CSÜRÖS, and Z. BRUCKNER (Ber., 1928, **61**, [*B*], 927—937; cf. Karrer, Widmer, and Staub, A., 1924, i, 713).—The action of a solution of trimethylamine in ethyl alcohol on acetobromocellobiose at 85—95° yields *hepta-acetylcellobiosidotrimethylamine* (I), m. p.

205—206° (decomp.), $[\alpha]_D$ —11·07° in chloroform, which very closely resembles Karrer's "cellal acetate" in properties. When hydrolysed by sodium methoxide in chloroform it gives homogeneous cellobiose in 50% yield. It does not react with hydrogen bromide in glacial acetic acid. It absorbs one atom of
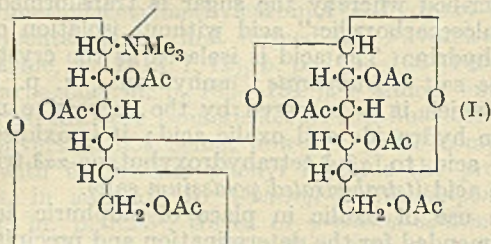
bromine in chloroform solution, giving *hepta-acetylcellobiosidotrimethylammonium bromide*, $C_{29}H_{44}O_{17}NBr$, m. p. 148—149°, $[\alpha]_D^{18}$ —7·53° in chloroform. Treatment of the bromo-compound with silver carbonate in absolute methyl alcohol or aqueous acetone, with silver acetate in anhydrous benzene, or with aqueous sulphurous acid leads to removal of the added bromine atom with regeneration of the original material.

Acetobromomaltose and trimethylamine solution at 70° give *hepta-acetylmaltosidotrimethylamine*, $C_{29}H_{41}O_{17}N$, m. p. 165°, decomp. 208°, $[\alpha]_D^{21}$ +65·59° in chloroform; it gives a non-crystalline *bromo*-derivative from which it is re-formed by the action of sulphurous acid. Acetobromomaltose and trimethylamine at 90—95° afford trimethylammonium bromide and hepta-acetylmaltose.   H. WREN.

Acetolysis of mannocellulose. Production of two new sugars, a tetra- and a penta-manno-holoside. G. BERTRAND and J. LABARRE (Bull. Soc. chim., 1928, [iv], **43**, 311—321).—See this vol., 157.

Starch. H. PRINGSHEIM and P. MEYERSOHN (Z. physiol. Chem., 1928, **173**, 211—219).—The results and conclusions of Peiser (A., 1927, 136) cannot be confirmed. Starch prepared, as by Peiser, by precipitation from starch paste with alcohol and washing with alcohol and ether, the alcohol and ether being removed rapidly in a vacuum over sulphuric acid, yields on acetylation a small amount of an acetate which has the acetyl content given by Peiser; if the alcohol and ether are removed by drying in the air, however, no hardening of the starch occurs, and the product is more readily acetylated, yielding an acetate with a slightly higher acetyl content and a significantly higher rotation ($[\alpha]_D^{17}$ +220° and 222·5°, compared with $[\alpha]_D^{17}$ +178—180° and +191—196° for acetates obtained from the hornified starch). Hydrolysis of the acetate by hot sodium hydroxide yields a non-reducing "starch," as claimed by Peiser, but this is due to the destruction of the reducing groups by the hot alkali. Hydrolysis in the cold yields products which have reducing powers of 4—5% of that of maltose, or 8% of that of maltose when the acetate with the highest acetyl content and rotation is employed. Peiser's acetylation is accompanied by the formation of dextrins which account for the high acetyl values, and the results are not inconsistent with

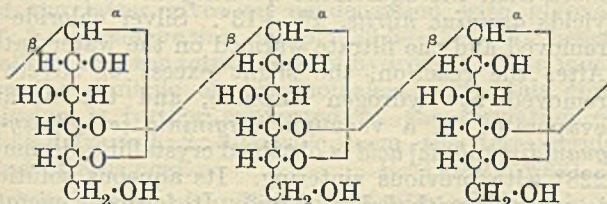the conception of the starch molecule as an aggregate of small molecules.   A. WORMALL.

Methylation of starch. L. SCHMID and M. ZENTNER (Monatsh., 1928, **49**, 111—117).—Potato starch after 27 methylations with diazomethane yields a methylated starch containing 21·5% of methoxyl (unchanged by further methylation). This methylated starch was hydrolysed with 1% methyl-alcoholic hydrogen chloride and the product extracted with acetone (*A*, 35·3% OMe), the acetone extract precipitated with ether (*B*, 25·23% OMe) and extracted with methyl alcohol (*C*, 20·01% OMe). Fraction *A* after hydrolysis with 5% hydrochloric acid yields a product of methoxyl content 29·7%, $[\alpha]_D$ + 83·58°, corresponding with a dimethylglucose. This, by oxidation with nitric acid (d 1·2), yields an acid the methyl ester of which contains only three methoxyl groups, and hence one of the methylated hydroxyl groups in the dimethylglucose is probably in position 6.   J. W. BAKER.

Inulin. VI. H. PRINGSHEIM and I. FELLNER (Annalen, 1928, **462**, 231—239).—In view of the many diverse opinions held as to the mol. wt. of inulin and its derivatives, further determinations have been made by the cryoscopic method in water. Inulin has M 1091—1172 in 0·8—1·1% solution. "Inulin" obtained by hydrolysing the products of heating inulin acetate in presence of tetrahydronaphthalene at various temperatures has M as follows: from acetate heated at 250°, 576—635 in 0·6—0·9% solutions (cryoscopic); from acetate heated at 260°, 457—461 in 0·8—1·36% solutions (cryoscopic); from acetate heated at 290°, 339—316 in 0·6—1·7% solutions (cryoscopic) (331—329 in 0·65—1·9% solutions, ebullioscopic determination). It is noted that the mol. wt. of molecules corresponding with 7, 4, 3, and 2 fructose anhydride units, respectively, are 1134, 648, 486, and 324.   E. E. TURNER.

Behaviour of cellulose when heated under pressure with water. E. BERL and A. SCHMIDT (Annalen, 1928, **461**, 192—220).—The products of the action of water, at temperatures from 150° to 350° and correspondingly high pressures, on pure cotton cellulose were examined as falling into one of the three groups: (*a*) water-insoluble, (*b*) water-soluble, and (*c*) gaseous products. The initial action of water under such conditions is hydrolytic in nature, this effect being greater as the hydrogen-ion concentration of the water increases, viz., with rise of temperature. Acids produced similarly accelerate hydrolysis. Dextrose appears as the first recognisable product, and this then undergoes charring—a fact elicited by control experiments with pure dextrose. Water-soluble, highly polymerised humalic acids are formed at this stage, these passing later into water-insoluble humic acids which are soluble, however, in ammonia. From the dextrose, hydroxymethylfurfuraldehyde is formed, and this undergoes scission through the functioning of 2 mols. of water to give lævulic acid and formic acid.

Debye–Scherrer diagrams obtained for the original cellulose and for cellulose after treatment as above are given.   E. E. TURNER.

Lignin and cellulose. VI. Methylcellulose. K. FREUDENBERG (Annalen, 1928, **461**, 130—131).— If the conclusions of Sponsler and Dore (cf. B., 1927, 934) are correct and are applied to Freudenberg's cellulose formula (this vol., 399), the latter becomes that annexed :

$$
\begin{array}{ccc}
{}^{\beta}\diagup\mathrm{CH-} & {}^{\beta}\diagup\mathrm{CH-} & {}^{\beta}\diagup\mathrm{CH-} \\
/\mathrm{H\cdot C\cdot OH} & /\mathrm{H\cdot C\cdot OH} & /\mathrm{H\cdot C\cdot OH} \\
\mathrm{HO\cdot C\cdot H} & \mathrm{HO\cdot C\cdot H} & \mathrm{HO\cdot C\cdot H} \\
\mathrm{H\cdot C\cdot O-} & \mathrm{H\cdot C\cdot O-} & \mathrm{H\cdot C\cdot O-} \\
\mathrm{H\cdot C\cdot O-} & \mathrm{H\cdot C\cdot O-} & \mathrm{H\cdot C\cdot O-} \\
\mathrm{CH_2\cdot OH} & \mathrm{CH_2\cdot OH} & \mathrm{CH_2\cdot OH}
\end{array}
$$

E. E. TURNER.

Isolation of lignin. L. KALB and T. LIESER [with R. HAHN, F. NEVELY, and H. KOCH] (Ber., 1928, **61**, [B], 1007—1022).—Exact information concerning the carbohydrates present in lignin obtained by incomplete treatment of wood can be obtained only by methods which permit the isolation of the carbohydrates in substance. Treatment of such lignin with chlorine dioxide and sodium sulphite, followed by characterisation of the carbohydrates by hydrolysis or fermentation with *Saccharomyces cerevisiæ* or *Schizosaccharomyces Pombe*, indicates the absence from them of galactose and presence of the components of the "skeleton substance" according to Schmidt's nomenclature. The chlorine dioxide–acetone process yields a greater quantity of carbohydrate than the sulphite method, the difference being probably due to the presence of hemicelluloses or dextrin-like products from the skeleton substance (due to the preliminary treatment with hydrochloric acid). The nature and mode of isolation of the carbohydrates from lignin permit the conclusion that they are residues of saccharifiable components of wood, mainly cellulose. This hypothesis is supported by the observation that they can be extracted (without destruction of the lignin) by ammoniacal copper oxide solution, from which they are precipitated, mixed with a little lignin, by acid. Hydrolysis and fermentation of the carbohydrates thus obtained proves their qualitative and approximately quantitative identity with those derived by the sodium sulphite process. During the extraction with ammoniacal copper oxide, the lignin does not acquire nitrogen or suffer oxidative degradation, since the process increases the methoxyl content to the characteristic value, 15—16%, of Willstätter's lignin, which can be raised by further methylation to about 30%. The observations further indicate that "hydrochloric acid lignin" is an individual substance approximating closely to native lignin and not a condensation product of a hypothetical "pure lignin" and carbohydrate. Comparison of the hydrolytic and chlorine dioxide–sodium sulphite processes (the latter is preferred to the acetone or ammoniacal copper oxide method, since it yields purer carbohydrates) for the determination of carbohydrate associated with lignin shows that the results obtained by the first method are invariably somewhat higher than those of the second, but the differences are very small when the carbohydrate content is low. Even after very prolonged hydrolysis a small amount of carbohydrate remains with the lignin; preparations which do not show more than 0·3% of carbohydrate by the chlorine dioxide–sodium sulphite process are, however, readily obtained and are regarded as "practically free from carbohydrate." Systematic experiments are recorded on the hydrolysis of wood by hydrochloric acid according to the procedure of Willstätter and Zechmeister (A., 1913, i, 955) and Willstätter and Kalb (A., 1922, i, 989). Modifications are introduced by diminishing the period of "main hydrolysis" with hydrochloric acid (d^0 1·222) to 2 hrs. and initiating the process at a lower temperature. After "subsequent hydrolysis" with rather more dilute acid, lignin "practically free from carbohydrates" is obtained. A variant of the method consists in replacing the "subsequent hydrolysis" by extraction with ammoniacal copper oxide, which yields a carbohydrate-free lignin provided that the primary hydrolysis has extended over 2—2½ hrs. Extraction of wood by ammoniacal copper oxide alone does not yield a pure lignin. It is doubtful if the more thorough shielding of the lignin by avoidance of the secondary hydrolysis compensates for the extra difficulty caused by the alkaline extraction. H. WREN.

True lignin. I. Acetylation of pine wood. W. FUCHS (Ber., 1928, **61**, [B], 948—951).—Pine meal, uniformly moistened with water, is gradually added to an ice-cold mixture of acetic anhydride and concentrated sulphuric acid. The temperature is gradually raised to 55—60°. The reaction mixture is diluted with benzene, filtered, and the product washed successively with benzene and alcohol. The yield is about 150% of the wood, whilst the original 2·7% of acetyl is increased to 41% by a single treatment; subsequent treatment increases this value only slightly. Pentosans, hexosans, etc. are almost completely absent from the acetylated wood, which consists to the extent of about 97% of lignin, cellulose, and acetic acid. The methoxyl content of the wood remains unchanged. Acetylated wood appears to consist almost exclusively of cellulose triacetate and an acetyl-lignin with about 33% of acetyl. Attempts to extract the former compound by means of solvents were unsuccessful. Treatment of the acetylated wood with chlorine and sodium sulphite affords a cellulose acetate with somewhat varying acetyl content approximating to that of cellulose triacetate; the product is sparingly and incompletely soluble in chloroform and insoluble in acetone. When hydrolysed with alcoholic potassium hydroxide it gives homogeneous, lignin-free cellulose. When the acetylated wood is treated with methyl-alcoholic hydrogen chloride under pressure, about half the lignin remains undissolved, whilst the remainder can be almost completely precipitated from the solution by addition of water. H. WREN.

Lignin acetals. II. E. HÄGGLUND and H. URBAN (Cellulosechem., 1928, **9**, 49—53; cf. A., 1927, 753; this vol., 277).—"Hydrochloric acid lignin," "phosphoric acid lignin," and "alkali lignin" all partly dissolve, forming semiacetals, after prolonged boiling with ethyl or amyl alcohol and hydrogen chloride, up to 80% of "hydrochloric acid lignin" being thus dissolved by amyl alcohol. The alcoholysis

of lignins is not dependent on a tautomeric hydroxyl group, since methylated lignins react similarly; *e.g.*, a methylated lignin formed, with amyl-alcoholic hydrogen chloride, a light brown *substance*, m. p. 70°. Experiments with carefully purified material now indicate that lignin has $M =$ about 400 and has the composition $C_{22}H_{20}O_{7-8}$ or $C_{19}H_{11}O_2(OMe)_2(OH)_2 \cdot CHO$.　B. W. ANDERSON.

αβ-Dialkylhydroxylamines. R. T. MAJOR and E. E. FLECK (J. Amer. Chem. Soc., 1928, **50**, 1479—1481; cf. A., 1914, i, 1167; Neuffer and Hoffman, A., 1925, i, 891).—Alkylation of hydroxyurethane in alkaline solution with 2·1 mols. of methyl or ethyl sulphate yields the αβ-dialkyl and a little of the α-monoalkyl derivatives (cf. Jones, A., 1898, i, 174; Hecker, A., 1914, i, 256). The dialkyl derivatives are hydrolysed and decarboxylated to the corresponding αβ-dialkylhydroxylamines by refluxing with 50% alcoholic potassium hydroxide. αβ-Diethylhydroxylamine forms a constant-boiling mixture, b. p. 74°, with water.　H. E. F. NOTTON.

Influence of the alcohol group of amino-acid esters on the rate of formation of 2 : 5-diketopiperazines and on the formation of guanidinocompounds by the action of guanidine on the various amino-acid esters. E. ABDERHALDEN and S. SUZUKI.—See this vol., 716.

Preparation of ethyl aminomalonate. R. LOCQUIN and V. CERCHEZ (Compt. rend., 1928, **186**, 1360—1362).—Reduction of ethyl oximinomalonate with magnesium or aluminium amalgam gives a 65% yield of *ethyl aminomalonate*, b. p. 116—118°/12 mm. The following derivatives have been prepared: *ethyl ureidomalonate*, m. p. 167°, *aminomalondiamide*, m. p. 196°, *ethyl benzamidomalonate*, m. p. 161°, and an *oxalate*, $NH_2 \cdot CH(CO_2Et)_2,(CO_2H)_2$, m. p. 138°.　E. A. LUNT.

Jaffé's reaction for creatinine. IV. Compound of creatinine, picric acid, and sodium hydroxide. I. GREENWALD (J. Biol. Chem., 1928, **77**, 539—546).—Addition of alcohol to the solution resulting from treatment of creatinine with picric acid and sodium hydroxide yields a precipitate, $2C_4H_7ON_3,C_6H_3O_7N_3,3NaOH,3H_2O$; treatment of the aqueous solution of this substance with basic lead acetate yields an analogous compound with lead hydroxide in place of the sodium hydroxide; on dissolution in boiling dilute acetic acid, creatinine picrate is obtained. Treatment with mineral acids causes destruction of the picric acid. The substance is not itself responsible for the red colour characteristic of Jaffé's reaction.　C. R. HARINGTON.

Isolation and function of phosphocreatine. C. H. FISKE and Y. SUBBAROW (Science, 1928, **67**, 169—170).—Calcium is used instead of barium in the isolation of phosphocreatine, the product having the composition $C_4H_8O_5N_3PCa,4H_2O$, and the constitution probably $PO(OH)_2 \cdot NH \cdot C(:NH) \cdot NMe \cdot CH_2 \cdot CO_2H$. This is the first substance containing phosphorus attached to nitrogen to be isolated from natural sources. The second dissociation constant of phosphocreatine is about $2 \cdot 5 \times 10^{-5}$; one of its functions in muscle is that of neutralising a considerable part of the lactic acid formed during muscular contraction.　A. A. ELDRIDGE.

Deamination of arginine. K. FELIX and H. MÜLLER (Z. physiol. Chem., 1928, **174**, 112—118).—Arginine hydrochloride when treated with rather more than the equivalent quantity of silver nitrite yields *arginine nitrite*, α_D^{20} $+13°$. Silver chloride is removed and the filtrate warmed on the water-bath. After the reaction, the slight excess of silver is removed by hydrogen sulphide, and the filtrate evaporated in a vacuum. *Argininic* [α-*hydroxy-δ-guanidinovaleric*] *acid* is obtained crystalline, decomp. 228° with previous sintering. Its aqueous solution is neutral, with $[\alpha]_D^{20}$ $-12·5°$. It forms a *picrate*, m. p. 145°, decomp. 205°; the *picrolonate* darkens at 223°, decomp. 227—228°. On boiling argininic acid with aqueous barium hydroxide, carbamide and α-hydroxy-δ-aminovaleric acid are produced. Evaporation of the original argininic acid solution at the ordinary pressure causes decomposition (loss of carbon dioxide).　H. D. KAY.

Synthesis of diethyl β-methyl-αγ-dicyanoglutaconate. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1928, **3**, 103—105; cf. A., 1927, 345, 1059; this vol., 158).—Ethyl orthoacetate, ethyl cyanoacetate, and acetic anhydride react to form ethyl β-ethoxy-α-cyanocrotonate, m. p. 74—75° (cf. Haller, A., 1900, i, 372). This compound condenses with ethyl sodiocyanoacetate to form ethyl α-sodio-αγ-dicyano-β-methylglutaconate, which is converted by dilute acid into ethyl αγ-dicyano-β-methylglutaconate.　A. McGOOKIN.

Preparation of guanidine derivatives starting from S-methylisothiocarbamide sulphate. V. PIOVANO (Gazzetta, 1928, **58**, 245—249).—S-Methylisothiocarbamide sulphate in boiling aqueous solution reacts with propylamine, evolving methylmercaptan and giving a 70% yield of *propylguanidine sulphate*, m. p. 220° (decomp.) [*picrate*, m. p. 177—178°; *chloroaurate*, m. p. 200° (decomp.); *chloroplatinate*, m. p. 195° (decomp.)]. With piperazine, *piperazine-guanidine sulphate*, m. p. 288—290° (decomp.), is obtained [*picrate*, m. p. 260—270° (decomp.); *chloroaurate*, m. p. 243° (decomp.); *chloroplatinate*, m. p. 265—268° (decomp.)].　E. W. WIGNALL.

Addition of ethyl sodiomalonate to aliphatic thiocarbimides. D. E. WORRALL (J. Amer. Chem. Soc., 1928, **50**, 1456—1459; cf. A., 1924, i, 208; 1925, i, 244).—The following *dicarbethoxythioacetalkylamides*, $NHR \cdot CS \cdot CH(CO_2Et)_2$, are obtained by treating ethyl sodiomalonate with alkylthiocarbimides and decomposing the enolic sodio-derivatives with acid: *methyl*, m. p. 49—50°; *ethyl*, m. p. 51—52°; *propyl*, m. p. 11°, and oily *butyl*, and the following *dicarbomethoxythioacetalkylamides* from methyl sodiomalonate: *propyl*, m. p. 42—43°; *butyl*, m. p. 62—63°, and *amyl*, m. p. 52—53°. With warm acids or alkalis these are completely hydrolysed, but with cold sodium hydroxide they give the following *sodium* salts, $NHR \cdot CS \cdot CH_2 \cdot CO_2Na$, of *carboxythioacetalkylamides*: *ethyl*, decomp. 148—149°; *propyl*, decomp. 155—156°; *butyl*, decomp. 156—157°, and *amyl*, decomp. 157—158°. *Carboxythioacetbenzyl-*

amide, m. p. 95—96°, with formation of *thioacet-benzylamide*, m. p. 62—63°, is prepared similarly.
<div align="right">H. E. F. NOTTON.</div>

Composition and structure of the polymeride of hydrocyanic acid. E. GRISCHKEVITSCH-TRO-CHIMOVSKI (Rocz. Chem., 1928, **8**, 165—174).—The polymeride of hydrocyanic acid formed from 4 mols. of the latter gives on condensation with glyoxal 2 : 3-*dicyanopyrazine*, m. p. 132·5—133°. It hence follows that the tetrameride of hydrocyanic acid must be the dinitrile of diaminomaleic acid; this conclusion is further supported by the formation of 4 : 5-dicyano-1 : 2 : 3-triazole from the tetrameride and nitrous acid.
<div align="right">R. TRUSZKOWSKI.</div>

Interaction of hydrogen sulphide with amino-and imino-acid nitriles. E. GATEWOOD and T. B. JOHNSON (J. Amer. Chem. Soc., 1928, **50**, 1422—1427).—The course of the reaction with a given nitrile cannot be predicted, but the products are of three types: (*a*) dithiopiperazines (cf. A., 1911, i, 696, 712), (*b*) iminonitriles (from aminonitriles), and (*c*) thiodeoxyhydantoins, a new class of substances. Thus, α-amino*iso*butyronitrile or α-iminodi*iso*butyronitrile in aqueous-alcoholic ammonia yields with hydrogen sulphide a *substance*, m. p. 153—155° (*mercury* salt, m. p. 175°), provisionally regarded as 5-*thio-2 : 2 : 4 : 4-tetramethyl-2-deoxyhydantoin*,
$\begin{matrix} CS-CMe_2 \\ NH\cdot CMe_2 \end{matrix}>NH$. This shows acidic and basic properties, is not desulphurised by mercuric oxide, and is hydrolysed by acids to α-amino*iso*butyric acid. α-Amino-α-methylbutyronitrile, α-amino-α-ethyl-butyronitrile, and α-iminodipropionitrile are not attacked by hydrogen sulphide under these conditions. α-Aminopropionitrile yields α-iminodipropionitrile with an unstable, oily by-product, whilst iminodiacetonitrile yields mainly *iminodiacetothioamide*, m. p. 124°, with (?) 5-*thio-2-deoxyhydantoin*, m. p. 186°, and an amorphous *substance*.
<div align="right">H. E. F. NOTTON.</div>

Action of cyanogen bromide on dimagnesium acetylene dibromide. A. S. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1927, **59**, 915—919).—See A., 1927, 1051.

Chelate compounds of thallium dialkyl. R. C. MENZIES, N. V. SIDGWICK, E. F. CUTCLIFFE, and J. M. C. FOX (J.C.S., 1928, 1288—1291).—By double decomposition of thallium dialkyl halides with thallous acetylacetone and corresponding compounds or by the action of thallium dialkyl ethoxide or carbonate on the appropriate diketone, the following were prepared: *thallium dimethyl acetylacetone*, m. p. 214—215° (some decomp.); *thallium diethyl acetylacetone*; *thallium dimethyl benzoylacetone*, m. p. 128—129°; *thallium diethyl benzoylacetone*, m. p. 116—118°; *ethyl thallium diethyl acetoacetate*, m. p. 88—90°, and *thallium dimethyl salicylaldehyde*, decomp. 200°. These are crystalline compounds which can be sublimed under reduced pressure and are soluble in benzene and hexane, and thus appear to be chelate co-ordinated compounds of the type
$CH\begin{matrix} CMe\cdot O \\ \\ CMe\cdot O \end{matrix}TlMe_2$. In water, however, they form
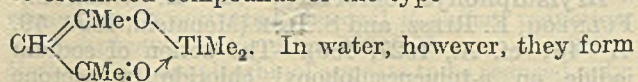
ionised solutions of alkaline reaction, in which the thallium dialkyl can be titrated quantitatively.
<div align="right">B. W. ANDERSON.</div>

Complex salts of β-methyltrimethylenediamine with bivalent platinum. F. G. MANN (J.C.S., 1928, 1261—1263; cf. this vol., 157).—A solution of β-methyltrimethylenediamine hydrochloride in aqueous sodium hydroxide when refluxed with aqueous potassium chloroplatinite yielded a solution which, after treatment with sodium bromide, yielded *bis-β-methyltrimethylenediamineplatinous dibromide*, $[Pt\{CHMe(CH_2\cdot NH_2)_2\}_2]Br_2$, m. p. 266—268° (decomp.). The corresponding *di-iodide*, m. p. 263—264° (decomp.), and *dinitrate* (deflagrates) were similarly obtained, and from the di-iodide the *di-d-camphor-β-sulphonate monohydrate*, m. p. 279—281° (decomp.), [α] +15°, *di-d-α-bromocamphor-π-sulphonate*, slow decomp. 278—285°, [α] +69·2°, and *ditartrate* were prepared. The above six compounds, although highly crystalline, showed no sign of *cis-trans*-isomerism; moreover, the last three mentioned could not be resolved into optically active forms; the observed rotations were due solely to the sulphonate ions.
<div align="right">B. W. ANDERSON.</div>

Complex compounds of platinum and palladium with organic sulphides. E. C. FRITZMANN (Ann. inst. platine, 1926, No. 4, 55—179).—Unpublished work by Tschugaev and Ilyin is reported. The *compound* $2CMe_2(CH_2SEt)_2,2PtCl_2$, rose, changes at 114—116° to a yellow *modification* (monomeric), m. p. 218—219°. The *compound* $C(CH_2SEt)_4,PtCl_2$, decomp. 235°, when heated yields the *compound* $C(CH_2SEt)_4,2PtCl_2$, yellow, m. p. <100°. The *compound* $2(EtSHC\!:\!CHSEt)_2,2PtCl_2$ and a monomeric *form* are recorded. In unpublished work by Tschugaev and Ivanov, the following *compounds* are recorded: $PdCl_2,2Et_2S$, yellow, m. p. 82°; $PdBr_2,2Et_2S$, m. p. 100°; $PdI_2,2Et_2S$, m. p. 104°; $PdCl_2,(CH_2SEt)_2$, m. p. 180°; $PdBr_2,(CH_2SEt)_2$, m. p. 159°; $PdI_2,(CH_2SEt)_2$, m. p. 154°. In unpublished work by Tschugaev and Malchevski the transition from the non-conducting type $[Pt,2Et_2S,Cl_2]$ to the electrolyte $[Pt,4Et_2S]Cl_2$ is traced. Tschugaev and Vladimirov (unpublished) have shown that compounds of the type $[Pt,2R_2S,X_2]$ existing in two isomeric forms show negligible conductivity in methyl alcohol, further addition of thioether yielding $[Pt,4R_2S]Cl_2$, the two compounds being in equilibrium.
<div align="right">CHEMICAL ABSTRACTS.</div>

*cyclo*Pentane derivatives. Preparation of 1 : 2-dimethyl*cyclo*pentane. G. CHAVANNE and (MLLE.) L. DE VOGEL (Bull. Soc. chim. Belg., 1928, **37**, 141—152).—Magnesium methyl iodide converts *cyclo*pentanone into 1-*methylcyclopentanol*, b. p. 135·6°/760 mm., m. p. 36° (*allophanate*, m. p. 157°), dehydrated by *p*-toluenesulphonic acid to 1-*methyl-Δ^1-cyclopentene*, b. p. 75·5—76°/760 mm., m. p. —127·2°, d_4^0 0·7979, n_D^{15} 1·4347. When this hydrocarbon is treated with monochlorocarbamide (cf. Detœuf, A., 1922, i, 236, 327) there are formed at least two *chlorohydrins* having b. p. about 75°/10 mm., d_4^{20} 1·1039, n_D^{20} 1·4785, and m. p. 35—37°, respectively. The mixture of chlorohydrins is converted by treatment with potassium hydroxide into

1-*methyl*-Δ^1-*cyclopentene oxide*, b. p. 110·8—111°/760 mm., m. p. —80·5°, $d_4^{13\cdot95}$ 0·9266, n_D^{15} 1·4311, which reacts with excess of magnesium methyl iodide to give the same stereoisomeric mixture of 1 : 2-dimethyl-*cyclo*pentanols as that obtained from 2-methyl*cyclo*-pentanone (van Rysselberge, A., 1926, 1238). When the theoretical quantity of the Grignard reagent is used and the reaction product is not distilled under reduced pressure the main product is 1 : 2-dimethyl-*cyclo*pentene, together with a small amount of 2-methyl*cyclo*pentanone.

Catalytic reduction of 1 : 2-dimethyl*cyclo*pentene in acetic acid using platinum-black affords 1 : 2-di-methyl*cyclo*pentane, b. p. 94—99°/760 mm., d_4^{20} 0·764, n_D^{20} 1·417 (cf. van Rysselberge, *loc. cit.*).

H. BURTON.

Catalytic action of mercury and bismuth [in nitration]. J. B. MENKE (Rec. trav. chim., 1928, 47, 668—672).—The nitration of benzene by metallic nitrates under varying conditions has been studied. When a mixture of benzene vapour and nitrogen oxides is heated in an atmosphere of mercury vapour or is passed over bismuth oxide at 400—500°, nitrobenzene and nitrophenol are formed. The formation of organo-metallic compounds which occurs when mercury is used is avoided by the second procedure, and in this case also, much less nitrobenzene is formed. Benzene is nitrated to nitrobenzene by a mixture of acetic anhydride and cupric, aluminium, ferric, cobalt, or nickel nitrate at 80°. Similar results are obtained with mercuric or mercurous nitrate, but in addition a little *o*-nitrophenol and (different) mercury compounds are obtained in these cases. When bismuth nitrate is used similar results are obtained but no metal complex compounds are formed. Thiophen is similarly nitrated by the action of aluminium nitrate and acetic anhydride at 60—65°. When acetic acid is substituted for its anhydride no nitration occurs except when the mercury or bismuth salts are used, and then only to a small extent, complex mercury compounds also being produced. Since phosphoric acid destroys its catalytic activity, bismuth cannot be used to replace mercury in the ordinary Kjeldahl or Gunning processes, nor in the oxidation of naph-thalene to phthalic acid. J. W. BAKER.

Comparative effects of the nitro-, carboxyl, and sulphonic acid groups on the hydrolysis of aryl halides. W. DAVIES and E. S. WOOD (J.C.S., 1928, 1122—1131).—The comparative activity of the chlorine atom in chlorobenzenes substituted in the 4-, 2 : 4-, and 2 : 4 : 6-positions by nitro-, carboxyl, and sulphonic acid groups, respectively, shows that the order of activation of the chlorine atom is $NO_2 > SO_3H > CO_2H$. The activity due to the nitro-group is, however, enormously (about 10^5 times) greater than that due to the other groups; the sulphinic acid group has an influence comparable with these latter. A nitro-group in the *o*-position also greatly increases the effect of a carboxyl or sulphonic acid group introduced into the *p*-position. The following compounds were prepared : *diphenylamine-2 : 4 : 6-trisulphonanilide*, m. p. 227° (decomp.); the *potassium* salts of chlorobenzene-2 : 4 : 6-trisulphonic acid and 1-chloro-2-nitrobenzene-4-sulphonic acid,

respectively, and the *ammonium* salt of chlorobenzene-*p*-sulphinic acid. B. W. ANDERSON.

Action of magnesium on *p*- and *m*-dibromo-benzenes. J. S. SALKIND and P. V. ROGOVINA (J. Russ. Phys. Chem. Soc., 1927, 59, 1013—1018).—An experimental refutation of older theories that only one halogen atom in an aromatic dibromo-compound reacts with magnesium in a Grignard synthesis.

m- and *p*-Dibromobenzenes were allowed to react with twice the theoretical quantity of magnesium; the products were hydrolysed, and the extent of the reaction was determined by dissolving the metal remaining and measuring the hydrogen evolved, and also by titrating the ionisable bromine. In each case, about 66—75% of the dihalogen magnesium derivative was formed.

The main product was tar, only about 23—31% of the theoretical yield of benzene being obtained.

M. ZVEGINTZOV.

Oxidation reactions. II. Oxidation of toluene with nitric acid and oxides of nitrogen in presence of oxygen. P. ASKENASY, E. ELÖD, and C. TROGUS (Annalen, 1928, 461, 109—130; cf. A., 1927, 635).—When toluene is boiled with nitric acid (*d* 1·4 ?) for 100 hrs., benzoic and *p*-nitrobenzoic acids are the main products, together with some *o*-nitrotoluene and carbon dioxide and traces of picric acid. Contrary to the statement of Fittig (Annalen, 1861, 117, 192; 120, 222), who probably used impure toluene, no hydroxybenzoic acids are formed. The absence of *p*-nitrotoluene is due to the comparatively ready oxidation of this substance by dilute nitric acid at a high temperature. On the other hand, *o*-nitro-toluene and -benzoic acid readily react with hydroxylamine formed during the heating process, to give *o*-toluidine and anthranilic acid, which undergo conversion into diazo-compounds in presence of nitrous acid. This would appear, at any rate, to be a source of, *e.g.*, nitrogen and phenol and thus of the picric acid actually identified.

Oxidation of toluene with nitric acid under con-siderable pressures (cf. Sachse, G.P. 216091) has also been investigated in detail. Oxidation proceeds in definite stages and the time interval between the beginning of reaction and the point when the toluene layer sinks to the bottom and begins to disappear with simultaneous evolution of nitric oxide has been plotted against temperature. Pressure as such has little effect on the reaction, but in so far as it leads to the attainment of a higher-boiling mixture it has a great effect. Reaction becomes explosive at temper-atures above 200°. Increase in concentration of the nitric acid from 5 to 30% causes increase in yield of total products, in the amount of carbon dioxide formed, and in the nitrogen content of the products. The rate of reaction increases also, 30% acid reacting violently. A number of tables are given showing the effect of different conditions on the reactions under investigation (temperature, pressure, catalysts, etc.).

E. E. TURNER.

Arylsulphonyl chlorides. II. E. GEBAUER-FÜLNEGG, E. RIESZ, and S. ILSE (Monatsh., 1928, 49, 41—46; cf. A., 1927, 139).—The action of sodium iodide on *p*-toluenesulphonyl chloride in acetone

solution yields sodium *p*-toluenesulphinate, di-*p*-tolyl-disulphone (Kohler and MacDonald, A., 1899, i, 904), and di-*p*-tolyldisulphoxide (Otto and Tröger, A., 1891, 718), iodine being liberated. The mechanism of formation of these compounds is discussed. The action of sodium iodide on *p*-diphenylsulphonyl chloride (obtained from the acid, which is produced in 90% yield by sulphonation with concentrated sulphuric acid at 50° in the presence of nitrobenzene as a diluent) similarly yields sodium *p*-diphenylsulphinate and di-diphenyldisulphone. J. W. BAKER.

Alternating effect in carbon chains. XXV. Mechanism of aromatic side-chain substitution. XXVI. Nitration of ω-chloro- and ω-bromo-*p*-xylene. C. K. INGOLD and E. ROTHSTEIN (J.C.S., 1928, 1217—1221, 1278—1280).—XXV. The side-chain bromination of nitro-*p*-xylene yields at least 76% of 3-*nitro-p-xylyl bromide*, m. p. 76°, showing that the reaction must proceed by preliminary attraction of potential bromine cations by electrons. The above bromide yielded the same 3-*nitro-p-xylyl-ω-trimethyl-ammonium picrate*, m. p. 138°, as was obtained through the corresponding quaternary *chloride*, from the known 3-nitro-*p*-xylyl chloride (m. p. 48°).

XXVI. In the nitration of ω-chloro- and ω-bromo-*p*-xylene substitution occurs chiefly in the position *ortho* to the methyl group. These results are of importance in the development of the theory of anionotropy. A mixture, b. p. 120°/3 mm., of 2- and 3-*nitro-4-methylbenzyl ethyl ethers* was incidentally obtained during the investigation. B. W. ANDERSON.
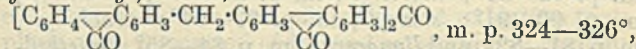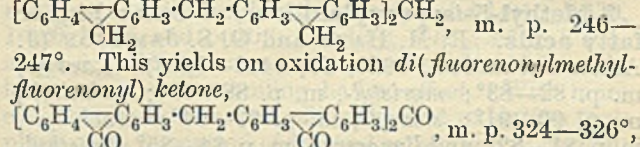
[Preparation of] styrene. T. W. ABBOTT and J. R. JOHNSON (Org. Syntheses, 1928, 8, 84—86).

Aromatic compounds containing a *tert*.-butyl group. A. E. TSCHITSCHIBABIN, S. ELGASINE, and V. A. LENGOLD (J. Russ. Phys. Chem. Soc., 1928, 60, 347—354).—See this vol., 404.

Production of condensed ring systems by catalytic dehydrogenation. II. Activated charcoal as reducing agent. N. D. ZELINSKI and M. V. GAVERDOVSKAJA (Ber., 1928, 61, [B], 1049—1053; cf. A., 1927, 47).—Triphenylcarbinol is converted by platinised charcoal at 150—180° into the labile form of triphenylmethane, m. p. 81°, and by activated charcoal at 300° into carbon dioxide and the stable variety of the hydrocarbon, m. p. 92°. Phenyldi-*cyclo*hexylcarbinol, m. p. 77°, in contact with platinised charcoal affords 9-*phenylfluorene*, m. p. 145°, whereas with activated charcoal at 300° it gives *phenyldicyclo-hexylmethane*, b. p. 210—212°/20 mm., $d_4^?$ 0·9890. Under similar conditions, diphenylmethylcarbinol yields 9-*methylfluorene*, m. p. 46°, and diphenylethane, b. p. 268—269°, $d_4^?$ 0·9875, respectively, whilst diphenylethylcarbinol affords 9-*ethylfluorene*, m. p. 108°, and diphenylpropane, b. p. 278—279°/759 mm. Dimethylbenzylcarbinol is converted into *isobutyl*-benzene, b. p. 170°/756 mm., d_4^{20} 0·8628, in presence of either catalyst. *Phenylmethylbenzylcarbinol*, b. p. 179°/14 mm., m. p. 51°, in contact with platinised charcoal gives 9-*methylphenanthrene*, m. p. 94°, whereas with activated charcoal it suffers reduction to αβ-*diphenylpropane*, b. p. 278°/751 mm., d_4^{20} 0·9807. Methylethylbenzylcarbinol appears to be reduced only

to β-*benzylbutane*, b. p. 113—115°/11 mm., d_4^{20} 0·868; the formation of a condensed system is not observed. *tert*.-Amyl alcohol is converted into pentane, b. p. 30—30·5°, d_4^{20} 0·6281. Phenol is converted into benzene by repeated passage over activated charcoal at 300°. In general reduction of oxygenated organic compounds in presence of activated or platinised carbon occurs at notably lower temperatures than are required with other forms of carbon. H. WREN.

Synthesis of two hydrocarbons of high mol. wt., derivatives of fluorene and methane. K. DZIEWOŃSKI and M. PANEK (Bull. Acad. Polonaise, 1927, A, 745—751).—The action of methylal on fluorene in presence of phosphorus pentoxide in boiling chloroform solution yields 2 : 2'-*difluorylmethane*, m. p. 201—202°. *Dinitro*-2 : 2'-*difluorylmethane*, m p. 256—257°, is obtained by nitration, and oxidation by sodium dichromate in acetic acid yields 2 : 2'-*di-fluorenone ketone*, m. p. 297—298° [*triphenylhydrazone*, m. p. 203° (decomp.)]. Fusion of the ketone with potassium hydroxide yields at 200—210° an *acid*, $C_{27}H_{20}O_7$, m. p. 262—265°, and at 260—270° diphenyl-2 : 4'-dicarboxylic acid. The formation of the last proves the constitution of the foregoing compounds. As a by-product in the first condensation there is formed *di*(*fluorylmethylfluoryl*)*methane*,
$$[C_6H_4{-}C_6H_3{\cdot}CH_2{\cdot}C_6H_3{-}C_6H_3]_2CH_2$$
m. p. 246—247°. This yields on oxidation *di*(*fluorenonylmethyl-fluorenonyl*) *ketone*,
$$[C_6H_4{-}C_6H_3{\cdot}CH_2{\cdot}C_6H_3{-}C_6H_3]_2CO$$
m. p. 324—326°, which is decomposed by fusion with potassium hydroxide at 280° to give an *acid*, $C_{27}H_{20}O_7$. R. K. CALLOW.

Closure of the fluorene ring in the di-α-naphthylmethane series. O. MAGIDSON (Trans. sci. chem.-pharm. Inst., 1926, [16], 32—48; Chem. Zentr., 1928, i, 58).—See A., 1925, i, 384.

Dissociation of phenanthrene by heat in the presence of hydrogen under pressure. N. A. ORLOV (J. Russ. Phys. Chem. Soc., 1927, 59, 895—902).—See A., 1927, 1060.

Photodecomposition of triphenylmethyl. S. T. BOWDEN and W. J. JONES (J.C.S., 1928, 1149—1158).—The region of the visible spectrum in which triphenylmethyl shows the strongest absorption, viz., the greenish-blue (5300—4000 Å.), is the most active in effecting its decomposition, ultra-violet light having little or no effect. The first products of the photochemical change are probably triphenyl-methane and phenyldiphenylenemethyl, the latter then undergoing association to diphenylbisdiphenyl-ene-ethane. The behaviour of the triphenylmethyl radical is shown to be different from that of the tri-phenylmethyl ion, since the latter (in liquid sulphur dioxide) is not photochemically reactive. The slight decolorisation noticed in "solid triphenylmethyl" exposed to sunlight is thought to be due to the presence of adsorbed solvent. B. W. ANDERSON.

Hydrogenation of tetraphenylmethane and *p*-hydroxytetraphenylmethane under pressure. V. N. IPATIEV and B. N. DOLGOV (J. Russ. Phys. Chem. Soc., 1927, 59, 1087—1091).—See this vol., 163.

Odour and constitution among the mustard oils [thiocarbimides]. III. G. M. DYSON (Perf. Ess. Oil Rec., 1928, **19**, 171—174; cf. this vol., 283, 514).—The odours of aromatic thiocarbimides containing both halogen and methyl substituent groups together are described. The results agree with the generalisation previously described. The nature of the odour is dependent more on orientation than on the nature of the substituent group, and where chlorine and methyl groups occur together in the same compound the effect of the chlorine is more strongly marked than that of the methyl group. The following substituted phenylthiocarbimides and their odours are described : 3-*chloro-4-methyl-*, b. p. 274° ; 4-*chloro-3-methyl-*, m. p. 22° ; 2-*chloro-5-methyl-*, b. p. 269° ; 5-*chloro-2-methyl-*, b. p. 272° ; 2-*chloro-4-methyl-*, m. p. 23° ; 4-*chloro-2-methyl-*, m. p. 34° ; 2-*bromo-4-methyl-*, m. p. 18°, and 4-*bromo-2-methyl-*, m. p. 32°. s-*Di-(2-bromo-4-methyl)*- and s-*di-(4-bromo-2-methyl)-thiocarbamides*, m. p. 192° and 178°, are described. *o-*, *m-*, and *p-*Nitrophenylthiocarbimides and four of the nitrotolylthiocarbimides have been prepared. With the exception of that of *p-*nitrophenylthiocarbimide, their odours are very faint.

E. H. SHARPLES.

2-Methyl-5-*iso*propylanilides of some higher fatty acids. R. M. HANN and G. S. JAMIESON (J. Amer. Chem. Soc., 1928, **50**, 1442—1443).—*Lauryl-*, m. p. 82—83° ; *myristyl-*, m. p. 88—89° ; *palmityl-*, m. p. 90—91° ; *stearyl-*, m. p. 93—94° ; *arachidyl-*, m. p. 81—82°, and *lignoceryl-*, m. p. 84—85°, 2-*methyl-*5-*iso*propylanilides have been prepared from the appropriate acid chlorides and cymidine.

H. E. F. NOTTON.

Molecular dissymmetry dependent on restriction of rotation about a single linking. Optically active benzenesulphonyl-8-nitro-1-naphthylglycine. W. H. MILLS and K. A. C. ELLIOTT (J.C.S., 1928, 1291—1302).—Benzenesulphonyl chloride reacts with 8-nitro-1-naphthylamine in pyridine, yielding 8-*nitro-1-benzenesulphonamido-naphthalene*, m. p. 198—199° (*dibenzenesulphonamido-*derivative, m. p. 199°), which is converted by ethyl bromoacetate in presence of sodium ethoxide into *ethyl* N-*benzenesulphonyl-8-nitro-1-naphthylaminoacetate*, m. p. 173°. Hydrolysis of this with dilute acetic and sulphuric acids gives N-*benzenesulphonyl-8-nitro-1-naphthylglycine*, $NO_2 \cdot C_{10}H_6 \cdot N(SO_2Ph) \cdot CH_2 \cdot CO_2H$ (I), m. p. 214°. If the rotation of the

$PhSO_2 \cdot N \cdot CH_2 \cdot CO_2H$ grouping is obstructed by the nitro-group (cf. Mills, Chem. and Ind., 1926, **45**, 884) it is probable that (I) will exist in two enantiomorphous modifications. When equivalent quantities of (I) and brucine are mixed in acetone solution *brucine l-benzenesulphonyl-8-nitro-1-naphthylaminoacetate* ($+H_2O$), m. p. 195—196°, is formed. This salt exhibits mutarotation in chloroform solution, the average period of half change at 15·5° being 5 min. When this salt is decomposed in chloroform solution with dilute sulphuric acid, the resulting chloroform solution of the *l*-acid is strongly lævorotatory, and the time of half change at 14·9° is 17 min. A solution of the brucine *l*-acid salt in

boiling methyl alcohol gives, on cooling, *brucine* d - *benzenesulphonyl* - 8- *nitro* - 1 - *naphthylaminoacetate* ($+3H_2O$), which is strongly dextrorotatory in chloroform solution, the rotation falling gradually to the final value of the brucine *l*-acid salt. If a chloroform solution of (I) is treated with a chloroform solution of brucine the initial lævorotation falls gradually to an equilibrium value. Decomposition in the usual way indicates the formation of the brucine *d*-acid salt, since the acid obtained shows dextrorotation.

In order to demonstrate that the optical activity found was not due to the asymmetric tervalent nitrogen atom, *benzenesulphonyl-1-naphthylglycine*, m. p. 188—189° (*ethyl* ester, m. p. 89°), was examined. The *quinine* salt of this acid exhibited no mutarotation under the conditions employed.

H. BURTON.

Oxidation of arylthiolarylides. E. GEBAUER-FÜLNEGG and E. RIESZ (Monatsh., 1928, **49**, 31—40 ; cf. A., 1927, 1060).—4-Chloro-2-nitro-1-chlorothiolbenzene has been condensed with *o*-aminophenol, *o*- and *p*-phenylenediamines, and *as*-dimethyl-*p*-phenylenediamine, and the action of oxidising agents on the resulting chloronitrophenylthiolanilides has been investigated. Condensation with *o*-aminophenol in ether yields 4-*chloro-2-nitrophenylthiol-o-hydroxyanilide*, m. p. 143°, which, on oxidation with sodium dichromate and acetic acid, or with hydrogen peroxide, yields 4-*chloro-2-nitrophenyl-o-benzoquinonethiolimine*, $C_6H_3Cl(NO_2) \cdot S \cdot N \dblcolon C_6H_4 \dblcolon O$, m. p. 134—135°. Similarly, *p*-phenylenediamine yields *bis-4'-chloro-2'-nitrophenylthiol-p-phenylenediamine* (I), m. p. 212°. This is converted by various oxidising agents or by heating with acetone or acetic acid into a red *substance*, m. p. 264—270°, which by chlorination with chlorine in chloroform suspension yields 4-chloro-2-nitrobenzenesulphonyl chloride, also obtained by the direct chlorination of (I). *o*-Phenylenediamine yields *bis-4'-chloro-2'-nitrophenylthiol-o-phenylenediamine*, m. p. 181°, together with 2 : 3-diaminophenazine hydrochloride. The former, by oxidation, yields a red *substance*, m. p. 172°. *as*-Dimethyl-*p*-phenylenediamine condenses to yield *p-dimethylamino-4'-chloro-2'-nitrophenylthiolanilide*, m. p. 152°, which by oxidation with concentrated nitric acid yields 4' - *chloro* - 2' - *nitrophenyl-p-benzoquinonethiol. iminedimethylimmonium nitrate*, $C_6H_3Cl(NO_2) \cdot S \cdot N \dblcolon C_6H_4 \dblcolon NMe_2 \cdot NO_3$, m. p. 102°, from which the free *base*, m. p. 186°, is obtained by the action of alcoholic ammonia. The base is also obtained when hydrogen peroxide replaces nitric acid as the oxidising agent, the corresponding *chromate* being obtained when chromic acid is used.

J. W. BAKER.

Preparation and constitution of thiocarbamides of fluorene. L. GUGLIALMELLI, A. NOVELLI, C. RUIZ, and C. ANASTASI (Anal. Asoc. Quím. Argentina, 1927, **15**, 337—362 ; cf. this vol., 629).—Fluorene derivatives are considered to show properties characteristic of 2 : 2′-disubstituted diphenyl derivatives, and may possess a configuration analogous to that proposed by Kaufler for diphenyl. The behaviour of 2 : 7-diaminofluorene as an *o*-diamine in thiocarbamide formation and the difficulty

of thiocarbamide formation by 2-amino-derivatives (*loc. cit.*) owing to steric hindrance may be explained on this basis.

By reaction with thiocarbonyl chloride in boiling toluene 2 : 7-diaminofluorene, m. p. 162°, yielded 2 : 7-*fluorylenethiocarbamide*, m. p. above 300°, for which an alternative bimolecular formula is possible, accompanied by (?) 7 : 7'-*diaminodi*-2 : 2'-*fluorylthiocarbamide*, which yielded an *azo-dye* on diazotisation and treatment with β-naphthol. Similarly 1 : 2-diaminofluorene (2 : 3-diaminofluorene, cf. Eckert and Langecker, this vol., 521) yielded 1 : 2(or 2 : 3)-*fluorylenethiocarbamide*, insoluble, m. p. above 300°; 1(or 3)-nitro-2-aminofluorene yielded 1 : 1'(or 3 : 3')-*dinitro*-2 : 2'-*fluorylthiocarbamide*, m. p. above 330°, also prepared by reaction with carbon disulphide in presence of pyridine and iodine; 2-nitro-7-aminofluorene yielded 2 : 2'-*dinitrodi*-7 : 7'-*fluorylthiocarbamide*, m. p. above 330°. R. K. CALLOW.

Action of cuprous hydride on diazonium salts. Combined Sandmeyer–Gattermann reaction. P. NEOGI and A. K. MITRA (J.C.S., 1928, 1332—1333).—Treatment of diazo-solutions at 0° with moist cuprous hydride and halogen acid yields halogenobenzenes as the main products, together with small quantities of the corresponding hydrocarbons. Crystalline cuprous halide is formed during the reaction. From diazonium sulphates, the main products are phenols, but small amounts of hydrocarbons are formed also.
H. BURTON.

Mechanism of the rearrangement of diazoaminobenzene into aminoazobenzene. II and III. N. YOKOJIMA (J. Soc. Chem. Ind. Japan, 1928, 31, 100—108, 109—116).—II. Rearrangement of diazoaminobenzene into aminoazobenzene in the absence of aniline could not be effected by heating alone, by heating with paraffin wax, by heating the hydrochloride in either an open or a sealed tube, or by mixing diazoaminobenzene and hydrochloric acid in alcoholic solution. By the addition of aniline and hydrochloric acid in alcoholic solution, part of the diazoaminobenzene changed into aminoazobenzene, the yield increasing with the amount of aniline added.

III. The mechanism of rearrangement of diazoaminobenzene into aminoazobenzene is explained as follows. In the aniline solution, hydrochloric acid combines with diazoaminobenzene, forming a yellow salt, NPh:N·NHPh,HCl. The hydrogen chloride intensifies the basic property of the amino-group and accelerates the separation of the diazo-group from it. Aminoazobenzene is formed by the direct attack of the separated diazo-compound on the *p*-position of the aniline nucleus. S. OKA.

Spectrochemical studies of hydroxyazo-compounds. VI. T. UEMURA and S. TABEI (Bull. Chem. Soc. Japan, 1928, 3, 105—107; cf. A., 1927, 1124).—The absorption curves of azobenzene and its *p*-amino- and *p*-acetamido-derivatives show that the auxochromic effect of the amino-group is diminished by acetylation. The two absorption bands of *m*-acetamido-*o*-hydroxyazobenzene are due to the hydroxyl group alone. A. McGOOKIN.

[Free] acyl radicals. J. LORENZO (Anal. Fís. Quím., 1928, 26, 98—117).—An account of work already abstracted on the decomposition of acetyl-, phenylacetyl-, and diphenylacetyl-azotriphenylmethane (Wieland and others, A., 1927, 237). The m. p. 137—138° is recorded for acetyltriphenylmethane. R. K. CALLOW.

Manufacture of halogen-substituted tertiary aromatic amines. I. G. FARBENIND. A.-G.—See B., 1928, 441.

New quaternary ammonium compounds from halogen-substituted tertiary aromatic amines. I. G. FARBENIND. A.-G.—See B., 1928, 361.

Manufacture of 2 : 5 : 6-trichloro-*m*-toluidine-4-sulphonic acid. I. G. FARBENIND. A.-G.—See B., 1928, 440.

Azo-dyes soluble in non-aqueous solvents. C. E. MAY and H. HUNT.—See B., 1928, 398.

Action of nitric acid on phenol in dilute aqueous solution. I. Mechanism of nitration of phenol. II. A. V. KARTASCHOV (J. Russ. Phys. Chem. Soc., 1927, 59, 819—832, 833—845).—I. The action of dilute nitric acid on phenol was investigated under different conditions to discover the factors which determine respectively the oxidation and nitration effects. Nitric acid of $d < 1·060$ (9% HNO_3) does not give any dinitrophenols, so acids of d 1·045, 1·030, 1·020, 1·015, and 1·010 (*i.e.*, 8·13%, 5·5%, 3·7%, 2·8%, and 1·9% HNO_3) were used. Acid of d 1·010, even in large excess and on boiling, had no effect. With more concentrated acids, on boiling, violent oxidation took place, with formation of tar and separation of carbon. Increased acid concentration lowered the initial reaction temperature, with a consequent diminution of the oxidation and an increase in the nitration reactions. Excess of nitric acid has a much more marked effect on the lowering of the initial reaction temperature than its concentration. Easily oxidised impurities in the phenol, such as pyrocatechol, benzaldehyde, formaldehyde, and lævulose, have a similar effect, and, further, strongly catalyse the oxidation reaction at the expense of the nitration.

II. A mechanism for the action of dilute nitric acid on phenol is suggested and tested. The initial reaction is oxidation, reducing the nitric acid to nitrous acid, which forms nitrosophenol, which, in turn, is oxidised to nitrophenol. By testing various reaction mixtures of phenol and nitric acid with Liebermann's reagent, blue and green colorations are obtained, indicating various quantities of nitrosophenol. Addition of free nitrous acid or nitrosophenol catalyses the reaction. Nitrosophenol itself is easily oxidised by nitric acid in the cold to nitrophenol, which, itself, is incapable of oxidation, any further reaction being one of nitration.
M. ZVEGINTZOV.

Halogenated *o*-anisidines. M. KOHN and R. KRAMER (Monatsh., 1928, 49, 146—159).—Bromination of 4-chloro-*o*-anisidine (Reverdin and Eckhard, A., 1900, i, 28) with bromine in acetic acid solution yields 4-*chloro*-3 : 5-*dibromo*-*o*-*anisidine*, m. p. 113°, from which by removal of the amino-group by diazotisation and subsequent demethylation are obtained, successively, 4-chloro-3 : 5-dibromoanisole (Kohn and Dömötör, A., 1927, 51) and 4-chloro-

3 : 5-dibromophenol (*benzoate*, m. p. 132°). Hence no wandering of the *p*-chlorine atom into the *ortho*-position occurs as in the case of the corresponding bromo-compound (Kohn and Karlin, A., 1927, 1182). 4-Chloro-3 : 5-dibromo-2 : 6-dinitroanisole (obtained by nitration of 4-chloro-3 : 5-dibromoanisole with a mixture of sulphuric and fuming nitric acids) when heated with pyridine is converted into the *N*-methyl-pyridinium salt of 4-chloro-3 : 5-dibromo-2 : 6-di-nitrophenol. 4-Chloro-2 : 6-dinitroanisole is similarly demethylated to the corresponding phenol. Nitration of the *acetyl* derivative of 4-chloro-3 : 5-dibromo-*o*-anisidine yields the 6-*nitro*-compound, decomp. 215°, which by hydrolysis yields 4-*chloro*-3 : 5-*dibromo*-6-*nitro*-*o*-*anisidine*, m. p. 82°. Demethylation of 2 : 4-dichloro-6-nitroanisole (Hugounenq, A., 1890, 240) with hydrobromic acid yields 2 : 4-*dichloro*-6-*nitrophenol*, m. p. 124°, whilst by reduction with tin and hydrochloric acid is obtained the oily 2 : 4-*di-chloro*-*o*-*anisidine* (*acetyl* derivative, m. p. 72°). This acetyl derivative is nitrated by a mixture of con-centrated sulphuric acid and fuming nitric acid to 2 : 4-*dichloro*-3 : 5-*dinitro*-*o*-*acetanisidide*, m. p. 219°, which is hydrolysed to 2 : 4-*dichloro*-3 : 5-*dinitro*-*o*-*anisidine*, m. p. 135°. Bromination of 2 : 4-dichloro-*o*-anisidine with bromine in acetic acid yields a *sub-stance*, m. p. 169°, from which by heating with water 2 : 4-*dichloro*-3 : 5-*dibromo*-*o*-*anisidine*, m. p. 83°, is obtained. J. W. BAKER.

Bromophenols. XXXI. 3 : 4 : 5-Trichloro-phenol. M. KOHN and R. KRAMER (Monatsh., 1928, **49**, 161—168).—When chloro-*o*-anisidine is treated in acetic acid solution with 4 mols. of dry chlorine diluted with carbon dioxide, a reddish-black, tarry product is obtained. This contains 3 : 4 : 5-*trichloroanisidine*, for when it is treated with alcohol and sulphuric acid, followed by sodium nitrite, the mixture yields on steam distillation and fractionation of the ethereal extract of the distillate 3 : 4 : 5-*tri-chloroanisole*, m. p. 63°, b. p. 256—261°, identified by hydrolysis by hydrobromic and acetic acids to 3 : 4 : 5-trichlorophenol, m. p. 91°, b. p. 271—277°/ 746 mm. (benzoyl derivative, m. p. 120°; cf. Holle-man, A., 1921, i, 102). This when treated with bromine yields 3 : 4 : 5-*trichloro*-2 : 6-*dibromophenol*, m. p. 180°, *d* 2·554; the crystallographic constants, $a : b : c = 2·0625 : 1 : 3·6962$, $\beta = 96° 13' 20''$, closely resemble those of *m*-chlorotetrabromo- and 3 : 5-di-chlorotribromo-phenol [K. HLAWATSCH]. The tri-chlorodibromophenol is oxidised by nitric acid to 2 : 6-*dichloro*-3 : 5-*dibromobenzoquinone*, stable at 240°.

3 : 4 : 5-Trichloroanisole is nitrated by nitric and sulphuric acids to 3 : 4 : 5-*trichloro*-2 : 6-*dinitroanisole*, m. p. 95—96°. E. W. WIGNALL.

Bromophenols. XXXIII. Chloro- and bromo-pyrogallol ethers. M. KOHN and (FRL.) E. GURE-WITSCH (Monatsh., 1928, **49**, 173—186).—4-Bromo-pyrogallol trimethyl ether (cf. Kohn and Grün, A., 1926, 284) is now obtained by the action of phosphorus penta-bromide. 4 : 6-Dibromo-5-nitropyrogallol trimethyl ether, m. p. 114° (cf. Kohn and Grün, *loc. cit.*), is also obtained by the action of bromine on 5-nitro-pyrogallol trimethyl ether (Will, A., 1888, 457). By the action of phosphorus pentachloride, pyrogallol

trimethyl ether yields the 4-chloro-derivative, b. p. 252—256°/748·5 mm. (cf. Gräbe and Suter, A., 1905, i, 703); this is nitrated in acetic acid by fuming nitric acid to 4-*chloro*-5 : 6-*dinitropyrogallol trimethyl ether*, m. p. 116—118°. The last is also prepared, m. p. 118—119°, from the 4-*chloro*-5-*nitro*-derivative, m. p. 77—78°, obtained by passing chlorine into the molten 5-nitro-derivative, which is further chlorinated, in presence of iron, to 4 : 6-*dichloro*-5-*nitropyrogallol trimethyl ether*, m. p. 103—104°. The 4-chloro-deriv-ative is converted by bromine into 4-*chloro*-5 : 6-*di-bromopyrogallol trimethyl ether*, m. p. 57—58°.

Pyrogallol dimethyl ether is chlorinated by sul-phuryl chloride to 4-*chloropyrogallol* 1 : 3-*dimethyl ether*, b. p. 270—275°/754 mm., 175°/18 mm.; this is identified by methylation and by nitration of the resultant trimethyl ether. This shows that the *p*-directive effect of the free hydroxyl group (cf. Peratoner and Genco, A., 1895, i, 342) is counteracted by the stronger influence of the methoxyl groups. Chlorination in carbon tetrachloride solution by rather more than 3 mols. of chlorine, diluted with carbon dioxide, yields *trichloropyrogallol* 1 : 3-*di-methyl ether*, m. p. 121—122° (*benzoyl* derivative, m. p. 102°); 4 : 5-dibromopyrogallol 1 : 3-dimethyl ether (Kohn and Grün, *loc. cit.*) is similarly converted into 4-*chloro*-5 : 6-*dibromopyrogallol* 1 : 3-*dimethyl ether* (*benzoyl* derivative, m. p. 119—120°). If only 2 mols. of chlorine are employed, 4 : 5-*dichloropyro-gallol* 1 : 3-*dimethyl ether*, m. p. 103—104° (*benzoyl* derivative, m. p. 122—123°), can be obtained; the product is brominated to the 6-*bromo*-derivative, m. p. 117—118°.

Tribromopyrogallol dimethyl ether (Kohn and Grün) is oxidised by chromic acid to 2 : 6-dibromo-3 : 5-dimethoxybenzoquinone (cf. Will, *loc. cit.*); the trichloro-compound gives similarly the 2 : 6-dichloro-analogue (cf. Gräbe and Hess, A., 1905, i, 698). The yields are poor. E. W. WIGNALL.

Condensation of chloral with substituted phenols. F. D. CHATTAWAY and F. CALVET (J.C.S., 1928, 1088—1094).—A republication of work already abstracted (this vol., 632). The following is new : anhydro-5-amino-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (6-amino-2 : 4-bistrichloromethyl-1 : 3-benzdioxin) on bromination in acetic acid yielded the 4-*bromo*-compound (7-*bromo*-dioxin derivative), m. p. 171—173° (*acetyl* derivative, m. p. 231—232·5°). R. K. CALLOW.

Nitration of aromatic thiocyanates and seleno-cyanates. F. CHALLENGER and A. T. PETERS (J.C.S., 1928, 1364—1375).—Nitration of *o*-tolyl thiocyanate at 3—8° with nitric and sulphuric acids yields mainly 5-*nitro*-*o*-*tolyl thiocyanate*, m. p. 117·5—118·5°, together with 4-*nitro*-*o*-*tolyl thiocyanate*, m. p. 70—71°, both of which have been prepared by the action of cuprous and potassium thiocyanate on the requisite nitrotoluenediazonium sulphate. Nitration of *phenyl selenocyanate*, b. p. 134°/10 mm., with nitric acid (*d* 1·5) gives chiefly *p*-nitrophenyl selenocyanate, m. p. 141° (cf. Bauer, A., 1913, i, 263), together with a small amount of the *o*-nitro-derivative, m. p. 143°. When *p*-tolyl selenocyanate is treated with nitric and sulphuric acids, 2-*nitro*-*p*-*tolueneseleninic acid* (I),

m. p. 151°, and *di-2-nitro-*p-*tolyl diselenide* (II), m. p. 69°, are obtained, but nitric acid (*d* 1·5) at −10° gives 2-*nitro-* (III), m. p. 69—70°, and 3-*nitro-*p-*tolyl selenocyanate*, m. p. 150°. Reduction of (I) with zinc and hydrochloric acid furnishes (II), also obtained by the action of potassium hydroxide on (III). Similarly, *p*-chlorophenyl selenocyanate yields either a mixture of di-*p*-chlorophenyl diselenide and *p*-chlorobenzeneseleninic acid (IV), or a mixture of 4-*chloro-2-nitrophenyl selenocyanate*, m. p. 127°, and (IV). *p*-Bromophenyl selenocyanate gives *p*-bromobenzeneseleninic acid. p-*Dithiocyanobenzene*, m. p. 106°, prepared by the Sandmeyer reaction from *p*-aminophenyl thiocyanate, is nitrated to a *nitrodithiocyanobenzene*, m. p. 143—144°, which is obtained together with 4-*bromo-*, m. p. 83°, and 4-*chloro-3-nitrophenyl thiocyanate*, m. p. 63°, by the action of cuprous and potassium thiocyanates on diazotised 4-bromo- and chloro-3-nitroaniline. Treatment of p-*thiocyanoselenocyanobenzene*, m. p. 109—110°, with nitric and sulphuric acids affords p-*thiocyanobenzeneseleninic acid*, m. p. 154°. *p*-Thiocyanoacetanilide on nitration furnishes 2-*nitro-4-thiocyanoacetanilide*, m. p. 138—139°, together with 2-*nitro-4-thiocyanoaniline*, m. p. 113°. When treated with alcoholic alkali, this last substance gives di-3-nitro-4-aminophenyl disulphide (?), m. p. 169°. 2-*Nitro-4-thiocyanophenyl selenocyanate* has m. p. 147°.

Selenocyanates containing an *o*-nitro-group give strong purple colorations with alcoholic potassium hydroxide (cf. Bauer, *loc. cit.*). H. BURTON.

Varying valency of platinum with respect to mercaptanic radicals. VII. (SIR) P. C. RÂY, K. C. BOSE-RÂY, and S. RAY-CHAUDHURY (J. Indian Chem. Soc., 1928, 5, 139—147).—Benzyl sulphide and platinic chloride react in alcohol solution, forming the compound $PtCl_2,2(CH_2Ph)_2S$ (I), m. p. 159°, together with the *substance* $PtCl_3,2(CH_2Ph)_2S$ (II), m. p. 183° (decomp.). If an excess of platinic chloride is used, a *complex*, $Pt_2Cl_5,4(CH_2Ph)_2S$, m. p. 158°, is first obtained which is separable into (I) and (II) by crystallisation from alcohol. The action of several bases on (II) has been examined. Ammonia, benzylamine, and ethylenediamine give tetramine-platinous dichloride, tetrabenzylammineplatinous dichloride, and the compound $PtCl_2,2C_2H_4(NH_2)_2$, respectively (cf. this vol., 44). Aniline yields $PtCl_2,2NH_2Ph$, whilst dimethylaniline gives (I). Piperidine affords the *substances* $PtCl_3,2C_5H_{11}N,(CH_2Ph)_2S$, m. p. 172°, and $PtCl_2,3C_5H_{11}N$, whilst pyridine gives the compounds $PtCl_2,4C_5H_5N$ (III) and $Pt_2Cl_7,4C_5H_5N$ (*loc. cit.*). The action of pyridine on (I) is to form (III) together with the compound $PtCl_2,2C_5H_5N$ (IV). The effect of heat on (III) is to furnish (IV). It is concluded that (II) is best represented by the formula $[2(CH_2Ph)_2S,PtCl_2]Cl$. H. BURTON.

Detection of β-naphthol. K. REBER (Schweiz. Apoth.-Ztg., 1927, 65, 589; Chem. Zentr., 1928, i, 384).—1 C.c. of a mixture of 25% hydrochloric acid (1 part) and 25% nitric acid (3 parts) is heated at 55—60° with 5 c.c. of aqueous β-naphthol; a carmine-red coloration, extractable with amyl alcohol, soon appears. 1 Part in 6000 parts can be detected. The red coloration produced when aqueous β-naphthol (5 c.c.), 0·03% aqueous sodium nitrite (2 c.c.), and dilute sulphuric acid (1 drop) are warmed together is not extractable with amyl alcohol.

A. A. ELDRIDGE.

Action of chlorosulphonic acid on phenols. V. [Naphthols.] J. POLLAK, E. GEBAUER-FÜLNEGG, and E. BLUMENSTOCK-HALWARD (Monatsh., 1928, 49, 187—202).—[With E. PETERTIL.] Chlorosulphonic acid acts on α-naphthol at the ordinary temperature (cf. B.P. 186,515; B., 1922, 933), and from the reaction mixture crystalline α-naphthol-2-sulphonic acid separates. With excess of chlorosulphonic acid, crystals of α-*naphthol-2 : 4-disulphonyl chloride*, m. p. 149°, separate (*disulphonanilide*, m. p. 228°). By the prolonged action of chlorosulphonic acid, a new α-*naphthol-*[2 : 4 : 7(?)]-*trisulphonyl chloride*, m. p. 172°, [$+0.5C_6H_6$, 160°], is obtained (cf. Claus and Mielcke, A., 1886, 716); this on alkaline hydrolysis loses one and on acid hydrolysis two chlorosulphonyl groups, yielding probably α-naphthol-7-sulphonic acid. The corresponding α-*naphtholtrisulphonanilide* has m. p. 240° (decomp.).

α-Naphthol with chlorosulphonic acid yields at 100° α-naphthol-4-sulphonic acid; at 160°, a black product, or, with excess of the reagent, a resinous product from which a yellow *trichloronaphthalene-sulphonyl chloride*, m. p. 214°, is isolated.

[With K. WINTER.] The action of chlorosulphonic acid on β-naphthol at the ordinary temperature does not yield a monosulphonyl chloride, but only β-naphthol-1-sulphonic acid; on keeping, a mixture of disulphonyl chlorides (see below) is obtained. With 1 mol. of chlorosulphonic acid in tetrachloroethane at 130°, β-naphthol yields β-naphthol-6-sulphonic acid. Excess of chlorosulphonic acid yields a mixture of two β-*naphtholdisulphonyl chlorides*, m. p. 111° (I) and 177° (II), respectively (see following abstract). These are almost insoluble in water; on treatment with phosphorus pentachloride in a sealed tube only octachloronaphthalene is obtained. With aniline the corresponding *disulphonanilides*, m. p., from (I) 191°, from (II) 231°, are obtained.

When β-naphthol is heated with excess of chlorosulphonic acid at 130—140°, a product is obtained from a carbon disulphide solution of which β-*naphthol-3 : 6 : 8-trisulphonyl chloride*, m. p. 196°, crystallises. The formulation is based on the preparation of the substance by the action of chlorosulphonic acid on β-naphthol-3 : 6-disulphonic acid, or -3 : 6 : 8-trisulphonic acid; the above-mentioned disulphonyl chlorides also yield the trisulphonyl chloride. The last gives the -3 : 6 : 8-*trisulphonanilide*, m. p. 140—145°, which can also be prepared, m. p. 152—155°, from O-*carbethoxy-*β-*naphthol-*3 : 6 : 8-*trisulphonyl chloride*.

β-Naphthol with great excess of chlorosulphonic acid at 150—160° yields a resinous product from which a substance, m. p. 120—122°, containing chlorine but not sulphur (? a dichloronaphthalene), and a product, m. p. 135—140°, containing sulphur, probably a naphthaquinone derivative, were isolated.

E. W. WIGNALL.

Constitution of the β-naphtholdisulphonyl chlorides. J. POLLAK and E. BLUMENSTOCK-

HALWARD [with A. SCHLESINGER, V. WEINMAYR, and K. WINTER] (Monatsh., 1928, 49, 202—212).— The two β-naphtholdisulphonyl chlorides, m. p. 111° (I) and 177° (II) (see preceding abstract) are investigated. The former is obtained by the action of chlorosulphonic acid on β-naphthol-6-sulphonic acid, and also from the 1-acid in the cold; it is therefore β-*naphthol*-1 : 6-*disulphonyl chloride*. It was thought that (II) might be obtainable from β-naphthol-8-sulphonic acid; the latter, however, yields the 6 : 8-*disulphonyl chloride* (III), m. p. 161—162°, from which the 6 : 8-*disulphonanilide*, m. p. 195°, is obtained. The constitution of the latter is established by preparing, from β-naphthol-6 : 8-disulphonic acid, the *potassium* salt of the *O*-carbethoxy-derivative, and thence, by the action of phosphorus pentachloride, *O - carbethoxy - β - naphthol*-6 : 8-*disulphonyl chloride*, m. p. 131°; this yielded the corresponding 6 : 8-*disulphonanilide*, m. p. 178°, and, by hydrolysis, the same disulphonanilide (m. p. 196°) as obtained from (III).

Similarly, from β-naphthol-3 : 6-disulphonic acid, the *O*-*carbethoxy-β-naphthol*-3 : 6-*disulphonyl chloride*, m. p. 125°, and the corresponding *disulphonanilide*, m. p., crude, 153—163°, have been prepared, and, from the latter, β-*naphthol*-3 : 6-*disulphonanilide*, m. p. 202°. This is not identical with the anilide prepared from (II), as might be expected from the conversion of (II) into β-naphthol-3 : 6 : 8-trisulphonyl chloride : it is, however, noteworthy that the latter is also obtained from (I), a process involving migration of the chlorosulphonyl group from the 1-position. It is therefore suggested that (II) may be β-*naphthol*-1 : 8-*disulphonyl chloride*. This formula is excluded by the rule of Armstrong and Wynne (Proc. C.S., 1890, 130), to which there are, however, exceptions (cf. Dressel and Kothe, A., 1894, i, 378).

The "β-naphthol-1-sulphonyl chloride" described by Anschütz and Maxim (A., 1918, i, 426), prepared by way of the acetyl derivative, does not form a sulphonylide. It was therefore thought that the substance described might actually have the chlorosulphonyl group in a different position. Accordingly, the *acetyl* derivatives of β-naphthol-6- and -8-sulphonic acids were prepared and converted by phosphorus pentachloride in chloroform into *O*-*acetyl-β-naphthol*-6- and -8-*sulphonyl chlorides*, m. p. 103° and 129°, respectively. Since these differ in m. p. from the compound described by Anschütz, and since in their case it is impossible to hydrolyse the acetyl group without affecting the chlorosulphonyl group, there is no reason to question the Anschütz formula. It is suggested, however, that the conditions for the formation of a sulphonylide cause a migration of the chlorosulphonyl group before condensation can occur.

O-*Acetyl-β-naphthol*-6-*sulphonanilide*, m. p. 95°, is hydrolysed to β-naphthol-6-sulphonanilide, m. p. 161° (cf. G.P. 278,091). Since the m. p. did not agree with that given by Zincke and Dereser (A., 1918, i, 220), viz., 100—105°, the substance was prepared by their method; it was found to contain 2 mols. of water, and after heating, or recrystallisation from benzene, to melt at 160—161°; but since recrystallisation of the anhydrous substance from an aqueous

solvent failed to yield the low-melting variety, the latter must be regarded as a labile form.

O-*Acetyl-β-naphthol*-8-*sulphonanilide* yields β-*naphthol*-8-*sulphonanilide*, m. p. 195°, also obtained by the hydrolysis of the *anilide* derived from *O*-*carbethoxy-β-naphthol*-8-*sulphonyl chloride*, m. p. 118°.

E. W. WIGNALL.

Dehydrogenation of sitosterol. L. SCHMID and M. ZENTNER (Monatsh., 1928, 49, 92—97).—A *hydrocarbon*, m. p. 245—247·5°, has been isolated from the mother-liquor of the product, m. p. 325°, obtained by the dehydrogenation of sitosterol with palladised charcoal (A., 1927, 661). A mixed-m. p. determination with the hydrocarbon chrysene, m. p. 246—248°, obtained in a similar manner from cholesterol (Diels and Gadke, *ibid.*, 241) gives no conclusive evidence, but on complete nitration it yields a *tetranitro*-derivative, decomp. 200°, which, although it contains the correct percentage of nitrogen, is not identical with tetranitrochrysene, m. p. above 300°. Crystallographic investigation (by MARCHET) of the hydrocarbon and of chrysene confirms the non-identity of the two substances.   J. W. BAKER.
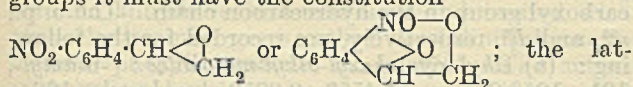
Plant sterols. L. SCHMID and G. BILOWITSKI (Monatsh., 1928, 49, 98—106).—Phytosterols isolated from various sources have been separated into stigmasterol and sitosterol by the action of bromine on their acetates. Thus the phytosterol, m. p. 132°, isolated from *Radix bardanæ* is acetylated with acetic anhydride, and addition of bromine in ether and acetic acid solution to the acetyl derivative precipitates the sparingly soluble tetrabromostigmasterol acetate identical with the corresponding derivative prepared from stigmasterol isolated from the calabar bean. The filtrate, after reduction with sodium amalgam, debromination by heating with zinc dust, and repetition of the process to remove all the stigmasterol, yields the sitosteryl acetate (*benzoate*, m. p. 144°) identical with a genuine specimen and yielding identical derivatives. By similar methods the sterols isolated from *Ficus carica* and *Ulmis campestris* are separated into stigmasterol and sitosterol. From the latter plant was also isolated a *substance*, m. p. 240°, which was not investigated.   J. W. BAKER.

Transformation of benzoylmethylcarbinol into acetylphenylcarbinol by sulphuric acid and under the conditions of alcoholic fermentation. (MLLE.) E. M. KOTCHERGINE (Bull. Soc. chim., 1928, [iv], 43, 573—575).—Benzoylmethylcarbinol (obtained in 81% yield by the action of alcoholic potassium acetate on *phenyl α-bromoethyl ketone*, b. p. 134—135°/18 mm., d_0^0 1·454) when heated with alcoholic sulphuric acid at 120—125° for 8 hrs. is converted into acetylphenylcarbinol; the same transformation takes place when the ketone is added to an aqueous solution of raffinose fermenting with brewer's yeast, some *s*-phenylmethylethylene glycol being also produced in the latter case. Accordingly the acetylphenylcarbinol obtained by Neuberg (A., 1921, i, 480) is regarded as a transformation product of the primarily formed benzoylmethylcarbinol.   R. BRIGHTMAN.

Syntheses with diazomethane. III. *o*-**Nitrophenylethylene oxide and the compounds derived**

therefrom. F. Arndt, B. Eistert, and W. Partale (Ber., 1928, 61, [B], 1107—1118).—The nitroso-compound obtained by the action of formic acid on "nitraldin" (A., 1927, 360) yields small amounts of N-hydroxyisatin, m. p. 201° (decomp.), under the influence of alkali hydroxide. It is identified as o-nitrosobenzoylcarbinol, since it is smoothly reduced by hydrazine carbonate to o-aminobenzoylcarbinol, m. p. 98° (N-acetyl derivative, m. p. 141°; diacetyl compound; dibenzoyl derivative, m. p. 167—168°; phenylhydrazone, m. p. 198°), which can be diazotised and is readily transformed by warm alkali hydroxide into indoxyl. Since nitraldin itself does not give reactions characteristic of the hydroxyl or carbonyl groups it must have the constitution

$$NO_2 \cdot C_6H_4 \cdot CH {<}^{O}_{CH_2} \quad \text{or} \quad C_6H_4 {<}^{NO-O}_{CH-CH_2}{>}O \,| \; ; \quad \text{the lat-}$$

ter structure involves an apparent, constitutive co-operation of the nitro-group which, however, is illusory, since other aldehydes are converted by diazomethane into ethylene oxides instead of the expected methyl ketones. "Nitraldin" is therefore regarded as o-nitrophenylethylene oxide. It is unaffected by phenylcarbimide at 130—140°, whilst profound decomposition ensues at higher temperatures. Reduction with tin and glacial acetic acid gives anthranil in small amount. Traces of indole are obtained by the action of hydrazine hydrate in boiling alcoholic solution. The action of hydrogen chloride on o-nitrophenylethylene oxide in pyridine affords o-nitrophenyl-ethylene chlorohydrin, $NO_2 \cdot C_6H_4 \cdot CH(OH) \cdot CH_2Cl$, m. p. 60—61°, b. p. 170°/17 mm. (decomp.), re-converted by sodium hydroxide into the parent substance and transformed by benzoyl chloride and alkali hydroxide into the benzoyl derivative, m. p. 87—88°. The corresponding acetyl compound, b. p. 186—188°/15 mm., m. p. 69—70°, is obtained by addition of o-nitrophenylethylene oxide to a solution of acetyl chloride in pyridine. ω-Chloro-o-nitroacetophenone, m. p. 66—67°, is obtained by oxidising o-nitrophenylethylene chlorohydrin with potassium dichromate and sulphuric acid. o-Aminophenylethylene chlorohydrin, m. p. 86—87°, prepared by reduction of the nitrocompound by stannous chloride and concentrated hydrochloric acid, appears to be converted by successive treatment with cold dilute acid and sodium hydroxide into a polymeric o-aminophenylethylene oxide, whereas if the treatment is followed by steam distillation it gives indole and, probably, polymerised indoles. o-Nitrophenylethylene oxide is converted by acetic anhydride containing anhydrous ferric chloride into o-nitroso-ω-acetoxyacetophenone, m. p. 104°.

o-Nitrophenylacetone, m. p. 26—27° [semicarbazone, m. p. 213—214° (decomp.)], and o-nitroacetophenone are identified among the by-products of the action of diazomethane on o-nitrobenzaldehyde. The former compound is prepared by the action of diazomethane on o-nitrophenylacetaldehyde in ether or by that of boiling dilute sulphuric acid on ethyl α-o-nitrophenyl-acetoacetate, m. p. 76—77°. o-Nitrophenylacetyl-acetone, m. p. 62—63°, is converted by hydrazine hydrate into 5-o-nitrophenyl-3-methylpyrazole, m. p. 120—121°. H. Wren.

Glycol from α-methyl-n-butaldehyde and benzaldehyde. A. Franke and R. Stern (Monatsh., 1928, 49, 21—26).—α-Methyl-n-butaldehyde condenses with benzaldehyde (2 mols.) in the presence of alcoholic potassium hydroxide, and the resulting aldol is reduced by the excess of benzaldehyde to yield γ-phenyl-β-methyl-β-ethylpropane-αγ-diol, b. p. 188—190°/17 mm. (diacetate, b. p. 189—191°/20 mm.). In two cases the cyclic benzylidene ether, $\begin{smallmatrix} CHPh \cdot CMeEt \cdot CH_2 \\ O\text{——}CHPh\text{——}O \end{smallmatrix}$, b. p. 214—215°/13 mm., m. p. 80—81°, was also obtained. The same compound is synthesised by the action of benzaldehyde on the glycol in the presence of concentrated hydrochloric acid. By oxidation the glycol is converted into phenyl sec.-butyl ketone, and when it is distilled in steam with 14% sulphuric acid it yields ωω-methylethylstyrene, b. p. 205—206° (dibromide, m. p. 57°), together with the methylene ether, b. p. 150°/13 mm., which is formed in accordance with the scheme: $CHPh(OH) \cdot CMeEt \cdot CH_2 \cdot OH$ (I) $\longrightarrow$ $CHPh(OH) \cdot CHMeEt + CH_2O$; (I) $+ CH_2O \longrightarrow$ $\begin{smallmatrix} CHPh \cdot CMeEt \cdot CH_2 + H_2O \\ O\text{——}CH_2\text{——}O \end{smallm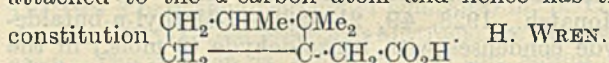atrix}$ (cf. Reik, A., 1898, i, 245). The same ether is synthesised by the action of a 40% formaldehyde solution on the glycol in the presence of an equal quantity of hydrochloric acid, d 1·19. J. W. Baker.

Reaction between magnesium compounds and ethylene oxides. I. I. Ribas (Anal. Fís. Quím., 1928, 26, 122—132).—α-Methoxypropylene βγ-oxide, b. p. 110°/751 mm., is prepared by treatment of α-chloro-γ-methoxyisopropyl alcohol (Fourneau and Ribas, A., 1927, 131) with sodium hydroxide solution. With magnesium phenyl bromide the oxide yielded α-bromo-γ-methoxyisopropyl alcohol, b. p. 90°/15 mm., and 25% of the theoretical yield of γ-methoxy-α-phenylisopropyl alcohol, b. p. 135—140°/15 mm. (phenylurethane, m. p. 56°; allophanate, m. p. 150—151°). The same compound was obtained by the action of magnesium phenyl bromide (2 mols.) on α-chloro-γ-methoxyisopropyl alcohol, and the constitution assigned to it was proved by its formation by the condensation of α-phenylpropylene βγ-oxide with methyl alcohol in the presence of sulphuric acid (cf. Fourneau and Ribas, loc. cit.).

R. K. Callow.

Constitution of isocampholic acid. J. von Braun and A. Heymons (Ber., 1928, 61, [B], 1089—1092).—isoCampholic acid is isolated with some difficulty from the campholic acid obtained with it by fusion of camphor with potassium hydroxide as the ethylamide, m. p. 41—42°. Campholethylamide, b. p. 160°/20 mm., m. p. 88°, is converted by an excess of phosphorus pentachloride into the corresponding imido-chloride, from which the original material is smoothly regenerated. isoCampholethylamide under similar conditions yields dichloroisocampholethylamide. $C_{12}H_{21}ONCl_2$, m. p. 73—77°, b. p. 125—127°/0·2 mm. (intermediate imidochloride, $C_{12}H_{20}NCl_3$, b. p. 145—150°/15 mm.). Hydrolysis of the ethylamide affords the unsaturated monochloro-acid, $C_{10}H_{15}O_2Cl$, b. p. 125°/0·5 mm. isoCampholic acid behaves therefore

as a compound containing two hydrogen atoms attached to the α-carbon atom and hence has the constitution

$$\begin{array}{c} CH_2 \cdot CHMe \cdot CMe_2 \\ | \qquad\qquad | \\ CH_2 \text{————} C \cdot CH_2 \cdot CO_2H \end{array}$$ H. WREN.

_cyclo_Pentylalkylacetic acids and β-_cyclo_pentylethylalkylacetic acids, and their action towards _B. lepræ_. XI. G. R. YOHE and R. ADAMS (J. Amer. Chem. Soc., 1928, **50**, 1503—1508; cf. following abstract).—As in the series previously examined, the toxicity of these acids towards _B. lepræ_ reaches a maximum with the members containing 16—18 carbon atoms. It is shown that with _cyclo_alkyl-alkylacetic acids of equal mol. wt. or having equally long side-chains, there is no marked difference in bactericidal power between _cyclo_hexyl, _cyclo_pentyl, and _cyclo_pentenyl derivatives. The following were successively prepared from _cyclo_pentyl bromide by standard methods : β-_cyclo_pentylethyl alcohol, b. p. 96·5—97°/24 mm., n_D^{20} 1·4577, d_4^{20} 0·9180, after purification through β-_cyclo_pentylethyl bromide, b. p. 75—77°/19 mm., n_D^{20} 1·4863, d_4^{20} 1·2860, and acetate; δ-_cyclo_pentylbutyl alcohol, b. p. 88—92°/2 mm., n_D^{20} 1·4613, d_4^{20} 0·9033; δ-_cyclo_pentylbutyl bromide, b. p. 110—111°/17 mm., n_D^{20} 1·4820, d_4^{20} 1·1872, from which δ-_cyclo_pentylvaleronitrile, b. p. 124—126·5°/17 mm., n_D^{20} 1·4542, d_4^{20} 0·8887, and δ-_cyclo_pentylvaleric acid, b. p. 124—128°/2 mm., n_D^{20} 1·4594, d_4^{20} 0·9752, are obtained; ethyl δ-_cyclo_pentylbutylmalonate, b. p. 154—160°/2·2 mm., n_D^{20} 1·4493, d_4^{20} 0·9934; δ-_cyclo_pentylbutylmalonic acid, m. p. 121—124°; and ε-_cyclo_pentylhexoic acid, b. p. 133—138°/1·8 mm., m. p. 33—33·5°, n_D^{25} 1·4549, d_4^{25} 0·9518. The following ethyl _cyclo_pentyl-alkyl-malonates (b. p., n_D^{20}, and d_4^{20} being given in this order) were obtained in 50—60% of the theoretical yields from ethyl _cyclo_pentylmalonate : -n-_heptyl_-, 143—146°/1 mm., 1·4548, 0·9749; -n-_octyl_-, 160—165°/1 mm., 1·4553, 0·9659; -n-_nonyl_-, 152—155°/0·6 mm., 1·4567, 0·9617; -n-_decyl_-, 169—171°/1 mm., 1·4571, 0·9560; -n-_undecyl_-, 186—189°/1 mm., 1·4580, 0·9522; the following ethyl β-_cyclo_pentylethyl-alkyl-malonates from ethyl β-_cyclo_pentylethylmalonate, b. p. 125°/2 mm., n_D^{20} 1·4478, d_4^{20} 1·0082 : -ethyl-, 126—129°/1·9 mm., 1·4511, 0·9924; -n-_propyl_-, 134—135°/1·7 mm., 1·4510, 0·9873; -n-_butyl_-, 136—140°/1·8 mm., 1·4523, 0·9783; -n-_amyl_-, 148—150°/1·1 mm., 1·4526, 0·9688; n-_hexyl_- 157—162°/1 mm., 1·4531, 0·9624; -n-_heptyl_-, 172—174°/2 mm., 1·4541, 0·9563, and -n-_octyl_-, 182—184°/1·2 mm., 1·4548, 0·9524. From these are prepared the following alkyl derivatives of β-_cyclo_pentylethyl-malonic acid, m. p. 126·5° : ethyl, m. p. 141—143°; n-_propyl_, m. p. 137—138°; n-_butyl_, m. p. 139—140·5°; n-_amyl_, m. p. 124—127°, and n-_hexyl_, m. p. 129·5—130°; the following _cyclo_pentyl-alkyl-acetic acids : -n-_heptyl_-, 155—160°/1·4 mm., 1·4594, 0·9312; -n-_octyl_-, 166—169°/2 mm., 1·4609, 0·9279; -n-_nonyl_-, b. p. 177—178·5°/1·4 mm., m. p. 37—37·5°; -n-_decyl_-, b. p. 189—190·5°/1·7 mm., m. p. 34·5—36°; -n-_undecyl_-, b. p. 193—197°/1·3 mm., m. p. 43·5—45·5°; and the following alkyl derivatives of β-_cyclo_pentyl-ethylacetic acid, b. p. 115—118°/2·4 mm., n_D^{20} 1·4575, d_4^{20} 0·9849 : ethyl, 122—124·5°/1·3 mm., 1·4590, 0·9602; n-_propyl_, 130—132°/1·9 mm., 1·4595, 0·9533; n-_butyl_, 136—137°/1 mm., 1·4608, 0·9435; n-_amyl_, 150—154°/1·9 mm., 1·4610, 0·9360; n-_hexyl_, 157—161°/1·9 mm.,

1·4616, 0·9303; n-_heptyl_, 167—169°/2 mm., 1·4621, 0·9252, and n-_octyl_, 173—176°/1·5 mm., 1·4629, 0·9210. H. E. F. NOTTON.

_cyclo_Hexyl- and _cyclo_hexylmethyl-alkylacetic acids and their action towards _B. lepræ_. X. R. ADAMS, W. M. STANLEY, and H. A. STEARNS (J. Amer. Chem. Soc., 1928, **50**, 1475—1481).—These have been prepared by methods previously described. As in other series, the acids containing 16—18 carbon atoms show a maximum toxicity towards _B. lepræ_. Comparison with the isomeric _cyclo_hexylalkyl-alkyl-acetic acids previously obtained (A., 1926, 1136, 1137; this vol., 62) indicates that the bactericidal power is almost independent of the position of the carboxyl group in the hydrocarbon chain. The b. p., n_D^{25}, and d_4^{25}, respectively, are recorded for the following : (a) ethyl _cyclo_hexyl-alkyl-malonates : -n-_amyl_-, 121—125°/2 mm., 1·4553, 0·9850; -n-_hexyl_-, 126—130°/2 mm., 1·4559, 0·9755; -n-_heptyl_-, 135—139°/2 mm., 1·4562, 0·9685; -n-_octyl_-, 144—148°/2 mm., 1·4564, 0·9638; -n-_nonyl_-, 149—154°/2 mm., 1·4567, 0·9574; -n-_decyl_-, 157—161°/2 mm., 1·4570, 0·9540; -n-_undecyl_-, 170—175°/2 mm., 1·4574, 0·9532, and -n-_dodecyl_-, 185—189°/2 mm., 1·4589, 0·9466; (b) _cyclo_hexyl-alkyl-acetic acids : -n-_amyl_-, 136—139°/3 mm., 1·4640, 0·9544; -n-_hexyl_-, 145—149°/3 mm., 1·4641, 0·9449; -n-_heptyl_-, 148—152°/2 mm., 1·4641, 0·9350; -n-_octyl_-, 158—161°/2 mm., 1·4642, 0·9298; -n-_nonyl_-, 167—171°/3 mm., 1·4645, 0·9245; -n-_decyl_-, 165—169°/2 mm., 1·4649, 0·9224; -n-_undecyl_-, 173—177°/2 mm., 1·4650, 0·9166; -n-_dodecyl_-, 187—191°/2 mm., 1·4653, 0·9129; (c) _cyclo_hexylmethyl-alkyl-acetic acids : -ethyl-, 131—132°/2 mm., 1·4623, 0·9814; -n-_propyl_- 141—143°/4·5 mm., 1·4628, 0·9720; -n-_butyl_-, 133—136°/3 mm., 1·4620, 0·9564; -n-_amyl_-, 139—142°/2 mm., 1·4630, 0·9516; -n-_hexyl_-, 174—175°/3 mm., 1·4627, 0·9448; -n-_heptyl_-, 202—204°/3 mm., 1·4632, 0·9393, and -n-_octyl_-, 186—190°/4 mm., 1·4640, 0·9331. The b. p., n_D^{20}, and d_4^{20} of the following ethyl _cyclo_hexylmethyl-alkyl-malonates are : -ethyl-, 143—145°/4·5 mm., 1·4542, 1·0104; -n-_propyl_-, 154—155°/3 mm., 1·4529, 1·0062; -n-_butyl_-, 157—159°/4·5 mm., 1·4548, 0·9910; -n-_amyl_-, 159—160°/4 mm., 1·4558, 0·9853; -n-_hexyl_-, 160—163°/2·5 mm., 1·4544, 0·9721; -n-_heptyl_-, 183—185°/5 mm., 1·4560, 0·9679; -n-_octyl_-, 178—181°/3 mm., 1·4570, 0·9612. The m. p. of the following _cyclo_hexylmethyl-alkyl-malonic acids are : -ethyl-, 127·5—130°; -n-_propyl_-, 145—147°; -n-_butyl_-, 132—134°, and -n-_amyl_-, 132—135°.

H. E. F. NOTTON.

β-Oxidation. I. Conjugation of benzoic and phenylacetic acids formed as end-products from the oxidation of phenyl-substituted fatty acids. A. J. QUICK (J. Biol. Chem., 1928, **77**, 581—593).—Previous workers on the subject of β-oxidation have confined themselves to determining hippuric and phenaceturic acids in the urine as indications of the benzoic and phenylacetic acids excreted. Quantitative results cannot be so obtained, since, in the dog, about 70% of the benzoic and 30% of the phenylacetic acid excreted is in conjugation with glycuronic acid. By determining the sum of the hippuric and benzoylglycuronic acids, or of the phenaceturic and phenylacetylglycuronic acids excreted, it is shown

that cinnamic and phenylpropionic acids give rise exclusively to benzoic acid, whilst phenyl*iso*crotonic and phenylbutyric acids give exclusively phenylacetic acid, so that, in these cases at least, oxidation must occur entirely in the β-position.
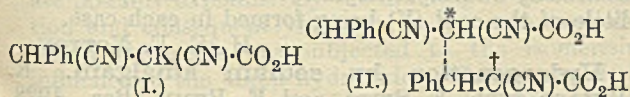
C. R. HARINGTON.

Oxidation of nitrophenylcyanoacetates. II. A. FAIRBOURNE and H. R. FAWSON (J.C.S., 1928, 1077—1080).—The compounds described previously (A., 1927, 244) as ethyl chloro- and bromo-2 : 4-dinitrophenylcyanoacetates are now shown to be *ethyl 2 : 4-dinitrophenylchlorocyanoacetate* (I), and *ethyl 2 : 4-dinitrophenylbromocyanoacetate* (II) since the action of warm 0·5N-sodium hydroxide solution is to yield a product which, when subsequently oxidised with chromic anhydride in acetic acid and treated with phenylhydrazine, gives ethyl 2 : 4-dinitrobenzoylformate phenylhydrazone, m. p. 170°. The action of chromic anhydride in acetic acid or of concentrated sulphuric acid at 80° on (I) and (II) is to form *ethyl 2 : 4-dinitrophenylchloro-*, m. p. 121°, and *ethyl 2 : 4-dinitrophenylbromo-malonamates*, m. p. 157°, and not intermediate hydroxycyanoacetates (cf. *loc. cit.*), whilst concentrated sulphuric acid at 120—130° furnishes 2 : 4-*dinitrophenylchloro-*, m. p. 134°, and 2 : 4-*dinitrophenylbromo-acetamides*, m. p. 160°, respectively. When the silver derivative of ethyl 2 : 4-dinitrophenylcyanoacetate is boiled either alone, or with iodine or (I) in presence of alcohol, there is produced in each case *ethyl αβ-bis-2 : 4-dinitrophenyl-αβ-dicyanosuccinate*, m. p. 156°. *Ethyl 2 : 4 : 6-trinitrophenylchlorocyanoacetate*, m. p. 118°, is formed by the action of chlorine on the corresponding cyanoacetate in sodium hydroxide solution.

Oxidation of ethyl *p*-nitrophenylcyanoacetate with hydrogen peroxide or 20% nitric acid affords ethyl αβ-di-*p*-nitrophenyl-αβ-dicyanosuccinate (cf. *loc. cit.*), whilst concentrated nitric acid oxidises ethyl 2 : 4-dinitrophenylcyanoacetate to ethyl 2 : 4-dinitrobenzoylformate.

H. BURTON.

Condensation of α-cyanocinnamic acid and potassium cyanide. M. HENZE (J. pr. Chem., 1928, [ii], 119, 157—172).—To elucidate the course of the reaction between chloroacetic acid, potassium cyanide, and benzaldehyde (Henze, A., 1926, i, 961; cf. Lapworth, J.C.S., 1922, 121, 1699), the interaction of α-cyanocinnamic acid, which is regarded as an intermediate product in the above reaction, and potassium cyanide in the presence of 1 mol. of sodium hydroxide has been studied. It is assumed that (I) is first formed and this adds on α-cyanocinnamic acid

$$\text{CHPh(CN)·}\overset{*}{\text{CH}}\text{(CN)·CO}_2\text{H}$$

CHPh(CN)·CK(CN)·CO$_2$H

(I.)　　　　(II.) PhCH:C(CN)·CO$_2$H

(Michael reaction) with the production of (II); carbon dioxide is then eliminated from either the carbon atoms marked * or † with the formation of the compound C$_{20}$H$_{17}$O$_2$N$_3$ (previously assumed to be C$_{20}$H$_{15}$O$_2$N$_3$) existing in two forms and now shown to be αγδ-*tricyano*-βδ-*diphenylvaleric acid*. Elimination of carbon dioxide from each of these acids by heating at 170° or preferably with zinc acetate and acetic acid led to a mixture of the two αγδ-*tricyano*-

βδ-*diphenyl*-n-*butanes*, m. p. 228° and 183°, respectively. Hydrolysis of the mixture of nitriles with aqueous baryta gave γ-*carboxy*-βδ-*diphenyladipic acid*, m. p. 220° (decomp.) (*methyl* ester, m. p. 61°), and a small quantity of an *isomeride*, m. p. 195—196° (decomp.). Heating the acid m. p. 220° at 220—230° led to 3-*keto*-2 : 5-*diphenylcyclopentane*-1-*carboxylic acid*, m. p. 158° (*oxime*, m. p. 183°; *methyl* ester, m. p. 99°), which gave 2 : 5-*diphenylcyclopentane*-1-*carboxylic acid*, m. p. 119—120°, on reduction with amalgamated zinc and hydrochloric acid. The constitution of the latter was established by oxidation with alkaline permanganate, when γ-benzoyl-β-phenylbutyric acid, m. p. 152°, was obtained. A compound, C$_{19}$H$_{15}$N$_3$, the exact constitution of which was not elucidated, was separated from the initial condensation product between α-cyanocinnamic acid and potassium cyanide.

I. VOGEL.

Asymmetric hydrolysis of esters by enzymes. I. R. WILLSTÄTTER, R. KUHN, and E. BAMANN (Ber., 1928, 61, [B], 886—895; cf. Rona and Ammon, A., 1927, 377).—Partial hydrolysis of ethyl *r*-mandelate by liver esterase leads to a mixture of (+)-mandelic acid and ethyl (−)-mandelate. The immediate hypothesis that the (+)-ester is more rapidly hydrolysed than the (−)-ester by the asymmetric enzyme is directly contradicted by experiments with the individual esters. The ratio of the rates with which the (+)- and (−)-ester in the racemic mixture are hydrolysed is considered to depend on (1) the ratio of the affinities of the esterase to the (+)- and (−)-esters and (2) the relative rates of decomposition of the compounds of the enzyme with the respective esters. Separate measurements of these factors show that, whereas the (−)-ester by itself is more rapidly hydrolysed than the (+)-ester, the latter substance is favoured during hydrolysis of the mixed esters, since its affinity towards esterase is 32 times that of its antipode, whereas the ratio of rates of hydrolysis is only 1·6 : 1 in favour of the compound of esterase and (−)-ester. Within the limits of the experiments (p_H 6·0—8·0) the optical activation of ethyl *r*-mandelate is independent of the hydrogen-ion concentration and of the quantity of enzyme used (1 : 3); the optical activity of the mandelic acid depends only on the extent to which hydrolysis has proceeded. From the linear relationship of the reaction it is to be expected that $[\alpha]_D$ for mandelic acid would remain constant for a considerable period in the early stages of the change and sink only when the greater part of the (+)-ester has been hydrolysed. An immediate rise in the $[\alpha]_D$ graph is not immediately explicable. The highest recorded value is $[\alpha]_D$ +70°, corresponding with the hydrolysis of 2·6 mols. of (+)-ester per mol. of (−)-ester in the initial stages.

H. WREN.

Condensation of formaldehyde with arylides of 2 : 3-hydroxynaphthoic acid. K. BRASS and P. SOMMER (Ber., 1928, 61, [B], 993—1002).—Stabilisation of "Naphthol AS" baths by formaldehyde is shown to be due to the production of methylenedinaphthols. 2-Hydroxynaphthalene-3-carboxylic acid is converted by formaldehyde in alkaline solution into *methylenebis-2-hydroxynaphthalene-3-carboxylic*

acid, decomp. above 280° (*diacetyl* derivative, unchanged below 295—300°). The constitution of the acid is established by reductive fission to 2-*hydroxy*-1-*methylnaphthalene*-3-*carboxylic acid*, m. p. 231° [*acetyl* derivative, m. p. 184—184·5° (cf. Fries and Hübner, A., 1906, i, 190)]. Methylenebis-2-hydroxynaphthalene-3-carboxylic acid is also produced when condensation is effected in glacial acetic acid, but the product is not completely identical with that formed in an alkaline medium. 2-Hydroxynaphthalene-3-carboxyanilide, formaldehyde, and sodium hydroxide afford *methylenebis-2-hydroxynaphthalene-3-carboxyanilide*, m. p. 263·5°; the anilide is obtained in small yield when condensation occurs in glacial acetic acid in the presence of concentrated sulphuric acid, but is then accompanied by a preponderating amount of a *product*, $C_{35}H_{26}O_4N_2$, m. p. about 284° after softening and darkening at 240°, which is insoluble in alkali hydroxide and cannot be acetylated. The *mono*- and *di-sodium* derivatives of the anilide are described. Coupling with benzenediazonium chloride is accompanied by loss of the methylene group and formation of benzeneazo-2-hydroxynaphthalene-3-carboxyanilide identical with that derived from "Naphthol AS." *Methylenebis-2-acetoxynaphthalene-3-carboxyanilide*, m. p. 252°, and 2-*acetoxynaphthalene*-3-*carboxyanilide*, m. p. 160°, are described. Condensation of the necessary naphthalide with formaldehyde in alkaline solution affords *methylenebis-2-hydroxynaphthalenecarboxy-α-naphthalide*, m. p. 268—269°, and the corresponding -β-*naphthalide*, m. p. 287—288°.

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Lichen substances. V. Synthesis of orsellinic acid. A. SONN (Ber., 1928, **61**, [*B*], 926—927).—Ethyl methylhydroresorcylate, prepared by the condensation of ethyl crotonate with ethyl acetoacetate in the presence of sodium ethoxide, is converted by bromine in glacial acetic acid into *ethyl dibromo-orsellinate*, m. p. 143—144°, which is transformed by hydrogen in the presence of palladium and calcium carbonate into ethyl orsellinate, m. p. 132°; hydrolysis of the ester by cold sodium hydroxide affords orsellinic acid identical with the natural product.　　　　　　　　　　　　　H. WREN.

Gallodeoxycholic acid. S. YONEMURA (J. Biochem. Japan, 1927, **8**, 79—84).—Gallodeoxycholic acid (from chicken bile) is identical with chenodeoxycholic acid (goose) and anthropodeoxycholic acid (man). The acid has $[\alpha]_D^{18}$ −33·04° in alcohol; oxidation yields gallodeoxybiliobanic acid, $[\alpha]_D^{18}$ −45·83° in alcohol, whilst reduction affords gallocholanic acid $[\alpha]_D^{18}$ −39·26° in alcohol.　　CHEMICAL ABSTRACTS.

5-Bromo-2 : 4-dimethoxybenzoylacrylic acid and its esters. G. P. RICE (J. Amer. Chem. Soc., 1928, **50**, 1481—1491).—Bromination of methyl 5-bromo-2 : 4-dimethoxybenzoylacrylate (this vol., 290) in chloroform affords a mixture (I), m. p. 127°, of the racemic *forms*, m. p. 150·5° (70—80% of crude product), and, m. p. 149—150°, of methyl *αβ-5-tribromo-2 : 4-dimethoxybenzoylpropionate*. These are converted by methyl-alcoholic potassium acetate into yellow *methyl* α(or β)-5-*dibromo*-2 : 4-*dimethoxybenzoylacrylate* (II), m. p. 139°, and a colourless *stereoisomeride*, m. p. 164°, which is formed from the yellow

derivative in sunlight. The mixture (I) and sodium methoxide probably yield first methyl 5-bromo-2 : 4-dimethoxybenzoylpropiolate, from which, according to the conditions, (*a*) *methyl 5-bromo-α-2 : 4-trimethoxybenzoylacrylate* (III), m. p. 157° (colourless *stereoisomeride*, m. p. 113°), the *dibromide*, m. p. 97°, of which is converted by methyl alcohol into β-5-*dibromo-α-2 : 4-trimethoxybenzoylacrylate* (IV), m. p. 123°; (*b*) *methyl 5-bromo-αα-2 : 4-tetramethoxybenzoylpropionate*, m. p. 128°, which is brominated to the ester (IV) and hydrolysed by cold hydrochloric acid to yellow *methyl 5-bromo-α-hydroxy-2 : 4-dimethoxybenzoylacrylate*, m. p. 168° (copper derivative), or (*c*) 5-*bromo-αα-2 : 4-tetramethoxybenzoylpropionic acid*, m. p. 152°, is formed together with a little 5-*bromo-α-hydroxy-2 : 4-dimethoxybenzoylacrylic acid* (V), m. p. 179° (*dibromide*, m. p. 170°), by addition and hydrolysis. Bromine titrations with the acid (V) and its methyl ester indicate that the enolic formulæ attributed to them are correct. The product (I) is converted by aqueous-alcoholic potassium hydroxide into a mixture containing the ester (III), the acid (V), and 5-*bromo-α-2 : 4-trimethoxybenzoylacrylic acid* (VI), m. p. 202°, whilst (II) or (III) give a mixture of the tetramethoxy-acid and (V). This indicates that (II) is an intermediate in the formation of the benzoyl-propiolic ester from (I).

A similar series of products has been prepared from ethyl 5-bromo-2 : 4-dimethoxybenzoylacrylate. Bromination gives a mixture of the racemic *forms*, m. p. 141° (80% of crude product) and m. p. 160—161°, and *ethyl αβ-5-tribromo-2 : 4-dimethoxybenzoylpropionate*, which give with potassium acetate mixtures of yellow *ethyl* α(or β)-5-*dibromo-2 : 4-dimethoxybenzoylacrylate*, m. p. 144°, and a colourless *isomeride*, m. p. 114°; and with sodium ethoxide, the acid (V), *ethyl 5-bromo-2 : 4-dimethoxy-α-ethoxybenzoylacrylate*, m. p. 162°, and *ethyl 5-bromo-2 : 4-dimethoxy-αα-diethoxybenzoylpropionate*, m. p. 132°, but not, as with the methyl ester, the acid corresponding with the last. The ethoxy-esters are hydrolysed with difficulty by cold hydrochloric acid to *ethyl 5-bromo-α-hydroxy-2 : 4-dimethoxybenzoylacrylate*, m. p. 143° (copper derivative). αβ-5-*Tribromo-2 : 4-dimethoxybenzoylpropionic acid*, m. p. 184·5° (also $+CHCl_3$, m. p. 177·5°), is less reactive than its esters, being converted by sodium acetate or methoxide into yellow, m. p. 200°, and colourless, m. p. 178—180°, *isomerides* of α(or β)-5-*dibromo-2 : 4-dimethoxybenzoylacrylic acid*, and by potassium hydroxide in methyl alcohol into the acid (VI) and in ethyl alcohol into 5-*bromo-2 : 4-dimethoxy-α-ethoxybenzoylacrylic acid*, m. p. 197°, a little of the acid (V) being formed in each case.

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Hydrogenation by sodium amalgam. R. WILLSTÄTTER, F. SEITZ, and E. BUMM (Ber., 1928, **61**, [*B*], 871—886).—Comparison of the effects produced by the reduction of organic compounds by sodium amalgam and water and by hydrogen activated by catalysts shows that the action of the amalgam cannot be ascribed to the evolution of nascent hydrogen which is subsequently added to the organic molecule. It is more probable that sodium is primarily added at the double linking yielding a product which is decomposed by water. Pure sodium amalgam is

conveniently prepared in quantity by heating mercury which has been twice distilled in a vacuum at 120° in a porcelain dish covered by a glass plate bored with two holes; through one orifice a rapid current of nitrogen is passed, whereas the other serves for the introduction of the sodium which is freed from the film of oxide and cut into suitable pieces under ether in a glass mortar with a glass knife. Such amalgam becomes oxidised superficially to only a very slight extent and the slight skin of oxide may be removed by passage through filter-paper in which a few holes have been pierced by a platinum needle. This amalgam differs widely in properties from that prepared in an iron vessel or a Hessian crucible. It does not react at a measurable rate with conductivity water prepared according to the directions of Baker and Parker (J.C.S., 1913, **103**, 2060). The action between the amalgam and water is accelerated by impurities present in either. Among readily amalgamated metals, copper, silver, magnesium, zinc, aluminium, tin, and lead act in order of increasing readiness; a negative catalyst could not be found. The "utilisation coefficient" for the hydrogen is determined by allowing reduction of the organic substance by sodium amalgam to occur in an atmosphere of nitrogen; the total hydrogen produced is determined by titration of the sodium hydroxide produced, whilst the evolved hydrogen is swept forward by the nitrogen through phosphoric oxide tubes and over red-hot copper oxide; the water formed is absorbed by phosphoric oxide and weighed. Oxygen must be completely excluded, since if present in sufficient amount it entirely prevents evolution of hydrogen. An indirect method of determination is based on the perhydration of the product with hydrogen and spongy platinum or on the more rapid measurement of bromine absorption.

Pure sodium amalgam reacts very rapidly and with very high utilisation of hydrogen on many aromatic and olefinic compounds. Whereas, according to von Baeyer, terephthalic acid is reduced exclusively to $\Delta^{2:5}$-dihydroterephthalic acid which cannot be hydrogenated further, the pure amalgam under otherwise similar conditions transforms terephthalic acid in cold solution into Δ^2-tetrahydrophthalic acid. Contrary to the views of von Baeyer and the postulates of Thiele's theory, the Δ^2-tetrahydro-acid is very much more readily hydrogenated than the corresponding Δ^1-acid; in cold solution at p_H 9—10·5 it gives the hexahydro-acid in 60—70% yield with 90% utilisation of hydrogen. The observed differences are possibly explained by the differing rates of reduction and consequent variation in the periods during which the acids are subjected to the isomerising influence of the alkali hydroxide. The course of the reduction is frequently greatly influenced by the
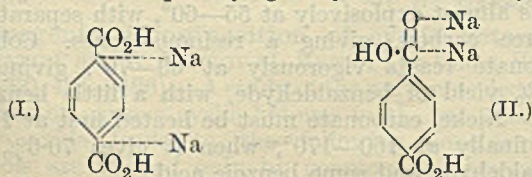
alkalinity of the medium. Thus at p_H 12—15 and above, terephthalic acid suffers hydrogenation in the

3 c

nucleus. If, however, the solution is buffered with phosphate or, preferably, sodium aminoacetate to p_H 9—9·8, p-toluic acid is obtained in 50% yield. It is suggested that primary addition of the sodium takes place according to (I) or (II) and that the partial affinities of the terephthalic acid molecule exercise their effects in various parts of the molecule in differing degree, according to the conditions of experiment and the reaction of the solution.

H. WREN.

Separation of phthalic and homophthalic acids. H. G. POOLE (J.C.S., 1928, 1378—1379).—When a mixture of sodium phthalate and homophthalate is treated in dilute solution with copper sulphate, *copper homophthalate* (solubility in water 1 in 5000 at 25°) is precipitated. The reaction must be performed in the cold, otherwise a basic copper phthalate is also formed. Decomposition of the copper salt with boiling hydrochloric acid gives pure homophthalic acid, m. p. 181°.

H. BURTON.

Photobromination of ethyl *m*-nitrobenzylidenemalonate. II. J. C. GHOSH, K. P. BASU, and S. C. BHATTACHARYYA (J. Indian Chem. Soc., 1928, 5, 183—190; cf. this vol., 176).—The addition of bromine to ethyl m-nitrobenzylidenemalonate under the influence of light in carbon disulphide solution is analogous to the reaction in carbon tetrachloride (*loc. cit.*). The equilibrium constant is approximately proportional to the square root of the intensity of incident light. The velocity in the initial stage is proportional to the concentration of bromine and increases considerably with increase in concentration of the ester. The values for the equilibrium constant and velocity are about seven times as great in carbon tetrachloride as in carbon disulphide.

H. BURTON.

Monoacyl derivatives of quinic acid. II. K. JOSEPHSON (Ber., 1928, 61, [*B*], 911—917; cf. this vol., 63; Karrer and Link, *ibid.*, 63).— Opening of the lactone ring of 4-benzoylquinide without simultaneous removal of the benzoyl group cannot readily be effected by alkali hydroxide. If, however, 4-benzoyl*iso*propylidenequinide dissolved in aqueous acetone at 55° is treated with hydrochloric acid, 4-*benzoylquinic acid*, m. p. 188° (corr.), $[\alpha]_D^{20}$ −3·9° in alcohol (also *monohydrate*), is easily prepared. Acyl migration does not occur during the change, since the product is re-converted by acetone containing a little hydrogen chloride into 4-benzoyl*iso*propylidenequinide. 4-Cinnamoyl*iso*propylidenequinide is similarly converted by hydrogen chloride in aqueous acetone into 4-*cinnamoylquinide*, m. p. 165° (corr.), $[\alpha]_D^{20}$ −18·3° in acetone, and 4-*cinnamoylquinic acid*, m. p. 188° (corr.), $[\alpha]_{Hg\ yellow}^{20}$ +5·9° in 95% alcohol. Hydrolysis of 4-cinnamoylquinide is also effected by sodium hydroxide in aqueous acetone, but the process is less advantageous. *iso*Propylidenequinide is transformed by acetic anhydride in the presence of pyridine at the ordinary temperature into 4-*acetyliso*propylidenequinide, m. p. 109°, $[\alpha]_{Hg\ yellow}^{20}$ −4·4° in chloroform, and by ethyl chloroformate in pyridine at 0° into 4-*carbethoxyiso*propylidenequinide, m. p. 108°, $[\alpha]_{Hg\ yellow}^{20}$ −4·7° in chloroform.

H. WREN.

Tautomerism of *cyclo*pentadienes. I. Derivatives of methyl*cyclo*pentadiene. F. R. Goss and C. K. Ingold (J.C.S., 1928, 1268—1278).—The formation of a sextuple valency group (cf. Bamberger, A., 1891, 1090) in the *cyclo*pentadiene series must be accompanied by appropriation of the electrons of one hydrogen atom, thus explaining why stable metallic derivatives of *cyclo*pentadiene, indene, and fluorene can be formed, and also the stability of the anion (I). In (I) each arrow denotes a contributing duplet. It has been shown that tautomeric (proto-

(I.)   (II.)   (III.)
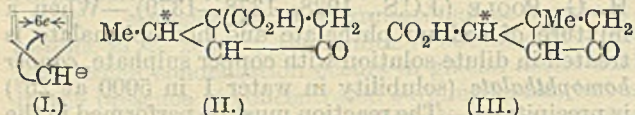
tropic) mobility exists in the indene series (Ingold and Piggott, J.C.S., 1923, **123**, 1469), and it is now demonstrated that the acids represented as (II) and (III) are identical, thus indicating that the nuclear hydrogen atom * is mobile in either or both compounds. Methyl malonate and methyl αα'-dibromo-β-methylglutarate condense in presence of sodium methoxide to form *methyl sodio-5-methyl-dicyclopenten*(or *cyclopentadien*)-*3-ol-1 : 2 : 4 - tricarboxylate* (IV), m. p. 270° (decomp.) (*hydroxy-*ester, b. p. 180°/1 mm.; *ethyl* ester), which on long treatment with 30% methyl-alcoholic potassium hydroxide gives *dimethyl potassium potassio-5-methyldicyclopentenoltricarboxylate.* Decomposition of this salt with acid affords *methyl hydrogen 5-methyldicyclopenten*(or *cyclopentadien*)-*3-ol-1 : 2*(or 1 : 4)-*dicarboxylate,* which when boiled with hydrochloric acid yields *5-methyldicyclopentan*(or *cyclopenten*)-*3-one-1-carboxylic acid* (II), m. p. 60° [*oxime*, m. p. 216° (decomp.)]. *Methyl 5-methyl-2*(or 4)-*ethyldicyclopentan*(or *cyclopenten*)-*3-one-1 : 2 : 4-tricarboxylate,* b. p. 210°/6 mm., is obtained by the action of ethyl iodide on (IV).

Methyl 3-methyl- Δ²-*cyclo*propene-1 : 2-dicarboxylate and methyl sodiocyanoacetate condense to form *methyl 3-methyl-1 : 2-dicarbomethoxycyclopropane-3-cyanoacetate,* b. p. 200°/20 mm., which when treated with sodium methoxide forms *methyl 3-amino-1-methyldicyclopentene*(or *cyclopentadiene*)-*2 : 4 : 5-tricarboxylate,* isolated in two forms, *A*, stable, m. p. 130° (decomp.), and *B*, m. p. 186° (decomp.). On keeping, *B* is converted into *A*. When *A* is hydrolysed with cold 3N-methyl-alcoholic potassium hydroxide a yellow *potassium potassio*-salt is produced which on acidification yields *dimethyl hydrogen 3-amino-1-methyldicyclopentene*(or *cyclopentadiene*)-*2 : 4 : 5-tricarboxylate,* m. p. 226° (decomp.). Hydrolysis of *A* with boiling hydrochloric acid yields *1-methyldicyclopentan*(or *cyclopenten*)-*3-one-5-carboxylic acid* (III), m. p. 60°. Oxidation of *A* with potassium persulphate and a small amount of silver oxide in 2N-sulphuric acid gives oxalic and fumaric acids, whilst hydrogen peroxide and a small amount of ferrous sulphate yields α- and β-methylglutaconic, and β-acetylacrylic acids.

Ethyl 3-amino-1-methyldicyclopentene (or *cyclopentadiene*)-*2 : 4 : 5-tricarboxylate* (V), m. p. 107° [*sodio*-derivative (VI); *diethyl hydrogen* ester, m. p. 199° (decomp.)], is described also. Treatment of (VI) with methyl and ethyl iodides yields the corresponding *methyl*, m. p. 113°, and *ethyl*, m. p. 118°, derivatives of (V). Hydrolysis of (V) with boiling hydrochloric acid gives (III).   H. Burton.

Polycyclic structures in relation to their homocyclic unsaturated isomerides. IX. Effect of the *spirocyclo*pentane grouping on the five-carbon intra-annular tautomeric nucleus. F. R. Goss (J.C.S., 1928, 1306—1310).—Oxidation of 5-*cyclo*pentane*spirodicyclo*pentan(or *spirocyclo*penten)-3-one-1-carboxylic acid (I) with alkaline potassium ferricyanide solution yields after esterification of the acids produced with methyl alcohol and sulphuric acid, 3-*methoxy*-5-*cyclo*pentane*spirocyclo*pentene-1 : 4-*dione*, m. p. 65°, hydrolysed by boiling hydrochloric acid to 5-*cyclo*pentane*spirocyclo*penten-3-ol-1 : 4-*dione* (II), m. p. 154°, and *methyl* 5-*cyclo*pentane*spirodicyclo*pentan(or *spirocyclo*penten)-4-ol-3-one-1-carboxylate, m. p. 145° [*free acid*, m. p. 110° (decomp.)]. Oxidation of 5-*cyclo*pentane*spirodicyclo*penten (or *spirocyclo*pentadien)-3-ol-1 : 2-dicarboxylic acid (III) with alkaline potassium ferricyanide gives (II). Oxidation of (I) with alkaline potassium permanganate yields αα-*dihydroxy*cyclopentane-1 : 1-*diacetic acid* (IV), m. p. 98°, which when heated at 90° affords α-keto*cyclo*pentane-1 : 1-diacetic acid (V). Similar oxidation of (III) gives a mixture of (IV) and (V). The ready production of (II), and the non-formation of substituted aconitic acids from this series of compounds, indicates that the bridged-ring phase predominates (cf. Ingold, Seeley, and Thorpe, J.C.S., 1923, **123**, 853).   H. Burton.

Colorimetric test for tannic acid. J. Rae (Pharm. J., 1928, **120**, 539).—Permanent reddish-brown colorations are given by solutions of tannic acid with 10% aqueous ammonium molybdate solution. Gallic acid and pyrogallol give the coloration also.   H. Burton.

Manufacture of carboxylic acids of acenaphthene. I. G. Farbenind. A.-G.—See B., 1928, 362.

Manufacture of 3 : 4-diaminobenzoyl-*o*-benzoic acid. R. Adams, J. M. Davidson, and J. Gubelmann, Assrs. to Newport Co.—See B., 1928, 440.

Manufacture of bromo-derivatives of 1 : 1'-dinaphthyl-8 : 8'-dicarboxylic acid. I. G. Farbenind. A.-G.—See B., 1928, 441.

Action of iron, cobalt, and nickel carbonates on benzylidene chloride. J. J. Vanin and A. A. Tschernojarova (J. Russ. Phys. Chem. Soc., 1927, **59**, 891—894).—The products of the action on warming of the carbonates of the metals of the iron group on benzylidene chloride in a stream of carbon dioxide were investigated. The activity of the metals decreases in their periodic order. Iron carbonate reacts almost explosively at 55—60°, with separation of free carbon, giving a resinous mass. Cobalt carbonate reacts vigorously at 60—70°, giving a 76·1% yield of benzaldehyde, with a little benzoic acid. Nickel carbonate must be heated first at 120° and finally at 160—170°, when it gives 70·6% of benzaldehyde and some benzoic acid. The mechanism of the reactions is discussed.   M. Zvegintzov.

Photolysis of benzaldehyde. M. DE HEMPTINNE.—See this vol., 720.

Tautomerism of o-nitrobenzaldehyde. F. ARNDT (Ber., 1928, **61**, [B], 1125—1126).—The assumption that o-nitrobenzaldehyde exists in tautomeric forms, $C_6H_4{<}^{CHO}_{NO_2} \rightleftharpoons C_6H_4{<}^{C(OH)}_{NO{-}{-}{-}}{>}O$ (cf. Tanasescu (A., 1926, 1247) is not in harmony with the following observations. (1) o-Nitrotriphenylmethane, for which a tautomeric form is impossible, resembles o-nitrobenzaldehyde in exhibiting a mobile hydrogen atom (for the detection of which the Zerevitinov method is inapplicable). (2) o-Nitrotriphenylmethane is isomerised to o-nitrosotriphenylcarbinol by light. (3) Solubility in alkali hydroxide is not peculiar to o-nitrobenzaldehyde, but is exhibited to a smaller extent by p-nitrobenzaldehyde. (4) o-Nitroacetophenone, which cannot yield a tautomeric form, is reduced to C-methylanthranil as readily as o-nitrobenzaldehyde is converted into anthranil.   H. WREN.

Benzylidene derivatives of glycols. A. FRANKE and E. GIGERL (Monatsh., 1928, **49**, 8—20).—A series of cyclic benzylidene derivatives of the type

$R''{<}^{O}_{O}{>}CHPh$ has been prepared by the condensation of benzaldehyde with various glycols. When anhydrous hydrogen chloride is passed into a mixture of benzaldehyde and the glycol at 0°, condensation occurs only in the case of the αγ-diols (αβ-diols not reacting under these conditions), and thus are obtained the cyclic *benzylidene* derivatives of ββ-dimethylpropane-αγ-diol, b. p. 123—124°/10 mm., m. p. 35° (yield, 68%); α-phenyl-ββ-dimethylpropane-αγ-diol, m. p. 98° (50%); β-methylpentane-βδ-diol, b. p. 124°/9 mm.; and βδ-dimethylpentane-βδ-diol, b. p. 127—128°/10 mm., m. p. 42° (20%). The yield is greatest with the diprimary glycol and decreases through the series primary-secondary, secondarytertiary, and ditertiary glycols. The cyclic *benzylidene* derivative, b. p. 126°/12 mm., m. p. 35°, of ββ-dimethylpropane-αγ-diol is obtained (yield, 65%) only by heating the glycol and benzaldehyde with a 1% alcoholic solution of hydrogen chloride for 1 hr. Pentane-αδ-diol by treatment with benzaldehyde and anhydrous hydrogen chloride at 0° yields only the αδ-oxide together with resinous products, and no derivative could be obtained from " camphor glycol " or decane-ακ-diol. In the absence of moisture the benzylidene derivatives develop intense colours in the presence of anhydrous hydrogen chloride (these colours also being observed during the preparation of the derivatives) which, it is suggested, are due to the formation of oxonium complexes with hydrogen chloride.   J. W. BAKER.

Pyrogenic decomposition of cyclic ketones. V. IPATIEV and A. PETROV (J. Russ. Phys. Chem. Soc., 1928, **60**, 491—496).—A study of the pyrogenic decomposition of various cyclic ketones in the presence of ferric oxide leads to the following conclusions. Phenols are yielded only by compounds possessing an ethylenic linking, whether in the nucleus or in the side-chain, such as homoisophorone and pulegone; the former substance loses more than one of its ethyl

groups, whilst the latter compound yields a mixture of phenols, unsaturated hydrocarbons, and cymol, as well as a number of aliphatic hydrocarbons produced by the breaking up of the ring, and liberation of carbon monoxide. Thymol, which is also produced, is further decomposed under the conditions of the experiment. 1-Methylcyclohexan-2-one, on the other hand, yields no phenolic products but a mixture of hydrocarbons, of which about 40% are unsaturated. These are probably of the amylene series, whilst the remainder are mainly saturated cyclic hydrocarbons, with a small admixture of toluene.
    R. TRUSZKOWSKI.

Pyrogenic decomposition of ketones at high pressures. V. N. IPATIEV and A. D. PETROV (J. Russ. Phys. Chem. Soc., 1927, **59**, 903—913).—The products of heating under pressure acetophenone and benzophenone between 270° and 430° and acetone above 500°, in an iron tube with alumina as a catalyst, were investigated. Acetophenone at 270—300° gives 30% of s-triphenylbenzene and diphenylfuran. At 380—420°, a 15% yield of benzene, toluene, ethylbenzene, and o-xylene is obtained, together with increasing quantities of tar containing a little benzoic acid. If hydrogen is added, the yield increases to 40%, showing that the ethylbenzene and o-xylene are formed by the direct reduction of acetophenone. Benzophenone and hydrogen at 400—430° yield 80% of diphenylmethane, with a little benzene and tar. When heated alone, benzophenone is unchanged even at 430°, but decomposes completely into carbon and gas above 500°. Acetone at 500—530° gives large quantities of paraffin hydrocarbons, including propane, phenols (1—2%, chiefly 1 : 3 : 5-xylenol), isophorone, xylitone, mesitylene, cymene, and ψ-cumene. The possible mechanism of the reactions is discussed, and its bearing on the composition of coal and low-temperature tars is emphasised.   M. ZVEGINTZOV.

Interaction of benzoyl chloride and diazomethane. Discussion of the reactions of diazenes. W. BRADLEY and R. ROBINSON (J.C.S., 1928, 1310—1318).—The reaction between benzoyl chloride and diazomethane in cold, dry ethereal solution takes place thus, $Ph \cdot COCl + 2CH_2N_2 \longrightarrow Ph \cdot CO \cdot CHN_2 + CH_3Cl + N_2$, diazoacetophenone, m. p. 48—48·5° (cf. Wolff, A., 1903, i, 203), being obtained in 91% yield. ω-Chloroacetophenone is not produced (cf. Clibbens and Nierenstein, A., 1915, i, 1602). Benzoyl bromide and diazomethane give diazoacetophenone also (cf. Lewis, Nierenstein, and Rich, A., 1925, i, 935). The mechanisms of the reactions of diazomethane are discussed on an electronic basis.   H. BURTON.

Syntheses with diazomethane. V. Action of acid chlorides with diazomethane. F. ARNDT and J. AMENDE (Ber., 1928, **61**, [B], 1122—1124; cf. Nierenstein, A., 1925, i, 34; Staudinger and Mächling, A., 1916, i, 855).—The nature of the product of the reaction of acid chlorides and diazomethane depends greatly on the conditions of the reaction. If the acid chloride is added to the diazomethane so that the latter is always present in excess, the liberated hydrogen chloride is absorbed by the diazomethane and the diazo-ketone remains mainly intact. If the

reactants are mixed in the reverse order, the primary diazo-ketone is decomposed by the liberated hydrogen chloride with formation of the chloro-ketone which then constitutes the main product. The nature and stability of the diazo-ketone cannot, however, be entirely neglected. Benzoyl chloride and an excess of diazomethane afford ω-diazoacetophenone, m. p. 49°, converted by warm, dilute sulphuric acid into benzoylcarbinol. The preparation of diazoacetone, b. p. 49°/13 mm., and *chlorodiazoacetone*, b. p. 75°/ 13 mm., m. p. +3°, is described. Benzoyl chloride and 1·5 mols. of diazomethane afford chiefly ω-chloro-acetophenone. H. WREN.

Conversion of hydroaromatic into aromatic compounds. II. Action of bromine on 5-chloro- and 5-bromo-1-phenyl-Δ⁴-cyclohexen-3-one. L. E. HINKEL and D. H. HEY (J.C.S., 1928, 1200—1204).—Phenyldihydroresorcinol is converted by phosphorus tribromide in presence of chloroform into 5-*bromo*-1-*phenyl*-Δ⁴-cyclohexen-3-one, m. p. 81·5°, which with bromine affords 4 : 5 : 5-*tribromo*-1-*phenyl*-*cyclo*hexan-3-one, m. p. 82° (decomp.). This compound exists in stable (from alcohol) and unstable (ether) forms which are probably *cis–trans* modifications. When the tribromoketone is heated on the water-bath there are formed as decomposition products 4 : 5-*dibromo*-3-*hydroxydiphenyl*, m. p. 81° (*benzoyl* derivative, m. p. 104°), and 5-*bromo*-3-*hydr-oxydiphenyl*, b. p. 208—210°/11 mm. (*benzoyl* deriv-ative, m. p. 108°), and a small amount of phenyl-dihydroresorcinol. When decomposed with alcoholic potassium hydroxide the tribromoketone furnishes in addition to the above hydroxy-compounds some 5-*bromo*-3-*ethoxydiphenyl*, m. p. 70—71°. 5-*Chloro*-4 : 5-*dibromo*-1-*phenylcyclohexan*-3-*one*, stable, m. p. 98·5° (alcohol), unstable, m. p. 88·5° (ether), is decomposed by alcoholic potassium hydroxide yield-ing an equimolecular *mixture*, m. p. 68—69°, of 5-chloro-and 5-bromo-3-ethoxydiphenyl, together with halo-genohydroxydiphenyl derivatives. H. BURTON.

Reactions of strongly electropositive elements with organic substances in liquid ammonia solution. VI. Reduction of benzophenone; hydrolysis of metal ketyls. C. B. WOOSTER (J. Amer. Chem. Soc., 1928, 50, 1388—1394; cf. Kraus and White, A., 1923, i, 456).—In liquid ammonia benzophenone readily forms mono- and di-sodio-derivatives (cf. Beckmann and Paul, A., 1892, 169) the colour of the latter being deep purple. The disodio-compound is quantitatively converted by excess of water or ammonia into benzhydrol. With ethyl bromide only one sodium atom is replaced by alkyl, giving diphenylethylcarbinol, whilst with iodobenzene, benzene, sodium iodide, and the sodio-derivative of α-aminobenzhydrol are formed. Di-potassiobenzophenone is formed analogously to the disodio-derivative, or from benzhydrol and potass-amide in liquid ammonia. Monosodiobenzophenone gives with ammonium chloride a mixture of benz-hydrol and benzophenone and with ethyl bromide a mixture of diphenylethylcarbinol and benzophenone. The disodio-derivative is converted by 1 mol. of ammonium chloride into a blue *ammoniosodio*-deriv-ative, CPh₂NH₄(ONa), which decomposes completely

in liquid ammonia in some 7—8 hrs. The same compound is formed from 1 mol. of ammonium chloride and 2 mols. of the monosodio-derivative, and appears as a transient green coloration in the decom-position of the sodio-derivatives by water. The primary reaction with the monosodio-derivative is, therefore, addition to the free valency and not replacement of the sodium atom (cf. Schlenk, A., 1911, i, 545). H. E. F. NOTTON.

Comparative stability of isomerides and their absorption spectra. (MME.) RAMART-LUCAS (Compt. rend., 1928, 186, 1301—1303).—Of two mutually interconvertible substances the absorption curve of the stable form is nearer to the visible than that of the labile form. Moreover, in a transformation involving separation of water, acid, or salt, with possible formation of two isomerides through a common unstable intermediate stage, it is, in general, possible to obtain either of the two forms at will if the conditions are known for the formation of the isomeride having its absorption curve further from the visible than the other. For example, the absorption curve of deoxybenzoin is nearer the visible than that of diphenylacetaldehyde, the usual dehydration product of hydrobenzoin; and by passing hydro-benzoin over kieselguhr at 300—400°/20 mm. an almost quantitative yield of deoxybenzoïn may be obtained. B. W. ANDERSON.

Benzopolymethylene compounds. XIV. Syn-theses of tetracyclic compounds and of pyrene. J. VON BRAUN and E. RATH (Ber., 1928, 61, [B], 956—963; cf. A., 1927, 666).—Further experiments on ring closure support the accuracy of the theory of Sachse and Mohr.

Tetraphthen ketone (I) is readily converted by zinc and ethyl bromoacetate into the *ester*, C₁₆H₁₈O₂, b. p. 214—215°/14 mm., of the unsaturated acid, which is smoothly hydrogenated in the presence of nickel to *ethyl tetraphthylacetate*, b. p. 196°/14 mm. *Tetraphthylacetic acid*, m. p. 108°, is described; as expected, its chloride is unaffected by aluminium chloride. Reduction of ethyl tetraphthylacetate by sodium and alcohol affords β-*tetraphthylethyl alcohol*, b. p. 188°/15 mm., m. p. 53°, converted successively into β-*tetraphthylethyl bromide*, b. p. 182—185°/15 mm., *tetraphthylpropionitrile*, b. p. about 205°/16 mm., m. p. 38°, and *tetraphthylpropionic acid*, m. p. 97°. The corresponding *chloride*, b. p. 215—220°/14 mm. (slight decomp.), is transformed by aluminium chloride in the presence of carbon disulphide into α-*keto-octahydromethylenephenanthrene* (II), b. p. 168—170°/0·5 mm., m. p. 104° (*oxime*, m. p. 213°; *semi-carbazone*, m. p. 266°), reduced by Clemmensen's method to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydro*-4 : 5-*methylenephenanthrene*, b. p. 130—132°/15 mm., m. p. 47°. This substance could not be dehydrogenated by lead oxide, zinc dust, palladium, nickel, or sulphur.

(I.) (II.) (III.)
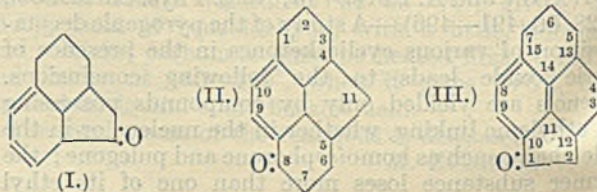
α-Ketohexahydrobenznaphthen, zinc, and ethyl bromoacetate afford the unsaturated *ester*, $C_{17}H_{20}O_2$, b. p. 218—219°/14 mm., smoothly hydrogenated to *ethyl hexahydrobenznaphthylacetate*, b. p. 196°/14 mm. The corresponding *acid*, b. p. 220—222°/13 mm., m. p. 93°, is converted through its *chloride* into the *ketone* (III), b. p. 170—172°/0·5 mm., m. p. 98° (*oxime*, m. p. 199°; *semicarbazone*, m. p. 256°), which is reduced to 3 : 4 : 5 : 6 : 12 : 13-*hexahydroperibenzoacenaphthen*, b. p. 130—132°/12 mm., m. p. 29°. Dehydrogenation of the last substance could not be effected. Reduction of ethyl hexahydrobenznaphthylacetate yields β - *hexahydrobenznaphthylethyl alcohol*, b. p. 192—194°/12 mm., m. p. 23—24°, converted successively into the corresponding *bromide*, b. p. 192—194°/12 mm., and *hexahydrobenznaphthylpropionitrile*, b. p. 212—214°/12 mm., which is hydrolysed to *hexahydrobenznaphthylpropionic acid*, b. p. 238—240°/12 mm., m. p. 118°. The *chloride* of the acid is very easily transformed by aluminium chloride into α-*ketodecahydropyrene*, b. p. 182—183°/0·4 mm., m. p. 63° (*oxime*, m. p. 158°; *semicarbazone*, m. p. 242°). *Decahydropyrene*, prepared by reduction of the ketone by Clemmensen's method, has b. p. 151—152°/12 mm., m. p. 34°, d_4^{20} 1·0612, n_D^{20} 1·5806; it is very readily dehydrogenated by passage over lead oxide–pumice to pyrene.   H. WREN.

Isomerism of styryl alkyl ketones. IV. 4-Hydroxy- and some derivatives of 2-hydroxystyryl alkyl ketones. A. McGOOKIN and D. J. SINCLAIR (J.C.S., 1928, 1170—1177).—Treatment of 5-bromo-2-hydroxystyryl methyl ketone with sodium hydroxide solution and subsequent acidification of the green sodium salt produced gives 5 : 5'-dibromo-2 : 2'-dihydroxydistyryl ketone, yellow, m. p. 188°, also obtained by interaction of the styryl methyl ketone or acetone and 5-bromosalicylaldehyde in presence of alkali. When the method of preparation using acetone is employed a colourless *modification*, m. p. 174·5°, of the distyryl ketone was isolated in addition to the yellow form. The following styryl ketones have been prepared by condensing substituted benzaldehydes with the appropriate ketone in presence of alkali hydroxide solution, and found to exist in yellow and colourless modifications with the same m. p.: 2-*hydroxy-4-methoxystyryl ethyl*, m. p. 123°, and *propyl ketones*, m. p. 111—112°; 4-*hydroxystyryl methyl*, m. p. 111—112°, *ethyl*, m. p. 115°, and *propyl ketones*, m. p. 90°; 2-*hydroxystyryl* iso*propyl ketone*, m. p. 107°; 2-*hydroxystyryl* tert.-*butyl ketone*, m. p. 128°, from salicylaldehyde and pinacolin, and 2-*hydroxystyryl isobutenyl ketone*, m. p. 141°, obtained in small yield together with 2-hydroxystyryl methyl ketone and 2 : 2'-dihydroxydistyryl ketone from salicylaldehyde and mesityl oxide. 2-*Hydroxy-3-methoxystyryl ethyl*, m. p. 86·5° (*hydrate*, m. p. 77—79°), and *propyl ketones*, m. p. 82·5°, and 3-hydroxystyryl methyl ketone, m. p. 97—98° (cf. Murai, A., 1925, i, 1157), are described. 4 : 4'-Dihydroxydistyryl ketone, m. p. 237—238°, can be prepared only from 4-hydroxybenzaldehyde and acetone or 4-hydroxystyryl methyl ketone by means of condensation in alcoholic hydrogen chloride. The condensation of salicylaldehyde or *p*-dimethylaminobenzaldehyde with 2-hydroxystyryl

ethyl ketone could not be effected in alkaline media.

Styryl alkyl ketones of the types >CH:CH·COMe and >CH:CH·CO·CH₂Alk give red solutions with boiling concentrated hydrochloric acid and undergo fission when treated with alkali. In the first type the fission products recombine, forming distyryl ketones, but in the second, high-melting, unsaturated substances of undetermined nature are obtained. 2-Hydroxystyryl tert.-butyl, isobutenyl, and phenyl ketones are unaffected by either acid or alkali. Examples of other cases of isomerism amongst styryl ketones recorded in the literature are given.
    H. BURTON.

Mononitrobenzils and heteronuclear dinitrobenzils. F. D. CHATTAWAY and E. A. COULSON (J.C.S., 1928, 1080—1088; cf. A., 1926, 728).—When a solution of benzoin in acetic anhydride and sulphuric acid is treated with powdered potassium nitrate at −10° to 0° and the resulting product oxidised with boiling nitric acid (*d* 1·5), there are obtained 4-nitrobenzil (I, 42%; *monophenylhydrazones*, m. p. 200° and 162°; *osazone*, m. p. 216°; *quinoxaline* derivative, m. p. 161°), and small amounts of 2-nitrobenzil (II), m. p. 102° (cf. List, A., 1894, i, 39), and 3-*nitrobenzil* (III), m. p. 120°. Nitration of (II) and (III) furnishes 2 : 2'- and 3 : 2'-dinitrobenzils and 3 : 2'- and 3 : 3'-dinitrobenzils, respectively, whilst from (I) there are obtained 3 : 4'-*dinitrobenzil*, labile, m. p. 127°; stable, m. p. 137° [*monophenylhydrazone*, m. p. 182°; *osazone*, m. p. 287° (decomp.); *quinoxaline* derivative, m. p. 221°], and 2 : 4'-*dinitrobenzil*, m. p. 135° (*monophenylhydrazones*, m. p. 224° and 201°; *quinoxaline* derivative, m. p. 186°). When benzoin or acetylbenzoin is nitrated at 25—30° with an excess of nitric acid and the resulting product oxidised, a mixture of 2 : 4'-, 3 : 4'-, and 4 : 4'-dinitrobenzils is produced. 2 : 2'- and 2 : 3'-*Dinitrobenzilmonophenylhydrazones*, m. p. 199° and 193° (decomp.), respectively, and 2-m-*nitrophenyl-3-o-nitrophenylquinoxaline*, m. p. 168°, are described. The constitutions of the above mono- and di-nitrobenzils are established by oxidation with chromic anhydride in acetic acid and subsequent identification of the benzoic or nitrobenzoic acids formed.   H. BURTON.

4 : 4'-Dinitrobenzil. F. D. CHATTAWAY and E. A. COULSON (J.C.S., 1928, 1361—1364).—Nitration of hydrobenzoin with nitric acid (*d* 1·5), and oxidation of the product with nitric acid of *d* 1·4, gives 4 : 4'-dinitrobenzil, m. p. 213° [*monophenylhydrazone*, m. p. 257°; *osazone*, m. p. 293° (decomp.); *quinoxaline* derivative, m. p. 201°], oxidised by chromic anhydride in acetic acid to *p*-nitrobenzoic acid. The group HO·CH·CH·OH exerts a strong *p*-directing influence as in benzoin (cf. this vol., 761). 4 : 5-Diphenylglyoxalone (Biltz, A., 1909, i, 740) is converted by fuming nitric acid into 3 : 3'-dinitrobenzil, but in presence of sulphuric acid gives a mixture of 3 : 3'- and 4 : 4'-dinitrobenzils.
    H. BURTON.

Some hydrochalkones and hydrochalkols. P. PFEIFFER, E. KALCKBRENNER, W. KUNZE, and K. LEVIN (J. pr. Chem., 1928, [ii], **119**, 109—130).—Chalkone on reduction with hydrogen and platinum-

black gives phenyl β-phenylethyl ketone, m. p. 72°, whilst with sodium amalgam hydrochalkol (αγ-diphenylpropan-γ-ol) (phenylurethane, m. p. 82—83°; p-*nitrobenzoate*, m. p. 89—90°, d^{21} 1·0614, n_{D}^{21} 1·5724, $[R_L]_D$ 65·8, calc. 66·1) is formed. Treatment of hydrochalkol with zinc chloride led to diphenylpropene : no phenylhydrindene was isolated. The undermentioned hydrochalkones were prepared by the reduction of the appropriate chalkones with hydrogen and platinum-black : *phenyl β-3 : 4-dimethoxyphenylethyl ketone*, m. p. 67·5—68·5° (*oxime*, m. p. 109°; *tertiary alcohol* with magnesium phenyl bromide, m. p. 102—103°); phenyl β-3 : 4-methylenedioxyphenyl ketone, m. p. 57—58° (Bargellini and Bini, A., 1912, i, 118, give m. p. 39—41°) (*tertiary alcohol* with magnesium methyl bromide, m. p. 50—52°); p-*anisyl β-3 : 4-dimethoxyphenylethyl ketone*, m. p. 57°; *phenyl β-2-chlorophenylethyl ketone* (from *phenyl 2-chlorostyryl ketone*, m. p. 51·5°), m. p. 46·5° (*oxime*, m. p. 113°); p-*anisyl β-2-chlorophenylethyl ketone* (from p-*anisyl 2-chlorostyryl ketone* from o-chlorobenzaldehyde and p-methoxyacetophenone, m. p. 91·5—92°), m. p. 48·5° (*oxime*, m. p. 90—91°); p-*anisyl β-2-bromophenylethyl ketone* (from p-*anisyl 2-bromostyryl ketone*, m. p. 79·5°), m. p. 65° (*oxime*, m. p. 99·5—100°); 1-*hydroxy-2-naphthyl β-phenylethyl ketone*, m. p. 98° (*acetyl* derivative, m. p. 89—90°); 1-*hydroxy-2-naphthyl β-p-anisylethyl ketone*, m. p. 108°; 1-*hydroxy-2-naphthyl β-3 : 4-methylenedioxyphenylethyl ketone*, m. p. 103—104°. 3-o-*Chlorobenzylidene-7-methoxychromanone*, m. p. 132°, is reduced to the corresponding o-*chlorobenzyl* derivative, m. p. 75° (*oxime*, m. p. 162—163°). Reduction of phenyl 2-chlorostyryl ketone with sodium amalgam gave α-*phenyl-γ-o-chlorophenylpropan-α-ol*, d^{21} 1·1636, $n_{D}^{18\cdot9}$ 1·5831, $[R_L]_D$ 70·83, calc. 71·06 (p-*nitrobenzoate*, m. p. 115°; *phenylurethane*, m. p. 100·5°); the latter yielded α-*chloro-α-phenyl-γ-o-chlorophenylpropane*, b. p. 151—154°/2 mm., on treatment with hydrogen chloride. The following compounds are described : 3-o-*bromobenzylidene-7-methoxychromanone*, m. p. 164°; *benzylidenenaphthachromanone*, from naphthachromanone and benzaldehyde, m. p. 131—132°; *piperonylidenenaphthachromanone*, m. p. 170—171°, from naphthachromanone and piperonal; *furfurylidenenaphthachromanone*, m. p. 145°, from naphthachromanone and furfuraldehyde.   I. VOGEL.

Active constituents of true coto-bark. Constitution of cotoin. E. SPÄTH and F. WESSELY (Monatsh., 1928, 49, 229—240).—Cotoin, regarded by Späth and Fuchs (A., 1922, i, 558) as 2 : 6-dihydroxy-4-methoxybenzophenone (I), might alternatively be 2 : 4-dihydroxy-6-methoxybenzophenone (II) (cf. Karrer, A., 1927, 564); the constitution (I) is, however, now established as follows. The monoalkylation of (I) can yield only one product, whereas (II) would be expected to yield two. Actually only one cotoin methyl ether (cf. Späth and Fuchs, *loc. cit.*) can be isolated from the product of the action of diazomethane in ether. This must be 2-hydroxy-4 : 6-dimethoxybenzophenone, since it yields 3 : 5-dimethoxy-2-phenylcoumarone (Motylewski, A., 1909, i, 822). Similarly, diazoethane in ether yields only one product, 2-*hydroxy-4-methoxy-6-ethoxybenzophen-*

on e, m. p. 91—92°, which when treated with sodium and ethyl bromoacetate in absolute alcohol yields a product hydrolysed by alcoholic potassium hydroxide to a mixture from which 5-*methoxy-3-ethoxy-2-phenylcoumarone*, m. p. 108—109·5°, is obtained by distillation.

Secondly, when cotoin methyl ether is ethylated, or the ethyl ether is methylated, the same product is obtained, viz., 2 : 4-*dimethoxy-6-ethoxybenzophenone*, m. p. 103—104°; this makes it probable that the two hydroxyl groups of cotoin are equivalent, *i.e.*, in the o-position to the keto-group; the methoxyl group is then in the p-position.

Lastly, the *cotoin diethyl ether*, m. p. 82—83°, b. p. 160—170°/0·001 mm., obtained by the action of excess of diazoethane, is shown to be 4-*methoxy-2 : 6-diethoxybenzophenone*, for it is reduced in alcoholic potassium hydroxide solution by zinc to 4-*methoxy-2 : 6-diethoxybenzhydrol*, m. p. 104—105°, of which the constitution is established by oxidation by chromic acid to 2 : 6-diethoxybenzoquinone, new m. p. 127—128°, identical with that obtained by oxidation of phloroglucinol diethyl ether, new m. p. 75—76°. The dimethoxyethoxybenzophenone is reduced by zinc and potassium hydroxide to 2 : 4-dimethoxy-6-ethoxybenzhydrol, m. p. 80—81°, which is oxidised by chromic acid to 2-methoxy-6-ethoxybenzoquinone, m. p. 135—136°, identical with that obtained by oxidation of *phloroglucinol methyl ethyl ether*, m. p. 50—51°, obtained by partial ethylation of phloroglucinol methyl ether with diazoethane.
                                          E. W. WIGNALL.

Dark-coloured dimeric keten. W. LANGENBECK and H. LANGENBECK (Ber., 1928, 61, [*B*], 938—942).—Benzilic acid which has been mixed with a small proportion of anhydrous sodium carbonate yields, when very energetically heated, a mixture of benzilide, m. p. 194°, and 3 : 3 : 4 : 4-*tetraphenylcyclobutane-1 : 2-dione*, m. p. 168°. The new compound is coloured red, the colour intensity being that of a true dye. It shows general absorption in the blue and violet. Proof of the constitution of the latter rests mainly on its oxidation by chromic acid to benzophenone (yield 49%). With alcoholic potassium hydroxide or potassium cyanide, phosphorus pentachloride, thionyl chloride, alcoholic bromine, zinc dust and glacial acetic acid, magnesium ethyl bromide, or phenylhydrazine it yields resinous, apparently highly polymerised products.
                                          H. WREN.

Preparation of phenolic ketones by the Hoesch method. A. KORCZYŃSKI and A. NOVAKOVSKI (Rocz. Chem., 1928, 8, 254—262).—See this vol., 523.

Synthesis of benzoquinone. J. F. DURAND (Compt. rend., 1928, 186, 1221).—The statement that benzoquinone was obtained from acetylene and carbon monoxide (A., 1927, 566) is withdrawn.
                                          J. D. FULTON.

Bromophenols. XXXII. Preparation of 2 : 6-dibromo-*m*-xyloquinone from s-xylenol. M. KOHN and M. K. FELDMANN (Monatsh., 1928, 49, 169—172).—s-Xylenol is brominated in acetic acid to tribromo-s-xylenol (methyl ether, m. p. 116°; cf. Blanksma, A., 1903, i, 164), which when oxidised
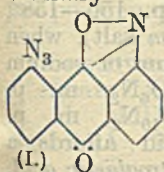
by fuming nitric acid yields 2 : 6-*dibromo*-m-*xylo-quinone*, m. p. 176°, rhombic prisms of angle 68° 4′, doubly refracting, α＝1·4804 [HLAWATSCH]. This is reduced by sulphurous acid to 2 : 6-*dibromo*-m-*xylo-quinol*, charring at 180° (*benzoyl* derivative, m. p. 253°; *methyl ether*, m. p. 116°, b. p. 309—311°/741 mm.).

E. W. WIGNALL.

Manufacture of a 2 : 3-dichloronitro-1 : 4-naphthaquinone. I. G. FARBENIND. A.-G.—See B., 1928, 441.

Diazides of anthraquinone. K. BRASS and F. ALBRECHT (Ber., 1928, 61, [*B*], 983—993).—The stability of diazides of anthraquinone depends on the position of the azido-groups in the anthraquinone nucleus and the manner in which they are distributed. Proximity to the carbonyl group causes instability in the α-derivatives which decreases from the 1 : 4- to the 1 : 5- and to the 1 : 8-compound. If, however, the residual affinity of the carbonyl group is engaged by the residue formed from the decomposition of one azido-radical, the second azido-group becomes stabilised. Anthraquinone-2 : 6-di-azide, on the other hand, is completely stable.

1 : 4-Diaminoanthraquinone is converted by diazotisation in concentrated sulphuric acid followed by treatment of the diazonium sulphate with bromine into the very unstable *perbromide* which, with ammonia, yields the corresponding *diazide*; this last compound, even when strongly cooled, steadily evolves nitrogen and passes into anthraquinone-1 : 4-dianthranil. Decomposition of the dianthranil by concentrated sulphuric acid at 200° gives about equal quantities of 1-amino-4-hydroxyanthraquinone, m. p. 208°, and 1 : 4-diaminoanthraquinone, m. p. 268°, contaminated by products of high mol. wt. The formation of the latter substance is explained by intermediate radical production, whereas that of the former remains unexplained, since it is not due to hydrolysis of the 1 : 4-diamino-compound. 1 : 5-Di-aminoanthraquinone is converted similarly into *anthraquinone*-1 : 5-*diazide*, which gradually passes at the atmospheric temperature into anthraquino-1 : 5-dianthranil. The freshly-prepared diazide is decomposed by 90% sulphuric acid into 4 : 8-di-aminoanthrarufin; 1 : 5-diaminoanthraquinone does not appear to be regenerated. When rapidly prepared at a low temperature, nearly homogeneous *anthraquinone*-1 : 8-*diazide* can be obtained from 1 : 8-diaminoanthraquinone; it gives a *compound* with triphenylphosphine. When preserved at the ordinary temperature, it gradually loses one third of its nitrogen, giving 1-*anthr-aniloanthraquinone*-8-*azide* (I), more rapidly prepared by crystallisation of the diazide on treatment of it with boiling water; with triphenyl-phosphine it affords *anthraniloanthra-quinonetriphenylphosphineimine*.

4 : 5-Diaminochrysazine comprises 90% of the products of the decomposition of the anthraniloazide by sulphuric acid, the remainder consisting of insoluble compounds of high mol. wt.; regeneration of 1 : 8-diaminoanthraquinone is not observed. *Anthraquin-one*-2 : 6-*diazide*, decomp. 202°, forms pale brown

crystals, sensitive to light; *anthraquinone*-2 : 6-di-*triphenylphosphineimine*, $C_{50}H_{36}O_2N_2P_2$, m. p. above 280°, is described. Decomposition of the diazide by sulphuric acid follows an ill-defined course, the sole isolable product being 2 : 6-diaminoanthrarufin.

H. WREN.

Anthraquinonedichlorodi-imine [1 : 4-dichloro-iminodihydroanthraquinone] and its compounds with amines. A. A. SANIN (J. Russ. Phys. Chem. Soc., 1927, 59, 867—875).—1 : 4-*Dichloroiminodi-hydroanthraquinone* was prepared by treating 1 : 4-diaminoanthraquinone with bleaching powder in aqueous suspension, and recrystallising the precipitate from carbon tetrachloride, when a reddish-brown *solid* was obtained, m. p. 155—156°, soluble in nitrobenzene and pyridine, less soluble in the other usual organic solvents. When warmed in alcohol or acetic acid solution, it was reduced to the amine. On reduction with hyposulphite, it showed the properties of a vat dye. Other diamines of the anthraquinone series, such as 1 : 4 : 5 : 8-tetra-aminoanthra-quinone, 1 : 5-diamino-4 : 8-dihydroxyanthraquin-one, 1-amino-4-hydroxyanthraquinone, as well as the *O*-substituted compounds, gave similar products.

On condensing the *dichloroimino*-compound with aniline in the presence of anhydrous sodium acetate or copper acetate, a *chloride* was obtained, of which the free base was a black *compound*, m. p. 204—206°, dissolving in concentrated sulphuric acid with a blue colour, and possessing, probably, the azonium structure (I). Besides this base, a dark *solid*, m. p.
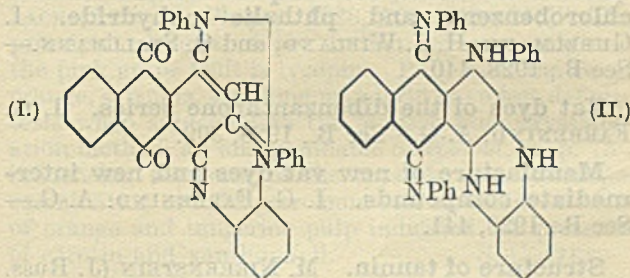
234—235°, easily soluble in aniline, pyridine, and nitrobenzene, was obtained, probably having the structure (II).

M. ZVEGINTZOV.

Rubiadin. I. Synthesis of 2 : 4-dihydroxy-1-methylanthraquinone. P. C. MITTAR, M. SEN, and P. K. PAUL (J. Indian Chem. Soc., 1927, 4, 535—540).—2 : 4 - Dihydroxy-*o*-toluic acid (cresor-sellenic acid), prepared by a slight modification of the method of Jacobsen and Wierss (A., 1883, 1121), when heated with benzoic and sulphuric acids at 125—130° for 12—15 hrs. yields 2 : 4-*dihydroxy*-1-*methylanthraquinone*, m. p. 265—266° (*diacetate*, m. p. 181—182°), which is not identical with rubiadin to which Schunck and Marchlewski (J.C.S., 1894, 65, 183) ascribed this constitution. Cresorsellenic acid by methylation yields 2 : 4-*dimethoxy*-*o*-toluic *acid*, m. p. 160°, the *methyl* ester, b. p. 289—291°, of which condenses with chloral hydrate in the presence of cold 90% sulphuric acid to yield 3 : 5-*di-methoxy* - 6 - *methyl* - 2 - *trichloromethylphthalide*, m. p. 176°, which is converted by heating with 20% sodium hydroxide solution on a water-bath for 5 hrs. into

3 : 5 - *dimethoxy* - 6-*methyl*-2-*phthalidecarboxylic acid*,
$C_6HMe(OMe)_2 < ^{CO}_{CH(CO_2H)} > O, H_2O$, m. p. 218—219°
(*ethyl* ester, m. p. 134°), which is decarboxylated by
heating with sulphuric acid at 225—235°, yielding
3 : 5-*dimethoxy*-6-*methylphthalide*, m. p. 249°. The
latter could not be oxidised to 3 : 5-dimethoxy-6-
methylphthalic acid. J. W. BAKER.

**Rubiadin. II. Synthesis of 1 : 3-dihydroxy-
2-methylanthraquinone.** P. C. MITTER and P.
GUPTA (J. Indian Chem. Soc., 1928, 5, 25—28; cf.
preceding abstract).—Repetition of the preparation
of 1 : 3-dihydroxy-2-methylanthraquinone (Schunck
and Marchlewski, J.C.S., 1893, 63, 969) shows that
the product obtained by those authors by the con-
densation of benzoic and 2 : 6-dihydroxy-*p*-toluic
acids probably contained traces of 1 : 3 : 5 : 7-tetra-
hydroxy-2 : 6-dimethylanthraquinone. When an
excess of benzoic acid is used, pure 1 : 3-dihydroxy-
2-methylanthraquinone, m. p. 290° (*acetyl* deriv-
ative, m. p. 225°), identical with rubiadin, is obtained.
In the preparation of 2 : 6-dihydroxy-*p*-toluic acid
by fusion of the corresponding sulphonic acid with
potassium hydroxide, small amounts of 2-hydroxy-
terephthalic acid are obtained. G. A. C. GOUGH.

**o-Aminocarboxylic acids of the anthraquinone
series and substitution products thereof.** I. G.
FARBENIND. A.-G.—See B., 1928, 361.

**Manufacture of 2 : 4-dichloro-1-aminoanthra-
quinone and intermediate products from *m*-di-
chlorobenzene and phthalic anhydride.** I.
GUBELMANN, H. J. WIELAND, and O. STALLMANN.—
See B., 1928, 440.

Vat dyes of the dibenzanthrone series. I. G.
FARBENIND. A.-G.—See B., 1928, 399.

**Manufacture of new vat dyes and new inter-
mediate compounds.** I. G. FARBENIND. A.-G.—
See B., 1928, 441.

Structure of tannin. M. NIERENSTEIN (J. Russ.
Phys. Chem. Soc., 1927, 59, 951—952).—A criticism
of Fischer's formula for tannin, in the light of the
author's researches. On exhaustive methylation with
diazomethane of Chinese tannin, followed by acid
hydrolysis, 2 : 3 : 5 : 6-tetramethylglucose, and not
dextrose as is demanded by Fischer's formula, is
obtained. Under the same conditions, synthetic
pentagalloyl-β-glucose also yields dextrose. Further,
brewer's yeast ferments tannin, giving an optically
active compound, free from sugar, possessing well-
defined tanning properties, without the formation of
either metadigallic or gallic acids.

M. ZVEGINTZOV.

Bile acids. XIX. M. SCHENCK and H. KIRCH-
HOF (Z. physiol. Chem., 1928, 175, 135—144).—The
dioxime of bilianic acid on treatment with sulphuric
acid yields an isomeride for which formula (I) is
suggested (cf. A., 1927, 665), although the position
of the nitrogen atoms is hypothetical. By the
action of nitric acid on this diisooxime two crystalline
products have been obtained, only one of which has
been examined carefully. This *compound*,
$C_{24}H_{34}O_8N_2$, m. p. 230—232° with frothing and

charring, is blue and is formed by the action of
nitric acid at the ordinary temperature. Analytical
data and the absence of heat production or gas
evolution suggest that no marked decomposition
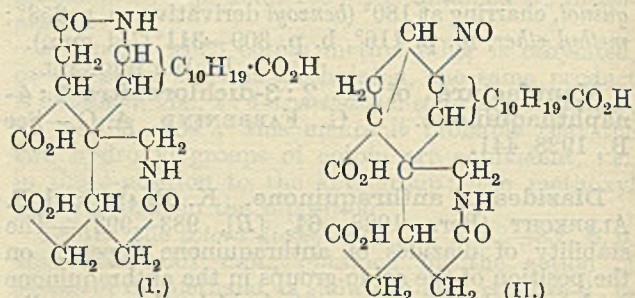
occurs, and it is considered probable that a change
occurs in the lactam grouping of the upper ring in (I)
with the production of a bridged ring; formula (II)
is tentatively suggested for this compound; the
latter decolorises alkaline potassium permanganate
only slowly, and is soluble in alkalis, the blue colour
being stable unless excess of alkali is present. If

the treatment with nitric
acid is more prolonged,
the blue colour disappears
and a colourless crystalline
product, which has not
been investigated further,
is obtained. The *diiso*-
oxime of *isobilianic* acid
(cf. this vol., 639), heated
with 25% hydrochloric
acid, yields a crystalline

substance, $C_{24}H_{35}O_9N, HCl$, m. p. about 248° after
sintering, and it is concluded that the nitrogen atom is
probably removed from the upper ring; formula
(III) is suggested for the corresponding free base,
but the latter has not yet been isolated.

A. WORMALL.

Nitration products of abietic acid. J. DUBOURG
(Bull. Inst. Pin, 1927, 241—246; Chem. Zentr.,
1928, i, 341—342).—Johansson's results (Ark. Kemi,
Min. Geol., 1917, No. 19) could not be repeated.
Addition of nitric acid (120 c.c.) to abietic acid (300 g.)
in boiling alcohol (600 c.c.) yields *dinitrodecahydro-
retenecarboxylic acid*, $C_{19}H_{26}O_2(NO_2)_2$, m. p. 162—
165°, $[\alpha]_{yellow}$ —115·2°, $[\alpha]_{green}$ —135·9° (in alcohol)
(*sodium, potassium, ammonium, zinc*, and *magnesium*
salts; *methyl* ester, m. p. 135—138°). *Aminodeca-
hydroretenecarboxylic acid*, $C_{19}H_{27}O_2NH_2$, has m. p.
226—228°. *Trinitro-octahydromethylphenanthrenecarb-
oxylic acid*, $C_{16}H_{16}(NO_2)_3 \cdot CO_2H$, m. p. 156—158°,
$[\alpha]_{yellow}$ —136·4°, $[\alpha]_{green}$ —157·2° (*sodium* salt), when
treated in alcoholic solution with sodium or sodium
ethoxide, yields an *acetal*, $C_{16}H_{17}O_6N_2$, m. p.
212—215°, and a *product*, $C_{20}H_{27}O_{10}N_2$, m. p.
120°; the latter with sulphuric acid affords a
product, $C_{16}H_{13}O_8N_2$, m. p. 97°. *Trinitroabietic acid*,
$C_{20}H_{27}O_2(NO_2)_3$, m. p. 177—178°, $[\alpha]_{yellow}$ —95°,
$[\alpha]_{green}$ —125°, is obtained by nitration of abietic acid
(20 g.) in carbon tetrachloride (200 c.c.) with ordinary
nitric acid (100 c.c.). An explosive *polynitro*-com-
pound is precipitated by water from a solution of
abietic acid in fuming nitric acid. A. A. ELDRIDGE.

Carotin. R. PUMMERER and L. REBMANN (Ber., 1928, **61**, [*B*], 1099—1102).—The absorption spectrum of carotin in *cyclo*hexane is compatible only with the presence of a large number of conjugated double linkings. When treated with perbenzoic acid in chloroform, carotin absorbs eight atoms of oxygen per mol., indicating the presence of eight double linkings if the normal course of the action be assumed. With iodine chloride, 11—11·5 mols. of reagent are absorbed per mol. of carotin. This value corresponds closely with the results expected from hydrogenation. The reaction does not, however, proceed normally, since it is accompanied by loss of about 3 mols. of halogen acid. The presence of eight double linkings appears definitely established, to which three "inert" double linkings may possibly be added. When similarly investigated, xanthophyll is found to have eight double linkings. H. WREN.

Rotenone, the active principle of the derris root. S. TAKEI (Ber., 1928, **61**, [*B*], 1003—1007; cf. A., 1925, i, 761).—Determinations of the mol. wt. of rotenone in benzene and camphor, combined with the isolation of a phenylhydrazone, m. p. 243—244°, and an *oxime*, m. p. 239°, lead to an alteration of the formula from $C_{19}H_{18}O_5$ to $C_{23}H_{22}O_6$. This change is applicable also to *iso*rotenone produced from rotenone by boiling 50% sulphuric acid or from *rotenone hydrochloride*, m. p. 188°, by the action of zinc dust and glacial acetic acid. Rotenic acid, $C_{12}H_{12}O_4$ (formerly $C_9H_{10}O_3$), is characterised by its *thallium* salt, m. p. 203°, and *acetyl* derivative, m. p. 155°. It is converted by ethereal diazomethane into the non-crystalline *methyl* ester of the methylated acid, from which the *methylated acid*, $C_{12}H_{11}O_3 \cdot OMe$, m. p. 115°, is obtained by hydrolysis; the latter substance yields a (?) *hydroxamic acid*, $C_{13}H_{14}O_3:N \cdot OH$, m. p. 120°. Nitration of rotenic acid gives ill-defined products from which *methyl nitromethylrotenate*, $NO_2 \cdot C_{11}H_9O(OMe) \cdot CO_2Me$, m. p. 120°, is obtained by aid of diazomethane. Distillation of rotenic acid causes loss of carbon dioxide and formation of a *phenol*, $C_{11}H_{12}O_2$, b. p. 271°/760 mm., m. p. 42°, and a *substance*, (?) $C_{22}H_{20}O_4$, m. p. 136°; the p-*toluene-sulphonyl* derivative, m. p. 105—106°, and the *methyl ether*, b. p. 137°/13 mm., of the phenol are described. An oxime could not be prepared from the phenol or its methyl ether. Oxidation of rotenic acid by aqueous permanganate affords *iso*butyric acid, whereas acetic acid is derived similarly from the phenol methyl ether. Rotenic acid is therefore regarded as a hydroxy*iso*propylcoumaronecarboxylic acid in which the position of the substituents remains undecided. H. WREN.

Constituents of *Myoporum lætum*, Forst. ("Ngaio"). III. Oxide rings of ngaione. F. H. McDOWALL (J.C.S., 1928, 1324—1331).—Ngaiol (A., 1927, 566), when treated with hydrogen and platinum-black in glacial acetic acid solution, gives an *oxido-glycol*, $C_{15}H_{28}O(OH)_2$, d_{20}^{20} 0·966, n_D^{20} 1·4664, differing in its colour reaction and in its physical constants from that obtained using Skita's colloidal palladium (*loc. cit.*). The oxide rings of the hydrogenated derivatives of ngaione can be opened by the action of hydrogen halides in glacial acetic

acid solution. Tetrahydrongaiene dioxide gives opening of only one oxide ring with formation of an oily *chloro-oxido-acetate*, $C_{15}H_{28}OCl \cdot OAc$. Tetrahydrongaiol with hydrogen iodide in glacial acetic acid suffers fission of both oxide rings with formation of an oily *polyiodide acetate*, probably $C_{15}H_{28}I_3(OAc)_3$, which cannot be reduced without the formation of an ethylenic linking. Hydrogenation of the product of reduction gives, after hydrolysis, a mixture of alcohols from which, by fractional distillation under reduced pressure, a paraffin *alcohol*, $C_{15}H_{31}OH$, b. p. 168—172°/29 mm., d_{20}^{20} 0·841, n_D^{20} 1·4474, was isolated. In one experiment, a paraffin *glycol*, $C_{15}H_{30}(OH)_2$, b. p. 200—215°/13 mm., n_{11}^{20} 1·4655, was obtained. The isolation of these last two compounds proves definitely the absence of carbocyclic rings from the molecule of ngaione. From the stability of ngaiol to water under pressure and of ngaiol and tetrahydrongaiol to acetic anhydride, it is concluded that an ethylene oxide ring is not present in ngaione. An *isomeride* of ngaiol, b. p. 188—190°/29 mm., d_{20}^{20} 1·013, n_D^{20} 1·4794, and a *sesquiterpene monoxide*, $C_{15}H_{24}O$, b. p. 160—170°, n_{20}^{20} 1·4894, d_{20}^{23} 0·9485, have been isolated from crude ngaiol.

The colour reaction given by furan derivatives with vanillin and concentrated hydrochloric acid (Asahina, A., 1924. i, 977) is also given by the majority of the oxides now described, as well as by ethyl ether, acetal, *iso*amyl ether, phenetole, anisole, diphenyl ether, and dimethylpyrone. M. CLARK.

Colouring matter of citrus juices. M. B. MATLACK (Amer. J. Pharm., 1928, **100**, 243—246).—The principal pigment of the Indian red pummelo and the pink grape fruit is lycopin. Pulp from the sweet orange, satsuma, and king mandarin gave less definite tests when subjected to the Molisch microcrystallisation method, an unsaponifiable *compound*, m. p. 75°, influencing the form of the crystals. Spectroscopic examination of light petroleum and alcoholic extracts of orange and tangerine pulp indicated the presence of carotin and xanthophyll. S. COFFEY.

Ultra-violet absorption curves of pulegone and *iso*pulegone. J. SAVARD (Compt. rend., 1928, **186**, 1436—1438, and Bull. Soc. chim., 1928, [iv], **43**, 524—529).—Whilst β-pulegone (A., 1926, 408) possesses the two absorption bands in the ultra-violet corresponding with those often observed in unsaturated and ketonic compounds, the bands of *iso*pulegone merge into each other. Pulegone obtained by distillation has a greater absorption in the band due to the double linking. Since this absorption is unchanged by treatment of the substance with potassium hydroxide, it is probably caused by the presence of the more unsaturated enolic tautomeride. G. A. C. GOUGH.

Optical activity and polarity of substituent groups. VIII. Growing-chain effects and *ortho*-effect in benzoic esters. H. G. RULE, W. HAY, and J. PAUL (J.C.S., 1928, 1347—1361).—The rotatory powers of a series of menthyl *n*-alkoxyacetates and menthyl hydrogen dicarboxylates have been measured for different wave-lengths both in solution and in the homogeneous state. The values for the alkoxy-acetates fall steeply to a minimum at propoxy-, rise

rapidly to a maximum at butoxy- and amyloxy-, and then fall to a minimum at heptyl- and octyl-oxy-acetates. The menthyl hydrogen dicarboxylates give a maximum for glutarate, a minimum for suberate, and another maximum for azelate. When these values are plotted against the length of the chain, which is measured from and includes the asymmetric atom, it is found that the maxima for one series almost coincide with the minima for the other. It is concluded from these results that the influence of o-substituents in optically active benzoates (this vol., 221) is propagated through space. A pronounced alternation in the rotatory powers of the menthyl hydrogen dicarboxylates is found, which disappears in the sodium salts. It is suggested that the alternation is a superimposed secondary effect due to association of the hydrogen esters through the carboxyl groups.

The following compounds are described : l-*menthyl propoxyacetate*, b. p. 161°/14 mm.; n-*butoxyacetic acid*, b. p. 115—116°/10 mm. (l-*menthyl* ester, b. p. 172·5°/14 mm.), from sodium butoxide and sodium chloroacetate; n-*amyloxyacetic acid*, b. p. 134°/12 mm. (*acid chloride*, b. p. 103°/64 mm.; l-*menthyl* ester, b. p. 148°/14 mm.); n-*hexyloxyacetic acid*, b. p. 143—144°/10 mm. (*acid chloride*, b. p. 106—108°/22 mm.; l-*menthyl* ester, b. p. 187°/10 mm.); n-*heptyloxyacetic acid*, b. p. 156°/10 mm., m. p. 7·5—8·5° (*acid chloride*, b. p. 116°/16 mm.; l-*menthyl* ester, b. p. 200°/11 mm.), and n-*octyloxyacetic acid*, b. p. 166°/10 mm., m. p. 12·5—13·5° (*acid chloride*, b. p. 125—126°/12 mm.; l-*menthyl* ester, b. p. 183°/2 mm.). l-*Menthyl hydrogen glutarate*, *adipate*, *pimelate*, *suberate*, *azelate*, and *sebacate* were obtained by partial hydrolysis of the corresponding dimethyl esters.   H. BURTON.

Carene. M. LAGACHE (Bull. Inst. Pin, 1927, 233—239; Chem. Zentr., 1928, i, 339).—The oil from *Pinus longifolia* has d^{20} 0·875, n_Y^{20} (Hg yellow) 1·4797, n_G^{20} (Hg green) 1·4803, α_Y −1·51°, α_G −1·18°, and yields l-pinene 24·8%, nopinene 9·7%, a terpene and carene 37·6%, an l-terpene 1·7%, oxidation products and longifolene 20·2%, and residue 6·8%. The carene has b. p. 70°/10 mm., d^{25} 0·8635, n_D^{25} 1·4678, n_G^{25} 1·4682, n_Y^{25} 1·4700, $[\alpha]_Y$ +17·13°, $[\alpha]_G$ +19·88° (nitrosochloride, m. p. 101—102°, $[\alpha]_Y$ +254·80°, $[\alpha]_G$ +288·62°); nitrosocarene has m. p. 89—90°, $[\alpha]_Y$ +160°, $[\alpha]_G$ +185°; carenenitrolmethylamine, m. p. 180°, $[\alpha]_Y$ +153·90, $[\alpha]_G$ +188·9°; carenenitrolethylamine, m. p. 155°, $[\alpha]_Y$ +135·6°, $[\alpha]_G$ +176°; carenenitrolpropylamine, m. p. 95°, $[\alpha]_Y$ +123·4°, $[\alpha]_G$ +181·4°.   A. A. ELDRIDGE.

Preparation of bromocamphor. F. CHEMNITIUS (Pharm. Zentr., 1928, 69, 307—309).—The slow addition of bromine (1 mol.) to camphor at 40—45° yields dibromocamphor, which loses hydrogen bromide when heated at 70° and finally at 120° for 3 hrs. The crude product is then poured into 10% potassium carbonate solution. By recrystallisation from alcohol and recovery from mother-liquors, a total yield of 80% of theory of bromocamphor, m. p. 76°, is obtained.   R. K. CALLOW.

Dynamic isomerism. XXVII. Absorption spectra of prototropic compounds. Physical properties of the stable and labile forms of benzoylcamphor. T. M. LOWRY, C. A. H. MACCONKEY, and H. BURGESS (J.C.S., 1928, 1333—1347).—Measurements have been made of the m. p., optical rotation, rotatory dispersion, solubility, and ultra-violet absorption of the enolic and ketonic forms of benzoylcamphor. Contrary to the statement of Morton and Rosney (A., 1926, 454) " that the two isomeric forms of benzoylcamphor give bands at the same wave-length but of unequal intensity," the absorption bands of the enol and ketone are shown to be of almost equal intensity, whilst differing widely in wave-length. The absorption of the equilibrium mixture in very dilute alcoholic solutions corresponds closely with that of a mixture of two parts of enol and one part of ketone. Van 't Hoff's relation between the solubilities of the two forms and their equilibrium concentrations has been tested for solutions in alcohol, acetone, and benzene and found to hold good within ±8%. The ratio of the initial and final solubilities of the enolic form indicates that the equilibrium mixture in a saturated alcoholic solution contains about 58% of enol, in close agreement with the proportion, 59%, deduced from the optical rotations of the solutions.

Improved methods of preparation of the enolic and ketonic forms of benzoylcamphor are described.   M. CLARK.

β-2-Furylethylamine. T. YABUTA and K. KAMBE (Proc. Imp. Acad. Tokyo, 1928, 4, 120—121).—β-2-Furylethylamine (*picrolonate*) (Windaus and Dalmer, A., 1921, i, 117) is conveniently prepared by reducing β-nitro-2-furylethylene with aluminium amalgam to 2-furylacetaldoxime (Asahina and Fujita, A., 1923, i, 239) and then the latter with sodium amalgam. The nitrofurylethylene is obtained by the action of nitrous fumes on β-2-furylacrylic acid in benzene solution.   J. STEWART.

Condensation products of furfuraldehyde with acid amides. K. BEAUCOURT (Monatsh., 1928, 49, 1—7).—Condensation of furfuraldehyde (1 mol.) with acid amides (2 mols.) by heating the components together for $3\frac{1}{2}$—4 hrs. on a water-bath in a current of carbon dioxide, occurs thus : $C_4H_3O\cdot CHO + 2NH_2\cdot COR = C_4H_3O\cdot CH(NH\cdot COR)_2 + H_2O$. In this way from the appropriate acid amide are prepared *furfurylidene-diacetamide* (yield 40%), m. p. 197° (decomp.); -*dipropionamide* (yield 35%), m. p. 195° (decomp.); -*di-n-butyramide* (yield 35—40%), m. p. 181° (decomp.); -*dibenzamide* (30—35% yield), decomp. 185°. With formamide only resinous products, from which no crystalline compound could be isolated, were obtained. The use of condensing agents (hydrochloric acid or pyridine) reduces the yields to nearly one half.   J. W. BAKER.

Esters of furoylacetic acid. J. E. ZANETTI and C. O. BECKMANN (J. Amer. Chem. Soc., 1928, 50, 1438—1442).—The *methyl* ester, b. p. 144—145°/20 mm. [*sodium*, *potassium*, and *copper* salts; *oxime*, m. p. 124—125°; *semicarbazone*, m. p. 141—142° (decomp.)]; n-*propyl* ester, b. p. 110—112°/1 mm. (*sodium* and *copper* salts; *oxime*, m. p. 120—121°; *semicarbazone*, m. p. 137—138°), and n-*butyl* ester, m. p. 25·2°, b. p. 136—138°/3 mm. (*copper* salt; *oxime*, m. p. 102°; *semicarbazone*, m. p. 127—128°),

of furoylacetic acid have been prepared. The m. p. of the above oximes are determined at a standard rate of heating (4°/min.), and are actually the temperatures of conversion into 3-furyloxazolone (A., 1910, i, 892). The stability of these oximes is not in accordance with the order of attraction of the furyl group for hydroxyl given by Hantzsch, whilst their relative stability is not in accordance with Abegg's theory (A., 1899, i, 327). H. E. F. NOTTON.

Action of ethyl formate on dibenzyl ketone. E. BENARY and G. A. BITTER (Ber., 1928, 61, [B], 1057—1060).—Dibenzyl ketone is converted by an excess of sodium ethoxide and ethyl formate in anhydrous ether into the disodium salt of di(hydroxymethylenebenzyl) ketone, recognised by its conversion by water and aniline hydrochloride into the *dianilide*, $CO(CPh:CH\cdot NHPh)_2$, m. p. 165—166°. If, however, the sodium salt is treated with dilute sulphuric acid, 3 : 5-*diphenyl* : 4-*pyrone*, m. p. 186—187°, is obtained. The latter substance is transformed by ammonium acetate into 4-*hydroxy*-3 : 5-*diphenylpyridine*, m. p. 376° after darkening, reduced by sodium and alcohol to 4-*hydroxy*-3 : 5-*diphenylpiperidine*, m. p. about 310° after darkening at 290°, and converted by distillation with zinc dust into 3 : 5-*diphenylpyridine*, m. p. 193—194° (*picrate*, m. p. 276°). If excess of sodium ethoxide and ethyl formate is avoided in the action on dibenzyl ketone, the main product is *hydroxymethylenedibenzyl ketone*, converted by phenylhydrazine into 1 : 4-*diphenyl*-5(3)-*benzylpyrazole*, m. p. 128°. Diethyl ketone gives only the monohydroxymethylene derivative when an excess of ethyl formate and sodium ethoxide is employed.

H. WREN.

Heteropolar carbon compounds. VI. *spiro*-**Pyrans.** W. DILTHEY and H. WÜBKEN (Ber., 1928, 61, [B], 963—968).—The development of colour in hot solutions of *spiro*dinaphthapyran, $\left(\begin{array}{c}CH{=}CR\\C_{10}H_6\cdot O\end{array}\right){>}C$ (cf. Löwenbein and Katz, A., 1926, 956; Dilthey and others, A., 1926, 1254; Dickinson and Heilbron, A., 1927, 251) has been ascribed by Dilthey to ionic dissociation, and this view has been shared by Dickinson and Heilbron (A., 1927, 884), who, however, find that coloration is not developed by 3 : 3′-dialkyl*spiro*naphthapyrans. Confirmation of the authors' theories is found in the observation that the ability of *spiro*pyrans to yield coloured solutions is paralleled by their tendency towards salt formation and that the phenomenon is not principal in nature. Thus 3 : 3′-diethyl*spiro*benzopyran appears incapable of forming a salt with hydrogen chloride and the diminished basicity goes hand in hand with a hypsochromic effect. Also the *spiro*dinaphthopyran from *cyclo*hexanone (I) (cf. Dickinson and Heilbron, *loc. cit.*) gives only violet salts which are not readily isolated; in alcohol, pyridine, xylene, or chlorobenzene it does not develop colour when heated, but this is due only to insufficiently high temperature, since in diphenyl ether (b. p. 250°) it is violet and

(I.) [structure: CH_2, CH_2 CH_2, $C_{10}H_6$ C $C_{10}H_6$, O O]

becomes colourless again when cooled. The inhibitive effect of 3 : 3′-disubstitution is therefore not absolute. Further, the development of colour by 3-amyl*spiro*dinaphthopyran in pyridine is greatly facilitated by the addition of a little water; the observation is more readily explained by an ionic dissociation than by a quinonoid transformation.

3-*Amyl*spiro*dinaphthopyran*, m. p. 182° [*perchlorate*, m. p. 256°; *perchlorate* of *acetylated base*, m. p. 204° (decomp.)], is prepared by saturating an alcoholic solution of 2-hydroxynaphthaldehyde and methyl hexyl ketone with hydrogen chloride. 3 : 3′-Trimethylene*spiro*dinaphthopyran forms colourless crystals, m. p. 238°; the normal *hydrochloride* and the *perchlorate*, complete decomp. 190°, are described. 3 : 3′-Dimethyl*spiro*dinaphthopyran, m. p. 237—238°, is obtained with certainty by the action of 2-hydroxynaphthaldehyde on diethyl ketone in glacial acetic acid saturated with hydrogen chloride; the unstable *picrate* is described. 3 : 3′-*Diphenyl*spiro*dinaphthopyran*, $C_{37}H_{24}O_2$, m. p. 247—248°, is prepared from dibenzyl ketone and a large excess of 2-hydroxynaphthaldehyde. In glacial acetic acid saturated with hydrogen chloride, the reactants give, after addition of perchloric acid, 3-*phenyl*-2-*benzylnaphthopyrylium perchlorate*, m. p. indef. 212—214°, which in boiling alcohol passes into 3-*phenyl*-2-*benzylidene*-5 : 6-*benzo*-2-*chroman*, m. p. 146°. H. WREN.

m-**Nitrobenzylidenedi-β-naphthol** [*m*-nitro-**phenyldi-2-hydroxy-α-naphthylmethane**]. O. DISCHENDORFER (Monatsh., 1928, 49, 133—145).—The formation of a yellow *compound*, m. p. 61·5°, of 1 mol. of β-naphthol with 1 mol. of *m*-nitrobenzaldehyde when the two substances are melted together at 70°, or heated in petroleum solution on a water-bath, is confirmed by thermal analysis. The eutectic mixture has m. p. 47·5° and contains 17·5% of β-naphthol. Since solutions of this compound are colourless it is assumed that it is completely dissociated in solution. *m*-Nitrophenyldi-2-hydroxy-α-naphthylmethane (I) (Zenoni, A., 1894, i, 136) yields a *monosodium* salt when it is dissolved in 6% sodium hydroxide solution, a *dibenzoate*, m. p. 193—194°, and a *dimethyl ether*, m. p. 216°. It is converted by oxidation with sodium hypobromite in

[structure (I.), labelled NO₂ and HO OH]
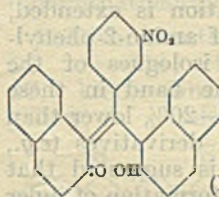
alcohol solution into *dehydro*-*m*-*nitrobenzylidenedi*-β-*naphthol* (annexed formula), m. p. 221—222° [*oxime*, m. p. 216—217° (decomp.)]. Dehydration of (I) with concentrated sulphuric acid yields 9-*m*-*nitrophenyl*-1 : 2 : 7 : 8-*dibenzoxanthen* (II) (Zenoni, *loc. cit.*), which is also obtained by heating *m*-nitrobenzaldehyde and β-naphthol in a mixture of acetic and concentrated sulphuric acids at 50°. It is oxidised by heating with concentrated sulphuric acid on a water-bath to the hydrogen sulphate of 9-*nitrophenyl*-1 : 2 : 7 : 8-*dibenzoxanthhydrol* (III), m. p. 286—287° (decomp.) (*ethyl ether*, m. p. 266—267°; *methyl ether*, m. p. 256—257°), which is best obtained by decomposition with aqueous acetone of the *ferric chloride double* salt, m. p. 264° (decomp.), of the pyrylium chloride (below), which is obtained by

oxidation of the pyran (II) with manganese dioxide in a boiling mixture of acetic and hydrochloric acids and treatment of the resulting solution with ferric chloride. When a chloroform solution of (III) is treated with acetyl chloride and anhydrous hydrogen chloride passed into the solution at the ordinary temperature, it is converted into 9-*nitrophenyldinaphthopyrylium chloride hydrochloride*, m. p. 281° (decomp.) [*mercurichloride*, m. p. 286° (decomp.); *perbromide*, m. p. 225° (decomp.); *perchlorate*, m. p. 307° (decomp.)]. When (II) is reduced with zinc dust and acetic acid it yields 9-m-*acetamidophenyl-1 : 2 : 7 : 8-dibenzoxanthen*, m. p. 246—247°, which, on hydrolysis, is converted into the corresponding 9-m-*aminophenyl* derivative, m. p. 242—243°.

J. W. BAKER.

Colour and chemical constitution. XXIII. The pigments of flowers. J. MOIR (Trans. Roy. Soc. S. Africa, 1928, **16**, 121—130; cf. this vol., 184).—The variation in colour of natural anthocyanidins and similarly constituted synthetic substances with the number and position of hydroxyl groups in the molecule has been investigated spectroscopically and the results are tabulated and discussed. A regular gradation of shade is found as the anthocyanidin is simplified down to the parent substance by the successive removal of hydroxyl groups. The presence of these groups in positions 4′ and 7 has the greatest effect in heightening the colour. When hydroxyl groups are present in these positions the presence of a hydroxyl group in positions 3 or 5 only broadens the absorption band without changing its position, but when they are absent the introduction of a hydroxyl group in position 3 has a marked effect. In acid solution, in which the compounds are supposed to exist as double oxonium chlorides, there is a gradual shift of colour from the yellow (flavylium chloride, λ 392) to the violet end of the spectrum (delphinidin, λ 545) as the number of hydroxyl groups is increased, this effect being due, probably, to loading by inactive (non-ionised) hydroxyl groups. In acid solution the methoxyl group has only a very slightly greater effect than the hydroxyl. A similar colour shift towards the violet occurs when the solution approaches neutrality, and the absorption spectra of nine derivatives in a medium of p_H 5—6 are recorded. The investigation is extended, in a medium of p_H 5, to a series of amino-2-phenylquinoline derivatives which are isologues of the anthocyanidins; the centre of the band in these derivatives occurs at a position 10—20% lower than that of the corresponding oxygen derivatives (*e.g.*, 2-phenylquinoline, λ 358), and it is suggested that this is due to the possibility of the formation of inner oxonium salts in the oxygen but not in the nitrogen derivatives. In alkaline solution the colour of the anthocyanidin is shifted towards the violet end of the spectrum (delphinidin, λ 690 and 590), this being due to the hydroxyl groups acting as positive centres and not as loading groups, the oxonium structure disappearing and the substances having the carbinol configuration. A displacement of the band towards the violet also occurs when the distance between the auxochrome group and the other active centre (oxonium atom) is increased by lengthening the side-chain,

and the positions of the bands of numerous flavylium, benzopyrylium, and carbocyanine derivatives are tabulated. The observation of Buck and Heilbron (J.C.S., 1922, **121**, 1204) that the absorption spectra of their styrylbenzopyrylium salts does not change when the colour changes from red to bluish-green is incorrect, the green phase possessing a strong band in the far red (λ 675 for the 4′-hydroxy-, and λ 700 for the 3′ : 4′-dihydroxy-compounds respectively) which was overlooked. The effect of replacing the quinoline ring by benzthiazole, benzoxazole, and benziminazole rings is also considered. The following new compounds have been prepared in the course of the investigation (no experimental details are given) : 7-*amino*- (λ 426), 4′-*amino*- (λ 407), 7 : 4′-*diamino*- (λ 430), 5 : 7 : 4′-*triamino* -2-*phenylquinolines*, which are obtained by condensation of the appropriate nitrobenzaldehyde with p-nitroacetophenone in the presence of potassium hydroxide, reduction of the resulting nitrophenyl styryl ketone with sodium hyposulphite, and closure of the quinoline ring by the action of acids.

J. W. BAKER.

Oxidation of phenols. X. Addition of triphenylmethyl to radicals with univalent oxygen and to aromatic peroxides. R. PUMMERER and F. LUTHER (Ber., 1928, **61**, [*B*], 1102—1107).—Confirmation of the views of Pummerer and Rieche (A., 1926, 1135) on the constitution of "dinaphthyldiperoxidnaphthylene oxide" (I) is found in the

(I.)
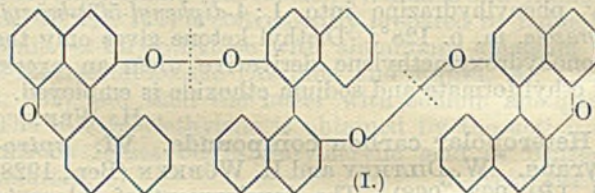
observation that it suffers fission at the dotted lines when treated with a solution of triphenylmethyl in benzene in complete absence of oxygen, the yield of the *ditriphenyl ether* of *dinaphthol*, m. p. 289° (from the middle portion), amounting to 60% if the triphenylmethyl is added to the compound. The ether, obtained also from β-dinaphthol and triphenylmethyl chloride in pyridine solution, is an unusually stable substance which is unaffected by permanganate, and hence undoubtedly contains the triphenylmethyl group attached to oxygen. The *triphenylmethyl ether* of *hydroxydinaphthylene oxide*, m. p. 237°, is more difficult to isolate. It is stable towards permanganate and therefore cannot be a derivative of the corresponding keto-methyl. It is unusually stable towards alcoholic potassium hydroxide or hydrogen chloride, but is converted by boiling concentrated sulphuric acid into triphenylcarbinol and hydroxydinaphthylene oxide, which is partly oxidised by the acid to dinaphthylene dioxide. Synthesis of the ether from hydroxydinaphthylene oxide and triphenylmethyl chloride could not be effected in pyridine or through the sodium compound. It is readily obtained from hydroxydehydrodinaphthylene oxide and triphenylmethyl in benzene. H. WREN.

2 : 7-Dimethylsulphonefluoran, 2′-hydroxy-5′-toluoylbenzene-2-sulphonic acid, and some of

their derivatives. W. R. ORNDORFF and I. T. BEACH (J. Amer. Chem. Soc., 1928, 50, 1416—1421).—o-Chlorosulphonylbenzoyl chloride and sodium p-tolyloxide give at 30—35° p-*tolyl o-chlorosulphonylbenzoate*, m. p. 138°; and at 100°, di-p-*tolyl o-sulphobenzoate** (* crystallographic data), m. p. 95·5°. When this is fused with zinc chloride and the product extracted with aqueous sodium carbonate, it affords the *sodium* salt* (+1·5EtOH) of 9-*hydroxy*-9-*phenyl*-2 : 7-*dimethylxanthen-o-sulphonic acid* [*barium* salt (+4H₂O); *methyl* ester; yellow *perchlorate*], which is converted by acid into orange 2 : 7-*dimethylsulphonefluoran**, decomp. 250°. This is probably similar in constitution to 3 : 6-dimethylsulphonefluoran (A., 1926, 1036); it is formed in poor yield from o-sulphobenzoic anhydride, p-cresol, and zinc chloride at 123°. With sodium hydroxide at 200—220° it gives 2 : 7-dimethylxanthone, and at 280—290°, 2-hydroxy-5-toluic acid, with hydrogen chloride, an unstable *monohydrochloride*, with bromine, products of indefinite composition, with zinc dust and boiling water, the *zinc* salt of 2 : 7-*dimethylhydrosulphofluoranic acid* (9-*phenyl*-2 : 7-*dimethylxanthene-o-sulphonic acid*), and with sulphuric acid at 200°, reddish-brown 2 : 7-*dimethylsulphonecœroxonol*, C₂₁H₁₆O₄S (cf. Decker and Ferrario, A., 1906, i, 687). 2′-*Hydroxy*-5′-*toluoylbenzene*-2-*sulphonic acid*, m. p. 90° (*ammonium* salt*), is obtained from o-sulphobenzoic anhydride and p-cresol in presence of tetrachloroethane and aluminium chloride at 100—110°. When heated with p-cresol it gives 2 : 7-dimethylsulphonefluoran.   H. E. F. NOTTON.

Cyclic disulphides derived from diphenyl. H. J. BARBER and S. SMILES (J.C.S., 1928, 1141—1149).—An improved method of preparing sodium 2-iodobenzenesulphonate is described. From this by treatment with copper powder (merely in boiling aqueous suspension) and then with phosphorus pentachloride are obtained successively diphenyl-2 : 2′-disulphonic acid and diphenyl-2 : 2′-disulphonyl chloride. Reduction of this disulphonyl chloride with zinc dust and hydrochloric acid yields 2 : 2′-*dithioldiphenyl*, m. p. 78—79°; oxidation of the dimercaptan with ferric chloride gives *diphenylene* 2 : 2′-*disulphide*, m. p. 113° (*disulphoxide*, m. p. 128°), converted by copper powder at 250° into dibenzthiophen. 2 : 2′-Dithioldiphenyl gives, with sodium chloroacetate, 2 : 2′-*dicarboxymethylthioldiphenyl*, m. p. 201—202°, with carbonyl chloride it gives *diphenylene*-2 : 2′-*dithiolcarbonate*, m. p. 101·5°, whilst it condenses with aldehydes and ketones, yielding, for example, *benzaldehyde diphenylene*-2 : 2′-*mercaptol*, m. p. 105—106°, *acetone diphenylene*-2 : 2′-*mercaptol*, m. p. 95°, and *benzil diphenylene*-2 : 2′-*mercaptol*, m. p. 198°. 4 : 4′-*Dimethyldiphenyl*-2 : 2′-*disulphonyl chloride*, m. p. 117—118°, prepared by general reactions from sodium-4-iodotoluene-3-sulphonate, cannot be reduced to a cyclic disulphide by zinc and hydrochloric acid, since m-tolylmercaptan (p-*nitrobenzoyl* derivative, m. p. 96°) is the main product. Diphenyl-3 : 3′-disulphonyl chloride gives the corresponding *dithiol* (*dimethyl* derivative, m. p. 50°) when reduced with zinc dust and acid, and this compound is converted into amorphous, insoluble products when

it is oxidised. 4 : 4′-*Dichlorodiphenyl*-3 : 3′-*disulphonyl chloride*, m. p. 179°, obtained from benzidine-3 : 3′-disulphonic acid, yields on reduction the corresponding *dithiol* (*dimethyl* derivative, m. p. 130°), which is converted by oxidation into amorphous, insoluble material.

Diphenyl-4 : 4′-*disulphinic acid*, m. p. 143°, prepared by reduction of the corresponding disulphonyl chloride with boiling alkaline sulphite solution, is converted by mineral acid into an amorphous material, probably a disulphoxide of high mol. wt. 1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonic acid* (*potassium* salt) is formed by the action of copper powder on potassium 1-iodonaphthalene-2-sulphonate in the presence of a little copper sulphate. Reduction of 1 : 1′-*dinaphthyl*-2 : 2′-*disulphonyl chloride*, m. p. 202—203°, with zinc dust and hydrochloric acid yields 2-naphthyl mercaptan. With alkaline sulphite followed by acidification, the cyclic *disulphoxide* is produced, and this on reduction with hydriodic acid gives 1 : 1′-*dinaphthylene* 2 : 2′-*disulphide*, m. p. 214°. When this substance is kept at 250° with copper powder, 1 : 1′-*dinaphthylene* 2 : 2′-*sulphide*, m. p. 202°, is obtained. It is pointed out that the fact that no cyclic disulphides are obtained from the 4 : 4′- and 3 : 3′-dithioldiphenyl derivatives, whereas 2 : 2′-dithioldiphenyl readily affords a cyclic disulphide, is in harmony with recent views on the stereochemistry of the diphenyl nucleus. The following compounds are described : *di*-2-*iodophenyl disulphide*, m. p. 133°; 2-*iodophenylsulphinic acid*, m. p. 108°; 2-*iodophenylmethylsulphone*, m. p. 109°; 2-*iodotoluene*-5-*sulphonic acid* [*barium* salt (+1½H₂O); *sulphonyl chloride*, m. p. 61—62°; *amide*, m. p. 135°]; 4-*iodotoluene*-3-*sulphonic acid* [*potassium* salt (+H₂O); *sulphonyl chloride*, m. p. 68°; *amide*, m. p. 161—162°]; *di*-4-*iodo*-m-*tolyl disulphide*, m. p. 104—105°; 1-*iodonaphthalene*-2-*sulphonic acid* (*barium* salt; *sulphonyl chloride*, m. p. 94°); 1-*iodonaphthalenesulphinic acid*, m. p. 143°; and *di*-1-*iodo*-2-*naphthyl disulphide*, m. p. 154°. Thianthren derivatives are formed when o-iodo-disulphides are heated with copper powder.

From di-o-iodophenyl disulphide, di-4-iodotolyl 3-disulphide, and di-1-iodonaphthyl 2-disulphide are thus obtained thianthren, 2 : 6-dimethylthianthren, and dinaphthathianthren, respectively.   M. CLARK.

*lin*Dithioxanthone. C. FINZI (Gazzetta, 1928, 58, 269—278; cf. Davis and Smiles, J.C.S., 1910, 97, 1290).—lin*Dithioxanthone* (I), m. p. 316°, yellow, is obtained by dehydrating by sulphuric

(I.)   (II.)
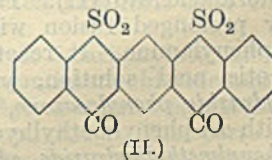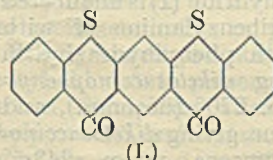
acid at 100° the m-*phenylenedithio*-2 : 2′-*dibenzoic acid* [1 : 3-*bis*(o-*carboxyphenylthiol*)*benzene*], C₆H₄(S·C₆H₄·CO₂H)₂, m. p. 270°, which is obtained by the condensation of thioresorcinol with diazotised anthranilic acid. (When the latter condensation is effected in an acid medium, m-*phenylenebis*[*thio*-o-*diazobenzoic acid*], C₆H₄(S·N₂·C₆H₄·CO₂H)₂, is obtained, unstable towards alkali.) The acid is

oxidised by peracetic acid to m-*phenylene bis-o-carb-oxyphenylsulphone*, m. p. 201°, with probably some sulphonic acid, and the dithioxanthone, stable to mild oxidising agents, by persulphuric acid to the corresponding *dibenzophenonedisulphone* (II), m. p. 305° (decomp.). When the dithioxanthone is dissolved in alcohol containing potassium ethoxide, and is treated with zinc, the colour of the solution changes through purple to green; on acidification, the *dithio-xanthhydrol*, m. p. 224° (decomp.), is obtained.

In either an acid or an alkaline medium, the sodium salt of dithioresorcinol reacts with diazotised o-amino-benzyl alcohol to give the stable m-*phenylenebis-(thio-o-diazobenzyl alcohol)*; in acid solution, diazotised 3-amino-β-naphthoic acid similarly reacts to give m-*phenylenebis(thio-3-diazo-β-naphthoic acid)*.

E. W. WIGNALL.

Imide ring closure in derivatives of diketo-succinic acid phenylosazone. F. D. CHATTAWAY and W. G. HUMPHREY (J.C.S., 1928, 1094—1098).—The formation of derivatives containing the imide ring by the action of ammonia, primary amines, and α-hydrazines on diketosuccinic anhydride phenyl-osazone (I) (A., 1927, 776) is described.

Fusion of the anhydride (I) with carbamide yields *diketosuccinimide phenylosazone*, m. p. 189°, which dissolves in boiling sodium hydroxide solution with evolution of ammonia, giving sodium diketosuccinate phenylosazone (II). The last-named compound is immediately converted by acids into 4 : 5-diketo-1-phenylpyrazoline-3-carboxylic acid 4-phenylhydr-azone (III). Benzylamine combines with the anhydride (I), yielding the *benzylamine* salt of *diketo-succinobenzylamic acid phenylosazone*, m. p. 165° (decomp.), from which the base is readily removed with regeneration of the anhydride by heating with acetic anhydride. Acidification of the benzylamine salt yields *diketosuccinobenzylimide phenylosazone*, m. p. 179°. Dibenzylamine reacts similarly, giving the *dibenzylamine* salt of *diketosuccinodibenzylamic acid phenylosazone*, m. p. 161—162° (decomp.), converted on acidification into *diketosuccinodibenzylamic acid phenylosazone*, m. p. 180°. Aniline reacts with the anhydride (I) giving a mixture of *diketosuccin-anilic acid phenylosazone* (IV), m. p. 201° (decomp.) (+AcOH, m. p. 135—200°, dependent on rate of heating), and *diketosuccinanil phenylosazone* (V), m. p. 252° (decomp.). The compound (IV) is converted by prolonged boiling with aniline into (V) and by prolonged boiling with aqueous-alcoholic hydro-chloric acid into (III). The anhydride (I) is unaffected by prolonged fusion with tribenzylamine or with diphenylamine. It reacts with phenylhydrazine in acetic acid solution, yielding *diketosuccinophenyl-hydrazide phenylosazone*, m. p. 270° (decomp.), and with as.-phenylmethylhydrazine, giving *diketosuccino-phenylmethylhydrazide phenylosazone*, m. p. 243·5° (decomp.). Analogous derivatives of certain sub-stituted phenylhydrazones and osazones of diketo-succinic anhydride have also been prepared. The tolylhydrazones yield with aniline the corresponding anils, the ketonic group remaining unchanged. Phenylhydrazine acts on the ketonic group as well as forming the hydrazide. The 2 : 4-dichloro- and 2 : 4-dibromo-anhydrides react with aniline less readily,

the products consisting entirely of the corresponding anils. The following are described : *diketosuccinanil* p-*tolylhydrazone*, m. p. 199° (decomp.); *diketosuccino-phenylhydrazide o-tolylphenylosazone*, m. p. 250° (decomp.); *diketosuccinanil 2 : 4-dichlorophenylosazone*, m. p. 308° (decomp.); *diketosuccinanil 2 : 4-dibromo-phenylosazone*, m. p. 309° (decomp.); *diketosuccino-phenylhydrazide 2 : 4-dichlorophenylosazone*, m. p. 280° (decomp.); *diketosuccinophenylhydrazide 2 : 4-di-bromophenylosazone*, m. p. 295° (decomp.). All the compounds described containing the succinimide ring are, like the parent substance, very stable towards acids, but are converted by boiling 10% sodium hydroxide solution into sodium diketo-succinate phenylosazones. M. CLARK.

Action of aniline on d-glutamic acid. W. H. GRAY (J.C.S., 1928, 1264—1267; cf. Hugounenq and others, A., 1924, i, 17).—Abderhalden and Schwab (A., 1926, 734) state that 2-hydroxypyrroline-5-carboxylic acid, the enolic form of 2-pyrrolidone-5-carboxylic acid, is obtained when d-glutamic acid is heated with aniline or diphenylamine. The product obtained in the first case is shown to be l-2-*pyrrolidone-5-carboxy-anilide*, m. p. 191°, $[\alpha]_D^{15}$ +17·9° in 80% alcohol (p-*bromo*-derivative, m. p. 212°; l-*acetyl* derivative, m. p. 166°; l-*dibenzyl* derivative, m. p. 158°). In the second case, only l- and dl-2-pyrrolidone-5-carboxylic acids could be isolated, and neither these nor the anilide could be reduced by catalytic hydrogenation. dl-2-*Pyrrolidone-5-carboxyanilide* has m. p. 204°.

M. CLARK.

Pirylene. J. VON BRAUN and W. TEUFFERT (Ber., 1928, 61, [B], 1092—1099).—The constitutions

$CH_2{:}C{<}^{CH}_{CH_2}{>}CH$ or $CH{<}^{CMe}_{C:CH_2}$, are rendered prob-

able for pirylene, the ultimate product of the Hofmann degradation of piperidine.

2-*Methylene*-N-*dimethylpyrrolidinium chloride*, m. p. 217° (corresponding chloroaurate, m. p. 265°), is converted by hydrogen in the presence of colloidal palladium or nickel into 2-*methyl*-N-*dimethylpyrrolid-inium chloride*, m. p. not below 280°. The methylene compound is smoothly transformed by distillation with potassium hydroxide into N-dimethylpiperideine, $CH_2{:}C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$, b. p. 136—138°, d^{19} 0·7979, n_D^{19} 1·4635 (chloroaurate; methochloride and the corresponding chloroplatinate and chloroaurate), the constitution of which is established by catalytic hydrogenation to α-dimethylamino-n-pentane. Treat-ment of dimethylpiperideine methiodide with potass-ium hydroxide affords pirylene, b. p. 60°, d_4^{19} 0·7443, n_D^{19} 1·4505. The hydrocarbon contains two double linkings, since it readily yields an oily tetrabromide and absorbs 2 mols. of hydrogen. It is oxidised by permanganate to a mixture of acetic and oxalic acids.

The initial stages of the transformation of tetra-hydroisoquinoline resemble closely those of piperidine. Thus, o-vinylbenzyldimethylamine is converted by bromine in chloroform into 2-*bromomethyl*-N-*dimethyl-dihydroisoindolium bromide*,

$C_6H_4{<}^{CH(CH_2Br)}_{CH_2}{>}NMe_2Br$, m. p. 181—182° (de-comp.) (corresponding chloride and chloroplatinate, decomp. 198°). It is converted by the successive action

of silver oxide and hydrochloric acid into 2-*methylene*-N-*dimethyldihydro*isoindolium chloride,

$$C_6H_4 {<}^{C(:CH_2)}_{-CH_2}{>}NMe_2Cl,$$ m. p. 159° (*chloroaurate*, m. p. 184°, decomp. 190°; *chloroplatinate*, m. p. 218—219°), which is catalytically hydrogenated to 2-*methyl*-N-*dimethyldihydro*isoindolium chloride, m. p. 229° (*chloroaurate*, m. p. 166°; *chloroplatinate*, m. p. 201°). Treatment of the unsaturated chloride with potassium hydroxide yields a highly unstable liquid (possibly a basic alcohol) and, mainly, the *ether*, [CH$_2$:C(NMe$_2$)·C$_6$H$_4$·CH$_2$]$_2$O, b. p. 180—190°/3 mm. (*methiodide*, C$_{24}$H$_{34}$ON$_2$I$_2$, m. p. 211°), which is indifferent to phenylhydrazine, semicarbazide, Fehling's and ammoniacal silver solutions. It is reduced to the corresponding *tetrahydro*-derivative, b. p. about 190—200°/3 mm. (*methiodide*, m. p. 188°).

H. WREN.

Isomerisation phenomena in heterocyclic nitrogen compounds. N. PUTOCHIN (J. Russ. Phys. Chem. Soc., 1928, **59**, 761—817).—A detailed *résumé* is given of former work on isomerisation reactions in heterocyclic nitrogen compounds, and an investigation of the effect of condensations with alkyl halides and formaldehyde on such reactions. It is suggested that condensation first occurs on the nitrogen atom, followed by a migration to a carbon atom of the nucleus, with or without a change in the size of the ring. Such reactions proceed the more easily the more active are the atoms taking part and the more readily are unstable intermediate ring systems formed.

The magnesium iodide derivatives of indole, 2-methylindole, and pyrrole were allowed to react in the cold with ethyl formate and ethyl acetate. With methyl formate, indole yielded 1-formylindole, $d_4^{18\cdot5}$ 1·175, $n_D^{18\cdot6}$ 1·62. On raising the temperature of the reaction to 70—75°, indole-3-aldehyde, m. p. 194°, is obtained. With 2-methylindole the reaction is analogous—1-formyl-2-methylindole, d_4^{16} 1·1353, n_D^{16} 1·617, and 2-methylindole-3-aldehyde resulting.

Under similar conditions, pyrrole does not give 1-formylpyrrole, but only pyrrolealdehyde, n_D^{16} 1·5939 (oxime, m. p. 163°). If with indole instead of ethyl formate, ethyl acetate is used, the corresponding 1-acetylindole, b. p. 144—145°/10 mm., is obtained in the cold, which when heated passes into 3-acetylindole, m. p. 189°.

On heating 1-formylindole in a sealed tube at 300—350° some crystalline *substance* is formed, which does not melt even at 300°.

Under similar conditions 1-acetylindole yielded a small quantity of quinoline.

Pyrrolidine condenses with formaldehyde at 140—150° in a sealed tube, giving 1-*methoxypyrrolidine*, 1:1′-dipyrrolidylmethane and 2-methoxypyrrolidine. Under similar conditions, piperidine yields small quantities of 1- and 2-methylpiperidines, and 1:1′-*dipiperidylmethane*, b. p. 120—125°/3·5 mm., d_4^{15} 0·9335, n_D^{15} 1·4883.

Trimethyleneimine, if prepared by Howard and Marckwald's method by reducing *p*-tolyltrimethylenesulphonimide with sodium in amyl alcohol, gives as a by-product a dihydric *amino-alcohol*, C$_6$H$_{15}$O$_2$N. On condensation with formaldehyde in a sealed tube at 120°, trimethyleneimine forms hexamethylenedi-imine, b. p. 185°, d_4^{19} 0·911, n_D^{19} 1·4685.

M. ZVEGINTZOV.

Organic catalysts. II. Reinforcement of the catalytic activity of isatin by nuclear substitution. W. LANGENBECK (Ber., 1928, **61**, [*B*], 942—947; cf. A., 1927, 546).—Comparison of the effect of isatin, isatin-1-acetic acid, 5-bromo-, 5:7-dibromo-, 5-chloro-isatin, and potassium isatinsulphonate on the decolorisation of methylene-blue by alanine shows that substitution of the imino-hydrogen atom has little influence, whereas the introduction of a halogen atom or a sulphonic group into the benzene nucleus causes enhanced catalytic activity. *Isatin*-1-*acetic acid*, m. p. 206—207°, is prepared in 72% yield by the action of chloroacetic acid and sodium carbonate on a boiling solution of isatin in 10% sodium hydroxide. *Isatin*-1-*acetyl chloride*, *isatin*-1-*acetamide*, m. p. about 260° (decomp.), l-*menthyl isatin*-1-*acetate*, m. p. 122°, and 5-*nitroisatin*-1-*acetic acid*, m. p. 207°, are incidentally described.

α-Amino*iso*butyric acid can be dehydrogenated to acetone, carbon dioxide, and ammonia by *p*-benzoquinone, but not by alloxan or isatin. Since the process cannot take place through the intermediate formation of an α-imino-acid, there must be a method of dehydrogenation of amino-acids differing from that previously assumed and probably depending on the formation of a radical with tervalent nitrogen.

H. WREN.

Reaction of disulphoisatides. A. WAHL and LOBECK (Compt. rend., 1928, **186**, 1303—1305).—Disulphoisatide, when gently heated with dry cuprous chloride in acetic acid suspension, forms a black precipitate and an orange solution, yielding 50—60% of *iso*indigotin with some free sulphur and isatin :

$$C_{16}H_{12}O_2N_2S_2 + 2CuCl = C_{16}H_{10}O_2N_2 + 2CuS + 2HCl.$$

The reaction may be applied to dimethyl- and dichloro-disulphoisatides (this vol., 428) and to the two *naphthodisulphoisatides* (insoluble substances, contaminated with excess of sulphur) prepared from the corresponding naphthoisatins. α-*Naphthodisulphoisatide* forms α-*dinaphtho*isoindigotin when thus treated.

B. W. ANDERSON.

Pyrrole and complex salts. H. FISCHER and B. PÜTZER (Ber., 1928, **61**, [*B*], 1068—1074).—2:4-Dimethylpyrrole is converted by bromine in glacial acetic acid into 3:5-dibromo-4-methylpyrryl-3-bromo-2:4-dimethylpyrrolenylmethane, oxidised by chromic acid in presence of concentrated sulphuric acid to bromocitraconimide, m. p. 170°.

Ethyl 4-methyl-2-ethylpyrrole-5-carboxylate and acetyl chloride in presence of aluminium chloride and carbon disulphide afford *ethyl 3-acetyl-4-methyl-2-ethylpyrrole-5-carboxylate*, m. p. 134°. The corresponding *acid*, m. p. 204° (decomp.), loses carbon dioxide when heated and yields 3-*acetyl-4-methyl-2-ethylpyrrole*, m. p. 122°. The ester is converted by sodium ethoxide and hydrazine hydrate in alcohol at 175° into 4-*methyl*-2:3-*diethylpyrrole*, b. p. 95—97°/20 mm. (*picrate*, m. p. 104·5°; additive *compound* with mercuric chloride; diazobenzenesulphonic acid *derivative*). 3:4-*Dimethyl-2-ethylpyrrole picrate*, m. p. 122·5° (corr.), is obtained from ethyl 3-aldehydo-

4-methyl-2-ethylpyrrole-5-carboxylate by the Wolff–Kishner method. Ethyl 2-methyl-4-hydroxymethyl-pyrrole-3 : 5-dicarboxylate is converted by bromine in glacial acetic acid at 18° into *ethyl 2-bromoethyl-2-hydroxymethylpyrrole-3 : 5-dicarboxylate*, m. p. 96·5° (corresponding *anilide*, m. p. 95°).

Treatment of ethyl 2-aldehydo-4-methylpyrrole-3 : 5-dicarboxylate with bromine yields *ethyl 2-bromo-4-methylpyrrole-3 : 5-dicarboxylate*, m. p. 147° (corr.). With hydrazine, the aldehyde gives the corresponding *hydrazone*, m. p. 100° (corr.), converted by a further portion of the aldehyde into the *aldazine*, $C_{24}H_{30}O_8N_4$, m. p. 196° (corr.), obtained directly from the aldehyde and hydrazine in acetic acid. The ester yields the complex *copper* derivative, $C_{24}H_{28}O_8N_4Cu$, m. p. 203° (corr.); it can be hydrolysed to the *tetracarboxylic acid*. The *aldazine* of 2 : 4-dimethylpyrrole-5-aldehyde has m. p. 251° (corr.). Treatment of ethyl 2-aldehydo-4-methylpyrrole-3 : 5-dicarboxylate with magnesium methyl iodide affords *ethyl 4-methyl-2-α-hydroxyethyl-pyrrole-3 : 5-dicarboxylate*, m. p. 95° (corr.).

Attempts to decarboxylate mesoporphyrin by means of piperidine lead to the isolation of a *substance*, $C_{44}H_{60}O_4N_6$, possibly a molecular compound of the reactants (1 : 2), which yields a crystalline *copper* salt, $C_{44}H_{54}O_2N_6Cu$, apparently derived from the dipiperidide of mesoporphyrin ; the corresponding *zinc* salt, m. p. 286° (corr.), is described. Mesoporphyrin dimethyl ester is converted by stannous chloride and sodium acetate in glacial acetic acid into the *compound* $C_{36}H_{42}O_4N_4,SnCl_2$, and in a mixture of glacial acetic acid and pyridine into the halogen-free *substance*, $C_{40}H_{52}O_{10}N_4Sn$.   H. WREN.

Reactions of ethyl 2-methylpyrrole-3-carb-oxylate, 2-methyl- and 2 : 3-dimethyl-pyrrole. H. FISCHER, H. BELLER, and A. STERN (Ber., 1928, **61**, [*B*], 1074—1083).—Ethyl 2-methylpyrrole-3-carboxylate is converted by 2 mols. of bromine in glacial acetic acid at 15—16° into *ethyl 4 : 5-dibromo-2-methyl-pyrrole-3-carboxylate*, m. p. 138—139°, whereas with 1 mol. of the halogen it affords a *substance*, $C_{16}H_{18}O_4N_2$, m. p. 255—256°. With ethyl cyanoformate, ethyl 2-methylpyrrole-3-carboxylate gives the *imino-chloride*, $C_{12}H_{17}O_4N_2Cl$, m. p. 180—181° (decomp.), converted by water into the *glyoxylic ester*, $C_{12}H_{15}O_5N$, m. p. 128°. 2-Methylpyrrole, b. p. 148°, obtained in 70% yield by decarboxylation of ethyl 2-methyl-pyrrole-3-carboxylate by potassium hydroxide at 170—200°, is converted through the Grignard compound with ethyl chloroformate into *ethyl 2-methyl-pyrrole-5-carboxylate*, m. p. 100°. 2-Methylpyrrole is also readily obtained by Wolff and Kishner's method from pyrrole-2-aldehyde, prepared by the action of chloroform and potassium hydroxide on pyrrole and isolated through the hydrogen sulphite compound. Bromination of ethyl 2-methylpyrrole-5-carboxylate in acetic acid at 40° affords a *dibromo*-compound, $C_8H_9O_2NBr_2$, m. p. 176° (decomp.); the ester condenses with formaldehyde, acetone, and ethyl meth-oxymethylmalonate, yielding, respectively, *di-5-carb-ethoxy-2-methylpyrryl-4-methane*, m. p. 195—196°, the corresponding *dimethylmethane*, m. p. 217°, and *ethyl 2-methyl-3-ββ-dicarbethoxyethylpyrrole-5-carboxylate*, m. p. 75°; bromination of the latter compound

affords a *substance*, $C_{16}H_{22}O_6NBr$, m. p. 105°. The successive action of water and chloroacetonitrile on ethyl 2-methylpyrrole-5-carboxylate yields the *compound* $C_{10}H_{12}O_2NCl$, m. p. 190°. *Ethyl 3-aldehydo-2-methylpyrrole-5-carboxylate*, m. p. 119° (corresponding *aldimide*, m. p. 215—216°; *semicarbazone*, m. p. 258°; *phenylhydrazone*, m. p. 216°), is readily prepared from ethyl 2-methylpyrrole-5-carboxylate and anhydrous hydrocyanic acid, it is converted by hydrazine hydrate and sodium ethoxide into 2 : 3-di-methylpyrrole, b. p. 63°/12 mm. (picrate, m. p. 144°). Similarly, ethyl 2-ethylpyrrole-5-carboxylate is converted into *ethyl 3-aldehydo-2-ethyl-pyrrole-5-carboxylate*, m. p. 89—90° (corr.) [*phenylhydrazone*, m. p. 188° (corr. decomp.); *oxime*, m. p. 194° (corr.)], reduced Wolff and Kishner's method to 3-methyl-2-ethyl-pyrrole. Ethyl 2-ethylpyrrole-5-carboxylate is converted by formaldehyde and concentrated hydrochloric acid into the *methane* derivative, $C_{18}H_{26}O_4N_2$, m. p. 197° (corr.).

5-Aldehydo-2-methylpyrrole-3-carboxylic acid is transformed in a vacuum at 220° into *2-methyl-pyrrole-5-aldehyde*, m. p. 68° (corr.). *3-Nitro-2 : 4-di-methylpyrrole*, m. p. 138° (corr.), obtained by heating 3-nitro-2 : 4-dimethylpyrrolecarboxylic acid in a vacuum at 200°, is converted by hydrocyanic acid and hydrogen chloride in ether into *3-nitro-2 : 4-di-methylpyrrole-5-aldehyde*. Ethyl 2 : 3-dimethylpyr-role-5-carboxylate is converted by bromine in carbon tetrachloride at 70° into the *compound* $C_9H_{12}O_2NBr$, m. p. 157° (corr.). 2 : 3-Dimethylpyrrole and propionyl chloride give the *substance* $C_9H_{13}ON$, m. p. 128° (corr.).   H. WREN.

Fission of pyridine nucleus by oxidation with alkaline potassium permanganate. B. D. SHAW and A. L. WILKIE (J.C.S., 1928, 1377—1378).—When pyridine is oxidised with aqueous potassium permanganate there are formed ammonium carbonate, potassium carbonate, oxalate, nitrate, and nitrite.   H. BURTON.

Crystallisation and absorption of moisture by quaternary pyridine bases. G. D. SYTSCHEV (J. Russ. Phys. Chem. Soc., **60**, 1928, 325—330).—Deals with the formation of the quaternary salts from pyridine and benzyl chloride, bromide, and iodide.   A. RATCLIFFE.

Iodination of 2-aminopyridine. O. MAGIDSON and G. MENSCHIKOV (Trans. Sci. Chem.-Pharm. Inst., 1926, [**16**], 23—30; Chem. Zentr., 1928, i, 63—64).—5-Iodo-2-aminopyridine (cf. A., 1926, 844), m. p. 129° (*picrate*, m. p. 240°), is produced by the action of hydrogen peroxide and hydrogen iodide, or of potassium iodide and iodate, on 2-aminopyridine in acid solution, or of iodine in aqueous potassium iodide; the periodide is converted into the base by means of hot alkali hydroxide solution. Pyrid-2-one is iodinated with difficulty. The following compounds were prepared : *5-iodopyridyl-2-nitroamine* (from 5-iodo-2-aminopyridine, 2 g., sulphuric acid, 15 c.c., water, 4 c.c., and nitric acid, d 1·4, 1 g., and cooling), m. p. 189° (decomp.); *5-iodopyrid-2-one* from 5-iodo-2-aminopyridine and nitrous acid, yellow, m. p. 183—189°; *5-iodo-2-chloropyridine*, m. p. 99°; *5-iodo-2-methoxypyridine*, b. p. 231° (*picrate*, m. p. 147°);

5-nitro-2-methoxypyridine, m. p. 110°; 5-amino-2-methoxypyridine. A. A. ELDRIDGE.

1-Dimethylaminopyridine and its derivatives. A. E. TSCHITSCHIBABIN and I. L. KNUNIANZ (J. Russ. Phys. Chem. Soc., 1928, **60**, 673—682).—See this vol., 427.

Nitro-2-acetamidopyridines. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 651—653).—See this vol., 301.

Nitration of 3-ethoxypyridine. E. KOENIGS, H. C. GERDES, and A. SIROT (Ber., 1928, **61**, [*B*], 1023—1030).—3-Bromopyridine is converted by methyl-alcoholic sodium methoxide into 3-*methoxypyridine*, b. p. 179° (*chloroplatinate*, m. p. 269°). Nitration of 3-ethoxypyridine by nitric acid (*d* 1·54) and concentrated sulphuric acid affords 6-*nitro-3-ethoxypyridine*, m. p. 31—32°, b. p. 175°/50 mm., which has no basic properties but is very sensitive towards alkalis. It is reduced by stannous chloride and concentrated hydrochloric acid to 6-*amino-3-ethoxypyridine*, m. p. 86° (*picrate*, m. p. 235°), hydrolysed by hydrogen bromide in glacial acetic acid at 130° to 6-*amino-3-hydroxypyridine* (*hydrobromide*, m. p. 173°; *hydrochloride*, m. p. 185°); attempts to diazotise the sulphate of the base were unsuccessful. Unexpectedly, 6-nitro-3-ethoxypyridine is converted by hydrogen bromide in glacial acetic acid at 130° into 6-*bromo-3-ethoxypyridine*, b. p. 257—259° [*hydrobromide*, m. p. 185° (decomp.)], and by concentrated hydrochloric acid at 130° into 6-*chloro-3-hydroxypyridine hydrochloride*, m. p. 208° (decomp.). 6-Bromo-3-ethoxypyridine is transformed by sodium ethoxide in alcohol into 3 : 6-*diethoxypyridine*, b. p. 215—217°/760 mm., hydrolysed by concentrated hydrochloric acid to 3 : 6-dihydroxypyridine, m. p. 248° (*hydrochloride*, m. p. 154°), thus establishing the position of the nitro-group in the nitro-3-ethoxypyridine. 3-Methoxypyridine is converted by energetic nitration into *dinitro-3-methoxypyridine*, m. p. 69°; a homogeneous mononitro-derivative could not be isolated.

Cautious nitration of 3 : 5-diethoxypyridine affords 2 : 6-*dinitro-3 : 5-diethoxypyridine*, m. p. 120°, reduced to 2 : 6-*diamino-3 : 5-diethoxypyridine*, m. p. 60° (decomp.). 2 : 6-*Dibromo-3 : 5-diethoxypyridine*, m. p. 165°, prepared from the dinitro-compound and hydrogen bromide in glacial acetic acid at 100°, appears to be converted by sodium ethoxide into unstable tetraethoxypyridine, b. p. 285—290° (partial decomp.). H. WREN.

Condensation products of homophthalimide [2 : 4-dihydroxy*iso*quinoline] and aromatic aldehydes. H. MEYER (Compt. rend., 1928, **186**, 1214—1216).—In order to compare the properties of derivatives of homophthalimide and 2 : 4-dihydroxyquinoline with those of oxindole, especially with regard to colour and constitution, condensation of these substances with aromatic aldehydes has been studied. Whilst homophthalimide is found to react readily, molecule for molecule, in alcohol or acetic acid solution in presence of diethylamine or hydrochloric acid with the aldehyde, 2 : 4-dihydroxyquinoline condenses only with difficulty, suggesting an enolic

3 D

formula for the substance. The condensation products of homophthalimide vary in colour from yellow to red, like the *iso*indogenides. The influence of the aromatic nucleus on the colour is pointed out. The following condensation products with 2 : 4-dihydroxy*iso*quinoline and aldehydes were prepared : p-*toluylidene*-, m. p. 199°; *cinnamylidene*-, m. p. 223°; o-*nitrobenzylidene*-, m. p. 236°; m-*nitrobenzylidene*-, m. p. 273°; p-*nitrobenzylidene*-, m. p. 263°; *furfurylidene*-, m. p. 210°; iso*phthalylidene*-, m. p. 292°; *terephthalylidene*-, m. p. 297—298°; *salicylidene*-, m. p. 215°; o-*methoxybenzylidene*-, m. p. 176°; m-*methoxybenzylidene*-, m. p. 176°; p-*hydroxybenzylidene*, m. p. 238°; *anisylidene*-, m. p. 195°; o-*vanillylidene*, m. p. 211°; *vanillylidene*-, in two forms, m. p. 178—180° and 165°; *piperonylidene*-, m. p. 218—219°, p-*dimethylaminobenzylidene*-, m. p. 195°.
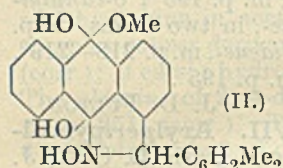
J. D. FULTON.

Free organic radicals. VII. Aryl*peri*pyrrolinoanthranolazyls. R. SCHOLL [with E. STIX, J. DONAT, and W. LEONHARDT] (Ber., 1928, **61**, [*B*], 968—972; cf. A., 1927, 675, 885).—Further investigation of aryl*peri*pyrrolinoanthranolazyls (I) shows that the electrolytic conductivity of pure alcohol and pyridine is not increased by the radical, so that disproportionation by electron displacement does not occur as with triarylmethyls in certain solvents. Alkaline solutions which have changed in colour from blue to red under the influence of the quartz mercury lamp in an atmosphere of nitrogen or from blue to yellow in the presence of air do not again become blue when placed in the dark or treated with cold phenylhydrazine and therefore probably do not contain aryl*peri*pyrrolinoanthrone; when heated with alcoholic, alkaline hyposulphite or phenylhydrazine they become impure blue, probably owing to re-formation of the radical from some unknown dehydrogenation or oxidation product. The stability of aryl*peri*pyrrolinoanthranolazyls, when crystalline, towards air and light, the ease with which they are re-formed from their closely related, non-radical oxidation and reduction products, and their ability to pass under ordinary conditions of reactions and without loss of radical nature into azylium salts, acyl derivatives, and *O*-ethers cause them to resemble very closely the dye molecules with normal valency fulfilment and ally them more closely to the normal, non-radical compounds than any other type of organic radicals.

Phenyl 1-anthraquinonyl ketoxime, m. p. 225° after darkening at 215—220°, prepared from 1-benzoyl-anthraquinone, is converted by the action of zinc dust and ammonia or its alcoholic solution into py-1-*phenyl-1 : 9-pyrrolinoanthranolazyl* (I. Ar=Ph), m. p. 266°. Anthraquinone-1-carboxylic acid is converted by the successive action of phosphorus pentachloride and a little sublimed ferric chloride in presence of toluene into *p*-tolyl 1-anthraquinonyl ketone, m. p. 207—208°, which is transformed into the corresponding *ketoxime*, m. p. 230—231°, when rapidly heated and thence into py-p-*tolyl-1 : 9-pyrrolinoanthran-10-olazyl* (I.Ar=*p*-C_6H_4Me), decomp. above 310°. Treatment of *m*-xylyl*peri*pyrrolinoanthranolazyl (*loc. cit.*) with
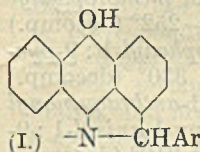
methyl sulphate and sodium hydroxide affords *py*-1-*m*-*xylyl*-1 : 9-*pyrrolinoanthranolazyl methyl ether*, m. p. 181° (*perchlorate*); the ether is much more closely related to the parent compound than is the benzoyl derivative (*loc. cit.*). It has a marked tendency towards solvate formation, yielding variously coloured solutions in ether, dioxan, xylene, pyridine, alcohol, and glacial acetic acid; the solutions become rapidly decolorised when exposed to light. The absorption curves of the ether and parent compound in alcohol or pyridine are closely similar. When titrated in nitrobenzene or acetic acid with permanganate and sulphuric acid until colourless, the methyl ether requires five equivalents of oxygen in place of the expected three. The compound (II) becomes decomposed into hydrogen peroxide, methyl alcohol, and *py*-*m*-xylylperipyrrolenino-anthrone and the liberated hydrogen peroxide utilises the additional two equivalents of oxygen. The preparation of p-*chlorophenyl* 1-*anthraquinonyl ketoxime*, m. p. 251—252° (decomp.) when rapidly heated, *py*-1-p-*chlorophenyl*-1 : 9-*pyrrolinoanthran*-10-*olazyl*, m. p. about 330° (decomp.) after softening at 310°, *anisyl* 1-*anthraquinonyl ketoxime*, m. p. 235—236°, and *py*-1-*anisyl*-1 : 9-*pyrrolinoanthran*-10-*olazyl*, m. p. about 310° (decomp.) after softening at 300°, is described.

[With L. WANKA.]—1-Amino-2-methylanthraquinone is converted by diazotisation in concentrated sulphuric acid and subsequent treatment of the *diazonium sulphate* with potassium cuprocyanide into 1-*cyano-2-methylanthraquinone*, m. p. 268°, hydrolysed by sulphuric acid to 2-*methylanthraquinone-1-carboxylic acid*, m. p. 263—264°; the acid *chloride* decomposes at about 192°.

[With H. DEHNERT.]—2-Methylanthraquinone-1-carboxyl chloride is converted with some difficulty by benzene in presence of ferric chloride but not of aluminium chloride into *phenyl 2-methylanthraquinonyl ketone*, m. p. 207—208°, from which *phenyl 2-methylanthraquinonyl ketoxime*, m. p. 239—240° after softening at 234°, and py-1-*phenyl*-1 : 9-*pyrrolino-2-methylanthran*-10-*olazyl*, m. p. 232—233°, decomp. about 285°, are successively derived. p-*Xylyl 2-methylanthraquinonyl ketone*, m. p. 192—193°, its *oxime*, m. p. 226—227·5° after softening, and py-1-p-*xylyl*-1 : 9-*pyrrolino*-2-*methylanthran*-10-*olazyl* have been prepared.

[With E. WEBER.]—m-*Xylyl 2-methylanthraquinonyl ketone*, m. p. 175°, its *oxime*, m. p. 232—233° after softening, and *py*-1-m-xylyl-1 : 9-pyrrolino-2-methylanthran-10-olazyl are described. H. WREN.

Red compounds of barbituric acid, picric acid, and sodium or lead hydroxide. I. GREENWALD (J. Amer. Chem. Soc., 1928, **50**, 1469—1474).—The red coloration obtained by adding excess of alkali to a solution of the two acids is not due to the formation of picramic acid (cf. Dox, A., 1926, 180), since the picric acid may be recovered almost quantitatively, but to an additive *compound* of approximate composition, $3C_4H_4O_3N_2.2C_6H_3O_7N_3,9NaOH,1$ or $2H_2O$, which is precipitated from the solution by alcohol. It dissociates in solution, since the colour-intensity is increased by adding excess of any of the components. It is converted by lead hydroxyacetate into a brick-red insoluble *substance*, $3C_4H_4O_3N_2.2C_6H_3O_7N_3,11Pb(OH)_2$.
H. E. F. NOTTON.

Reactions of carbohydrazide. II. A. M. MUNRO and F. J. WILSON (J.C.S., 1928, 1257—1261).—The view previously expressed (A., 1927, 232) that in the thermal decomposition which carbohydrazones (or δ-aminosemicarbazones) undergo at their m. p. the hydrazidicarbohydrazone (or hydrazidicarbohydrazide itself) is the intermediate product has now been confirmed by investigation of the thermal decomposition of dibenzaldehydehydrazidicarbohydrazone, *diacetonehydrazidicarbohydrazone* (I), m. p. 256°, and hydrazidicarbohydrazide. In each case, the end-products were those anticipated. The decomposition of diacetonecarbohydrazone (II) and *dipinacolincarbohydrazone* (III), m. p. 188°, both in boiling alcoholic solution and at the m. p., is also found to conform to the general scheme. The compound (II) yields (I) and thence dimethylketazine and 4-aminourazole. The compound (III) yields *dipinacolinhydrazidicarbohydrazone*, m. p. 230°, and thence pinacolinazine and 4-aminourazole. Equimolecular proportions of ethyl acetoacetate and carbohydrazide react in boiling alcohol, giving *ethyl acetoacetate δ-aminosemicarbazone* (IV), m. p. 219°. When 2 mols. of the ester react with 1 mol. of carbohydrazide, *di(ethyl acetoacetate) carbohydrazone* (V), m. p. 196°, and 3-*methyl-5-pyrazolone-1-carboxy-α-carbethoxy*iso*propylidenehydrazide*, m. p. 230° (decomp.), are obtained. In one instance only, the compound (V) and 3 : 3'-*dimethyl-5* : 5'-*dipyrazolonyl* 1 : 1'-*ketone*, m. p. 183°, were obtained. In boiling alcoholic solution, the compound (IV) yields hydrazine and *di(ethyl acetoacetate) hydrazidicarbohydrazone* (VI), m. p. 213°. When heated at its m. p. it gives hydrazine, 4-aminourazole, and 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone (VII). After prolonged boiling in alcoholic solution, the compound (V) yields (VI) and (VII). When heated at its m. p. it gives 4-aminourazole and (VII). M. CLARK.

Reduction of saturated by unsaturated amino-acids. M. BERGMANN and H. ENSSLIN (Z. physiol. Chem., 1928, **174**, 76—93).—The ethyl ester of glycylaspartic acid anhydride (ethyl 2 : 5-diketo-piperazine-3-acetate) condenses with benzaldehyde by Sasaki's method to give the *ethyl* ester of *benzylideneglycylaspartic anhydride* (ethyl 2 : 5-diketo-6-*benzylidenepiperazine-3-acetate*) converted by hydrochloric acid into 2 : 5-*diketo-6-benzylidenepiperazine-3-acetic acid* (*methyl* ester, m. p. 204°; position of double linking established by hydrolysis with hydrochloric acid, when no phenylalanine or pyruvic acid is produced). If the ester is saponified with sodium hydroxide, however, an *anhydride* isomeric with the above is obtained, but the double linking is now in the αβ-position to the carboxyl group (*methyl* ester, m. p. 147°; position of double linking established by ozonisation), i.e., a derivative of aminofumaric or aminomaleic acid is produced. This may be regarded as a carboxyl derivative of aminoacrylic acid, and it is

suggested that derivatives of acrylic acid play an important part in the metabolism of amino-acids. The above example of the reduction of a saturated amino-acid (aspartic acid portion of molecule) by an unsaturated amino-acid (aminocinnamic portion of the molecule) is typical of a labile equilibrium which probably exists in the animal body between saturated and unsaturated amino-acids. H. D. KAY.

Transformations of peptide substances. XXIII. Histidine. Peptide formation by acyl wandering. XXIV. Synthesis of a *dl*-histidyl-glycine. M. BERGMANN and L. ZERVAS (Z. physiol. Chem., 1928, **175**, 145—153, 154—157).—XXIII. *Methyl hippurylbenzoyl-1-histidine* (I : R= ·CO·CH$_2$·NHBz), m. p. 157° (corr.), dissolved in chloroform and treated with 1 mol. of glycine in *N*-sodium hydroxide (1 mol.) at the ordinary temperature and shaken for 12 hrs. yields benzoylglycylglycine (35% of theoretical) and methylbenzoylhistidine (I : R=H).

$$CO_2Me\cdot CH(NHBz)\cdot CH_2\cdot C{<}^{N=CH}_{CH\cdot NR} \quad (I.)$$
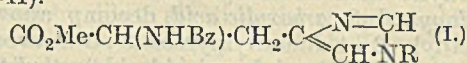
Methyl acetylbenzoyl-1-histidine (I : R=Bz), m. p. 168° (corr.), under similar conditions also loses its ring acyl group and with *d*-arginine yields acetyl-*d*-arginine (55% yield) and with glycine, acetylglycine (65% yield). 1-Benzoyltheobromine similarly gives up its acyl group to glycine yielding hippuric acid (75% yield). The acyl groups may be transferred to compounds other than amino-acids and an acetyl-histidine derivative and tetra-acetylglucosamine yield penta-acetylglucosamine.

XXIV. Acetyl-*dl*-histidine warmed with acetic anhydride and treated with glycine ethyl ester yields *ethyl acetyl-*dl-*histidylglycine* (II), m. p. 180°,

$$CO_2Et\cdot CH_2\cdot NH\cdot CO\cdot CH(NHAc)\cdot CH_2\cdot C{<}^{N=CH}_{CH\cdot NH} \quad (II.)$$
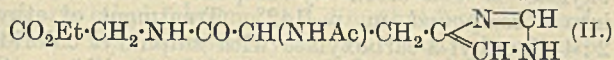
which when heated with *N*-hydrochloric acid yields *dl*-histidylglycine, m. p. 235° (corr.) with frothing and charring. A. WORMALL.

2 : 2′-Dipyridylamine and its nitration products. A. E. TSCHITSCHIBABIN and V. A. PREO-BRASHENSKY (J. Russ. Phys. Chem. Soc., 1928, **60**, 641—650).—See this vol., 307.

3 : 4 : 5 : 6 - Tetrahydro - 4 - carboline. J. N. ASHLEY and R. ROBINSON (J.C.S., 1928, 1376).—Reduction of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (I), m. p. 185—186°, with sodium and *n*-butyl alcohol yields 3 : 4 : 5 : 6-tetrahydro-4-carboline (Asahina, Irie, and Ohta, J. Pharm. Soc. Japan, 1927, No. 545). β-3-Indolylpropionhydrazide (II) has m. p. 140—141°. Erroneous m. p. were previously recorded for compounds (I) and (II) (Manske and Robinson, A., 1927, 256). M. CLARK.

Quinazolines. I. Mechanism of the reaction between formaldehyde and *p* - substituted aromatic amines in presence of acids. G. MAFFEI (Gazzetta, 1928, **58**, 261—269).—Mainly theoretical. The reaction between a *p*-substituted amine and formaldehyde is considered to give a methylene-di-*p*-amine (I), which undergoes an inversion to an *o*-aminobenzylphenylamine (II). The latter reacts

with formic acid (produced, with methyl alcohol, from the formaldehyde) to give a 2-hydroxy-3-aryltetra-hydroquinazoline (III); loss of water now yields the dihydroquinazoline (IV) and methyl alcohol [which also yields the *N*-methyl derivative (V) of the original amine] converts the latter into the methohydroxide (VI). Products of types (I) to (VI) have been isolated (cf. Lepetit, Maffei, and Maimeri, this vol., 284).

From *p*-nitroaniline the product 3-nitro-6-amino-benzyl-*p*-nitroaniline (VII) of type (II) has been isolated by Meyer and Stillich (A., 1902, i, 319), who also obtain an alternative product (VIII) of m. p. 207—208°, which they regard as 3-nitro-6-amino-5-methylolbenzylidene-*p*-nitroaniline. The author regards this as of type (III), since he obtains it by heating (VII) with formic acid in a sealed tube at 140°; it is renamed 6-*nitro*-2-*hydroxy*-3-p-*nitrophenyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 3-*quinazoline* (*acetyl* derivative, m. p. 223—235°). The product of the elimination of water, held by Meyer and Stillich to be 3-nitro-5 : 6-methyleneiminobenzylidene-*p*-nitroaniline, obtained by the action of glacial acetic acid on (VIII), is correspondingly renamed 6-*nitro*-3-p-*nitrophenyl*-3 : 4-*dihydro*-1 : 3-*quinazoline* (m. p. 243—246°).

From *p*-toluidine the base of m. p. 158° (Lepetit, Maffei, and Maimeri, *loc. cit.*) is regarded as 3-p-*tolyl*-6-*methyl*-3 : 4-*dihydro*-1 : 3-*quinazoline*, and that of m. p. 97—98° as the corresponding *methohydroxide*. From *p*-phenetidine the base of m. p. 140° is 6-*ethoxy*-3-p-*ethoxyphenyl*-3 : 4-*dihydro*-1 : 3-*quinazoline*, which has been synthesised; the compound of m. p. 210° (*loc. cit.*) is regarded as the corresponding 4-ketone, also obtained (cf. Busch, A., 1895, i, 306) by oxidising the compound $C_{18}H_{18}O_2N_2S$, m. p. 192—193° (Lepetit, A., 1917, i, 198), which is thus the thio-analogue of the ketone. E. W. WIGNALL.
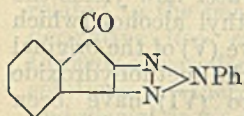
Manufacture of acid dyes of the phenonaphtha-safranine series. J. R. GEIGY A.-G.—See B., 1928, 441.

Manufacture of alkylpyrazolanthrones. I. G. FARBENIND. A.-G.—See B., 1928, 441.

Sulphoxytriazines [ketothiontriazines]. J. BOUGAULT and L. DANIEL (Compt. rend., 1928, **186**, 1216—1218).—5 - *Keto* - 3 - *thiol* - 6 - *methyl* - 1 : 2 : 4 - *tri-azine*, m. p. 220°, is readily prepared by dehydrating pyruvic acid thiosemicarbazone in faintly alkaline solution. When treated with sodium hypobromite followed by removal of excess of the latter with sodium hydrogen sulphite and subsequent acidification, 5-keto-3-thion-6-benzyl-1 : 2 : 6-triazine gives the corresponding dihydroxytriazine. The formation of an intermediate compound, *e.g.*, the 3-sulphonic acid, is suggested, as the dihydroxytriazine is itself decomposed by hypobromite (cf. A., 1916, i, 609). In a similar manner, 3 : 5-diketo-6-methyltriazine is obtainable (cf. A., 1914, i, 1004) from the corresponding hydroxythiol compound. J. D. FULTON.

Phenylene 2 - aryltriazolylene ketones and phenylene-2-phenyltriazolylenemethane. (1:2:3-Triazole analogues of fluorene and fluorenone.) G. CHARRIER [with C. SALA] (Gazzetta, 1928, **58**, 254—260).—The action of chromic acid on sodium

phenylene-2-phenyltriazolyleneglycollate (Charrier and Gallotti, A., 1925, i, 306) yields *phenylene 2-phenyl*-1 : 2 : 3-*triazolylene ketone* (annexed formula), m. p. 158° (*oxime*, m. p. 223°; *phenylhydrazone*, m. p. 214°; p-*chlorophenylhydrazone*, m. p. 226°; *semicarbazone*, m. p. 309°), which is reduced by hydriodic acid and phosphorus to *phenylene-2-phenyl*-1 : 2 : 3-*triazolylenemethane*, m. p. 128°.

When 2-N-p-*tolylnaphthotriazolequinone*, m. p. 216—217°, is treated with boiling aqueous sodium hydroxide, *phenylene-2-p-tolyl*-1 : 2 : 3-*triazolyleneglycollic acid*, m. p. 194°, is obtained; the *sodium* salt, m. p. 205° (decomp.), of the latter is oxidised by chromic acid to *phenylene 2-p-tolyl*-1 : 2 : 3-*triazolylene ketone*, m. p. 196° (*phenylhydrazone*, m. p. 207°; *semicarbazone*, m. p. 228°). E. W. WIGNALL.
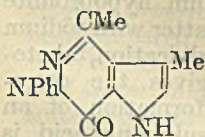
Manufacture of new pharmaceutical compounds [alkyloxymethyltheobromines]. I. G. FARBENIND, etc.—See B., 1928, 427.

[Porphyrins and their syntheses.] O. SCHUMM (Ber., 1928, **61**, [*B*], 784—787).—In his general account of this subject, Fischer (*ibid.*, 1927, **60**, [*B*], 2611) has made little or no reference to the results obtained by Schumm and his co-workers.
H. WREN.

Porphyrin syntheses. XV. Synthesis of 2 : 2′-disubstituted pyrroles and porphyrin syntheses from simple pyrroles. H. FISCHER, E. STURM, and H. FRIEDRICH (Annalen, 1928, **461**, 244—277).—An improved method is described for the preparation of aminoacetone hydrochloride by the reduction of *iso*nitrosoacetone. This method is more convenient for laboratory purposes than that of Gabriel starting with chloroacetone and potassium phthalimide, which is suitable for production on a larger scale. The condensation in alkaline solution, described by Piloty (Ber., 1912, **45**, 3749), of aminoacetone with ethyl acetopyruvate has been re-investigated. Three products result : (1) 3-acetyl-4-methylpyrrole-2-carboxylic acid, (2) 2 : 4-dimethyl-3-glyoxylic acid, and (3) the *ethyl* ester, m. p. 124°, of (2). The yields depend greatly on the purity of the aminoacetone and increase in the amount of alkali used increases the amount of (2). The potassium salt of (2) is converted into (3) by ethyl sulphate, whilst diazomethane converts (1) into the *methyl* ester, m. p. 100°. The acid (1) or its esters reacts with phenylhydrazine in 50% acetic acid at 100° to give the *pyridazinopyrrole* (annexed formula), m. p. 297° (corr.), whilst the acid is converted by hydrazine hydrate in presence of sodium ethoxide into opsopyrrole.

3-*Acetyl-4-methylpyrrole*, m. p. 117°, results when acid (1) is distilled at 50 mm. pressure or (2) is heated with 10% sodium hydroxide solution at 140°. The acetylmethylpyrrole, when heated at 170° with alcoholic sodium ethoxide and hydrazine hydrate, is converted into 3-methyl-4-ethylpyrrole (opsopyrrole). Decarboxylation of (2) gives a *dimethylpyrrolealdehyde* (?), m. p. 88—89°, reduced by the sodium ethoxide–hydrazine method to a *base*, $C_7H_{11}N$, b. p. 74—75°/11 mm., named iso*opsopyrrole*. This with diazotised sulphanilic acid affords a yellow *azo-dye* containing one azo-grouping.

When the above methylethylpyrrole is heated with formic acid or with similar compounds at 160° it is transformed into ætioporphyrin, whilst when excess of formic acid is used and the condensation is stopped when the product becomes red, opsopyrrolemethene, isolated as the *perchlorate*, results. The hydrobromide of the methene is converted by bromine in acetic acid at 30—40° into a "dibromide," the free base derived from which is identical with the methene, m. p. 175—176°, from hæmocarbethoxypyrrole.

Sulphuryl chloride (5 mols.) converts ethyl 2 : 5-dimethylpyrrole-3-carboxylate in ethereal solution into a product which, when decomposed with steam, affords *ethyl 4-chloro-2 : 5-dialdehydopyrrole-3-carboxylate*, m. p. 131°. 2 : 5-Dimethylpyrrole-3-carboxylic acid similarly affords 4-*chloro*-2 : 5-*dialdehydopyrrole-3-carboxylic acid*, decomp. above 237°, and ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate affords (6 mols. of sulphuryl chloride) *ethyl 2 : 4-di-(trichloromethyl)pyrrole-3 : 5-dicarboxylate*, m. p. 72° (crystallographic data by STEINMETZ; monoclinic prismatic; $a : b : c = 1.4041 : 1 : 1.6005$; $\beta = 111°\ 20'$), converted (1) by concentrated potassium hydroxide at 60—70° into a *compound*, m. p. 187°, (2) by chromic anhydride in acetic acid into a *pentachloro-hydroxy*-compound, $C_{12}H_{12}O_5NCl_5$, m. p. 110° (also formed by oxidising the hexachloro-compound with concentrated nitric acid or by treating it with concentrated sulphuric acid), and (3) by zinc dust in acetic acid into *ethyl 4-methyl-2-hydroxymethylpyrrole-3 : 5-dicarboxylate*, m. p. 116°. Ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate is converted by sulphuryl chloride etc. into a *compound*, m. p. 142°. Treatment of ethyl 2 : 4-dimethyl-3-carboxylate with sulphuryl chloride in ether, without subsequent decomposition with steam, gives (3-*carbethoxy*-2 : 4-*dimethylpyrryl*)-(5-*chloro-3-carbethoxy-4-methylpyrryl*)*methene hydrochloride*, m. p. 143°.

Phenylsulphur chloride converts ethyl 2 : 4-dimethylpyrrole-3-carboxylate into *ethyl 5-phenylthiol-2 : 4-dimethylpyrrole-3-carboxylate*, m. p. 111°, ethyl 2 : 4-dimethylpyrrole-5-carboxylate into *ethyl 3-phenylthiol-2 : 4-dimethylpyrrole-5-carboxylate*, m. p. 157°, and ethyl 2 : 5-dimethylpyrrole-3-carboxylate into *ethyl 4-phenylthiol-2 : 5-dimethylpyrrole-3-carboxylate*, m. p. 143°.

When ethyl 2 : 4-dimethyl-3-ethylpyrrole-5-carboxylate is treated with 2 mols. of sulphuryl chloride (ether; 0°) there is formed *ethyl 4-methyl-3-ethyl-2-chloromethylpyrrole-5-carboxylate*, m. p. 130° (corr.), converted by boiling water into the known bis(5-carbethoxy-4-methyl-3-ethylpyrryl)methene. Using 3 mols. of sulphuryl chloride and boiling the initial product with aqueous alcohol, 5-*carbethoxy-4-methyl-3-ethylpyrrole-2-carboxylic acid*, m. p. 211°, results, together with some ethyl 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylate, m. p. 90° (corr.). The last-named acid is readily hydrolysed to 4-*methyl-3-ethyl-2 : 5-dicarboxylic acid*, m. p. 232°, is converted by boiling acetic anhydride in presence of anhydrous sodium acetate into a *pyrocoll*, $C_{22}H_{26}O_6N_2$, m. p. 150°,

whilst when it is heated at 215—220° it affords *opsocarbethoxypyrrole* (*ethyl 3-methyl-4-ethylpyrrole-2-carboxylate*), m. p. 25°. The last-named is converted by hydrogen cyanide and hydrogen chloride into a product which affords 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylic acid when hydrolysed with dilute alkali. Bromination of opsocarbethoxypyrrole in acetic acid gives *ethyl 2-bromo-4-methyl-3-ethylpyrrole-5-carboxylate*, m. p. 103° (corr.), also formed when the carbethoxy-acid, m. p. 211°, is brominated in acetic acid solution. Opsopyrrole is conveniently prepared either by heating the carbethoxy-acid, m. p. 211°, with hydriodic acid or by heating it with 10% sodium hydroxide at 160°.
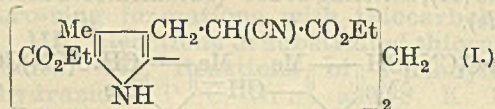
The oxime of ethyl 2-aldehydo-4-methyl-3-ethyl-pyrrole-5-carboxylate is converted by boiling acetic anhydride in presence of sodium acetate into *ethyl 2-cyano-4-methyl-3-ethylpyrrole-5-carboxylate*, m. p. 131° (corr.), hydrolysed by boiling 10% sodium hydroxide to the corresponding dicarboxylic acid. Ethyl 2-alde-hydo-4-methyl-3-ethylpyrrole-5-carboxylate is readily hydrolysed by dilute alkali to the expected aldehydo-acid (above), and condenses in alcoholic hydrobromic acid with cryptopyrrole, with methyl hæmopyrrole-carboxylate, and with cryptopyrrolecarboxylic acid to give *methenes* melting respectively at 160°, 168°, and 197°.

When cryptopyrrole is heated either alone or in presence of its carboxylic acid with hydrogen bromide in acetic acid, no porphyrin formation occurs, but when cryptopyrrole is heated under pressure at 100° with formic acid and perchloric acid, a quantitative yield of cryptopyrrolemethene perchlorate is obtained. On the other hand, porphyrin formation does occur when ethyl cryptopyrroleglyoxylate (ethyl 2 : 4-di-methyl-3-ethylpyrrole-5-glyoxylate) is heated with hydrogen bromide in acetic acid, and the same reagent converts ethyl 5-bromo-2 : 4-dimethyl-3-ethyl-2-carb-oxylate into *ætioporphyrin*, and converts 5-carb-ethoxy-4-methyl-2-bromomethylpyrrole-3-propionic acid into a mixture of coproporphyrin ("III") and (the tetramethyl ester of) *iso*coproporphyrin, separable only with difficulty and then melting, respectively, at 250° (corr.) and 139°. The carbethoxy-propionic acid also affords a mixture of porphyrins when heated with succinic acid. Porphyrin formation occurs when 5-carbethoxy-2 : 4-dimethylpyrrole-3-propionic acid is heated with hydrogen bromide in acetic acid, but not when carbethoxyxanthopyrrolecarboxylic acid is so treated.   E. E. TURNER.

Porphyrin syntheses. XVI. Syntheses of porphyrins with nitrile function. H. FISCHER and H. WASENEGGER (*Annalen*, 1928, **461**, 277—295).—Ethyl 3-aldehydo-2 : 4-dimethylpyrrole-5-carb-oxylate condenses with ethyl cyanoacetate in presence of boiling alcoholic aniline to give ethyl 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole-5-carboxylate (A., 1924, i, 543) (yield 90—95%), which is reduced by sodium in alcoholic solution containing some acetic acid to ethyl 2 : 4-dimethyl-3-(β-cyano-β-carb-ethoxy)ethylpyrrole-5-carboxylate. The latter is converted by alcoholic hydrogen chloride into ethyl 2 : 4-dimethyl-3-ββ-dicarbethoxyethylpyrrole-5-carb-oxylate and by hydrobromic and acetic acids into ethyl

acetate and the substance previously obtained (A., 1925, i, 834) from alkali and ethyl 2 : 4-dimethyl-3-ββ-dicarbethoxyethylpyrrole-5-carboxylate, and on bromination affords *ethyl 4-methyl-2-bromomethyl-3-(β-cyano-β-carbethoxy)ethylpyrrole-5-carboxylate*, m. p. 129°, which is converted by methyl alcohol, ethyl alcohol, and aniline into the -2-*methoxymethyl-* (m. p. 113°), the -2-*ethoxymethyl-* (m. p. 123°), and the -2-*anilinomethyl-* (m. p. 138°) compounds, respectively, and transformed by boiling water into formaldehyde and *bis-[2-carbethoxy-3-methyl-4-(β-cyano-β-carbethoxy)ethylpyrryl]-5-methane* (I). The latter is brominated in

$$\begin{bmatrix} \text{Me} \underset{\text{NH}}{\overline{}} \text{CH}_2 \cdot \text{CH(CN)} \cdot \text{CO}_2\text{Et} \\ \text{CO}_2\text{Et} \underset{}{} \text{CH}_2 \end{bmatrix}_2 \quad \text{(I.)}$$

acetic acid solution to give a *dibromo*-derivative, m. p. 131°, and is converted by warm dilute aqueous alcoholic alkali into *bis-[2-carbethoxy-3-methyl-4-(β-cyano-β-carboxy)ethylpyrryl]-5-methane*. The latter, when melted in a vacuum, affords *bis-(2-carbethoxy-3-methyl-4-β-cyanoethylpyrryl)methane*, m. p. 194°, also obtained by boiling with water for 8 hrs. (with air bubbling through) *ethyl 4-methyl-2-bromomethyl-3-β-cyanoethylpyrrole-5-carboxylate*, m. p. 185°, which is the product of brominating ethyl 2 : 4-dimethyl-3-β-cyanoethylpyrrole-5-carboxylate, and reacts with methyl alcohol, ethyl alcohol, and aniline to give the -2-*methoxymethyl*, -2-*ethoxymethyl*, and -2-*anilino-methyl* compounds, these melting, respectively, at 140°, 113°, and 188°. Ethyl 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)ethylpyrrole-5-carboxylate is converted by acetic and hydriodic acids into cryptopyrrolecarb-oxylic acid, m. p. 138°.
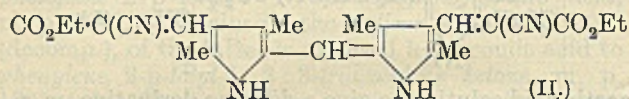
When (I) is treated in alcoholic solution with hydrogen chloride, bis-(2-carbethoxy-3-methyl-4-ββ-dicarbethoxyethylpyrryl)-5-methane, m. p. 126°, separates, and this substance, when boiled in aqueous alcoholic alkali, affords a mixture of bis-(2-carbethoxy-3-methyl-4-β-carboxyethylpyrryl)-5-methane and bis-(2-carboxy-3-methyl-4-β-carboxy-ethylpyrryl)-5-methane.

Bromination of ethyl 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole-5-carboxylate gives a bromo-compound which is not crystalline but clearly contains bromomethyl groups, since methyl and ethyl alcohols convert it respectively into a *methoxy-* (m. p. 101°) and an *ethoxy-* (m. p. 120°) compound. The desired *ethyl 4-methyl-2-bromomethyl-3-(β-cyano-β-carbethoxy)vinyl-pyrrole-5-carboxylate*, m. p. 135°, is, however, obtained by treating the last-named ethoxy-compound with hydrogen bromide in acetic acid. The bromo-com-pound is not convertible into a methane by the general methods.

Condensation of 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylic acid with ethyl cyanoacetate in boiling alcoholic aniline solution gives 2 : 4-*dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole-5-carboxylic acid*, m. p. 242°, which is converted by boiling acetic anhydride into a *pyrocoll*, m. p. 276°, hydrolysed by hot con-centrated alkali to give 3-aldehydo-2 : 4-dimethyl-pyrrole-5-carboxylic acid.

Hydrolysis of 2 : 4-dimethyl-3-(β-cyano-β-carbeth-oxy)vinylpyrrole with alcoholic alkali produces the

corresponding β-*carboxylic acid*, m. p. 210°. 2 : 4-Di-methyl-3-(β-cyano-β-carbethoxy)vinylpyrrole-5-carb-oxylic acid passes, when heated in a vacuum, into 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole, converted by hydrogen cyanide and chloride in chloro-form solution into 2 : 4-*dimethyl-3-(β-cyano-β-carb-ethoxy)vinylpyrrole-5-aldehyde* (oxime, m. p. 185°; *semicarbazone*, m. p. 253°; *azlactone*, m. p. 185°), which, when heated in alcoholic hydrochloric acid with the pyrrole from which it is prepared, affords the *bis-[2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrryl]-methene* (II), sintering at 250° (obtained from the *hydro-chloride*).

$$CO_2Et \cdot C(CN) : CH \underset{Me}{\underset{|}{\fbox{ }}} Me \quad Me \underset{Me}{\underset{|}{\fbox{ }}} CH : C(CN) CO_2Et$$
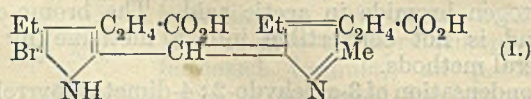$$NH \qquad\qquad NH \qquad (II.)$$

In cold alcoholic hydrochloric acid solution, crypto-pyrrolealdehyde condenses with 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole to give the *hydro-chloride*, m. p. 220°, of the expected *methene*, m. p. 132°. The last-named vinylpyrrole reacts with aqueous formaldehyde (boiling solution) to give green and colourless forms of *bis-[2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrryl]-5-methane*, m. p. 217° (corre-sponding β-*carboxylic acid*, m. p. 268°).

The condensation product of 2 : 4-dimethyl-3-(β-cyano-β-carbethoxy)vinylpyrrole and cryptopyrrole-aldehyde condenses with bis-(2-bromo-3-methyl-4-ethylpyrryl)-5-methene when heated with succinic acid, to give ætioporphyrin.
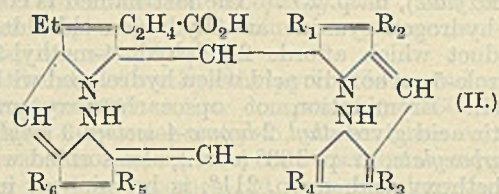
2 : 4-Dimethyl-3-(β-cyano-β-carbethoxy)vinylpyr-role-5-aldehyde when heated with a little alkali affords the corresponding β-*carboxylic acid*, m. p. 240°, and when heated with concentrated (1 : 1) potassium hydroxide is converted into 2 : 5-*dimethylpyrrole-3 : 5-dialdehyde*, m. p. 166°.　　E. E. TURNER.

Porphyrin syntheses. XVIII. Synthesis of three tetraethylporphintetrapropionic acids (homologous coproporphyrins). Xanthopor-phinogen from ætioporphyrin III and one of the homologous opsopyrrolecarboxylic acids. H. FISCHER and G. STANGLER (Annalen, 1928, 462, 251—267).—2-*Methyl-4-ethylpyrrole-3-propionic acid*, m. p. 78° (*picrate*, m. p. 140°), is obtained by heating its 5-carbethoxy-derivative with hydrogen iodide in acetic acid at 100°, and is converted by bromine into (2-*bromo-3-ethyl-4-β-carboxyethylpyrryl)(2'-methyl-4'-ethyl-3'-β-carboxyethylpyrrolenyl)methene hydrobromide* (as I), decomp. about 230°. The latter when heated

$$Et \underset{Br}{\underset{|}{\fbox{ }}} C_2H_4 \cdot CO_2H \quad Et \fbox{ } C_2H_4 \cdot CO_2H$$
$$\quad CH \qquad\qquad Me \qquad (I.)$$
$$NH \qquad\qquad N$$

with succinic acid (cf. this vol., 651) affords a product which with methyl-alcoholic hydrogen chloride gives the *methyl* ester, m. p. 193°, of a *tetraethylporphin-tetrapropionic acid* (II; $R_1 = R_3 = R_5 = Et$; $R_2 = R_4 = R_6 = \cdot[CH_2]_2 \cdot CO_2H$), also obtained but with m. p. 180° (isomeride?) by heating 4-ethyl-2-bromomethyl-5-carbethoxypyrrole-3-propionic acid with succinic acid and subsequently esterifying. The methyl ester, m. p. 193°, depresses the m. p. of the isomeride (below) of

m. p. 182°, and forms a *copper* salt, $C_{44}H_{52}O_8N_4Cu$, m. p. 265°, and an *iron* salt, $C_{44}H_{52}O_8N_4ClFe$, m. p.

$$Et \fbox{ } C_2H_4 \cdot CO_2H \quad R_1 \fbox{ } R_2$$
$$CH$$
$$N \qquad\qquad N \quad CH \quad (II.)$$
$$CH \quad NH \qquad NH$$
$$CH$$
$$R_6 \fbox{ } R_5 \qquad R_4 \fbox{ } R_3$$

170°. Hydrolysis of the ester, followed by heating in a high vacuum at 300° gives a sublimate consisting of ætioporphyrin and acid porphyrins, the main product, however, being a black material from which *octa-ethylporphin*, m. p. 292—293° [mixed with synthetic compound of m. p. 312—314° (Fischer and Bäumler; details to appear shortly), m. p. was 302—303°], is isolable.

5-Carbethoxy-2-methyl-4-ethylpyrrole-3-propionic acid undergoes bromination in ethereal solution to give 5-*carbethoxy-4-ethyl-2-bromomethylpyrrole-3-pro-pionic acid*, m. p. 174°, converted by boiling water into formaldehyde and *ethyl bis-(4-ethyl-3-β-carboxy-ethylpyrryl)methane-2 : 2'-dicarboxylate*, m. p. 161°, which on hydrolysis affords the not very stable free tetracarboxylic *acid*, decomp. 180°. The latter is converted by formic acid into a poor yield of the corresponding homologous iso*coproporphyrin* (II; $R_2 = R_3 = R_6 = Et$; $R_1 = R_4 = R_5 = \cdot[CH_2]_2 \cdot CO_2H$), the *methyl* ester of which has m. p. 170°. Bromine con-verts the last-named tetracarboxylic acid in acetic acid into *bis-(2-bromo-3-ethyl-4-β-carboxyethylpyrryl)-methene hydrobromide*, decomp. indef. above 200°. *Bis-(2-methyl-4-ethyl-3-β-carboxyethylpyrryl)methene hydrobromide* is formed when 2-methyl-4-ethylpyrrole-2-propionic acid is heated in formic acid with bromine, and when heated with bromine in acetic acid is con-verted into *bis-(4-ethyl-2-bromomethyl-3-β-carboxy-ethylpyrryl)methene hydrobromide*, whilst when it is heated with bis-(2-bromo-3-ethyl-4-β-carboxyethyl-pyrryl)methene hydrobromide it affords an acid (II; $R_2 = R_4 = R_5 = Et$; $R_1 = R_3 = R_6 = \cdot[CH_2]_2 \cdot CO_2H$) which on esterification gives the *methyl* ester, m. p. 182°.

The three new methyl ester porphyrins (methyl esters of tetraethyl-tetrapropionic acid porphins) are spectroscopically similar to their lower homologues, the coproporphyrins (methyl esters of tetramethyl-tetrapropionic acid porphins), three of which have been synthesised by Fischer, the fourth to be described shortly.

5-Carbethoxy-4-ethyl-2-bromomethylpyrrole-3-pro-pionic acid is converted by sulphuryl chloride in ethereal solution into a *chloro-compound*, m. p. 118°, which when boiled with water gives 5-*carbethoxy-4-ethyl-3-β-carboxyethylpyrrole-2-carboxylic acid*, m. p. 248° (decomp.), the latter affording 3-*ethylpyrrole-4-propionic acid*, m. p. 133°, when heated with aqueous sodium hydroxide at 165—170°, under pressure.

A second synthesis of the ætioporphyrin (" III "), m. p. 360°, described previously (A., 1927, 1206), has been effected by heating the methene from opso-pyrrole with (3-methyl-4-ethyl-2-bromomethyl)(4'-methyl-3'-ethyl-2'-bromomethylpyrrolenyl)methene

(hydrobromides) in presence of succinic acid. The aetioporphyrin, which is the basis of the blood colouring matter, is converted by lead dioxide in chloroform–acetic acid into the corresponding xanthoporphinogen, decomp. 298°. The latter is converted back into the aetioporphyrin by reduction in methyl-alcoholic solution with sodium amalgam.

Mesoporphyrin, m. p. 206°, is obtained (cf. this vol., 76) when a mixture of (3-methyl-4-ethyl-2-bromomethylpyrryl)(4'-methyl-3'-ethyl-2'-bromomethylpyrrolenyl)methene hydrobromide is added to concentrated sulphuric acid. Isolation is effected through the sodium salt. E. E. TURNER.

Isomerisation of an *iso*oxazole to a triazole derivative. G. WITTIG, F. BANGERT, and H. KLEINER (Ber., 1928, 61, [B], 1140—1143).—4 : 5-Diphenyl-3-methyl*iso*oxazole cannot be prepared by the action of hydroxylamine on *acetyldeoxybenzoin*, m. p. 99—99·5°, prepared by the action of acetyl chloride and sodamide on deoxybenzoin in ether, since the diketone is either not attacked or suffers extensive decomposition. A possible source of the desired compound appeared to be 4-benzeneazo-5-phenyl-3-methyl*iso*oxazole, which, however, when distilled in the presence of copper powder or sand, becomes isomerised to 5-*benzoyl-2-phenyl-4-methyl*-1 : 2 : 3-*triazole*, m. p. 74° (p-*nitrophenylhydrazone*, m. p. 231—231·5°). Isomerisation also occurs vigorously at 180—240°, but is not observed in solvents of lower b. p., whereas with media of high b. p. (phenol, dimethylaniline, nitrobenzene) smeary products are obtained. The identity of the triazole is established by its production from acetic anhydride and any of the stereoisomeric forms of the *phenylmethylhydrazone* of *oximinobenzoylacetone*. The a-*form*, m. p. 126°, of the latter compound is prepared from oximinobenzoylacetone and *as*-phenylmethylhydrazine in cold ether, the b-*variety*, m. p. 150—151°, being isolated from the mother-liquors or obtained directly from the components in boiling methyl alcohol. The stable c-*form*, m. p. 164—165°, is prepared by more extended action under the latter conditions. The b- and c-isomerides with acetic anhydride afford an *acetate*, m. p. 119°, hydrolysed to the c-variety by cold methyl-alcoholic sodium methoxide. The *phenylhydrazone* of *oximinobenzoylacetone*, m. p. 170—171° (decomp.), is converted when heated into 4-nitroso-1 : 5-diphenyl-3-methylpyrazole. H. WREN.

Azoxines. V. Application of the Turpin reaction to aminonaphthols. H. GOLDSTEIN and A. WARNÉRY (Helv. Chim. Acta, 1928, 11, 489—495). —When a mixture of 1-amino-β-naphthol and picryl chloride is treated with alcoholic potassium hydroxide there is formed 9 : 11-*dinitro-βα-naphthaphenoxazine* (I), decomp. 279° (cf. Turpin, J.C.S., 1891, 59, 714),
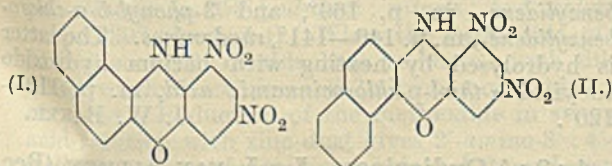
which when reduced and subsequently oxidised with ferric chloride yields 11-*amino-βα-naphthaphenoxazine*-

9-*imine* [*perchlorate*; *hydrochloride*; *acetyl* derivative (*perchlorate*)]. Similarly, 2-amino-α-naphthol furnishes 8 : 10-*dinitro-αβ-naphthaphenoxazine* (II), which yields 10-*amino-αβ-naphthaphenoxazine*-8-*imine* (*perchlorate*). 3-Amino-β-naphthol affords 1 : 3-*dinitro-ββ-naphthaphenoxazine*, m. p. 313° (decomp.), from which 1-*amino-ββ-naphthaphenoxazine*-3-*imine* [*perchlorate*; *acetyl* derivative (*perchlorate*)] is obtained.

3-(2 : 4 : 6-*Trinitrophenyl*)*amino-β-naphthol* and 3-(2 : 4-*dinitronaphthyl*)*amino-β-naphthol* have m. p. 205° (decomp.) and 205°, respectively.

H. BURTON.

Hetero-ring formations with thiocarbohydrazide. III. Reactions of substituted thiocarbohydrazides. IV. Reactions of 1-phenylthiocarbohydrazide. P. C. GUHA and S. K. ROY-CHOUDHURY (J. Indian Chem. Soc., 1928, 5, 149—161, 163—174).—III. Substituted thiocarbohydrazides have been prepared by the action of hydrazine on dithiocarbazinates, $NH_2 \cdot NH_2 + NRR' \cdot NH \cdot CS_2Me(Et)$ $\longrightarrow NRR' \cdot NH \cdot CS \cdot NH \cdot NH_2(I) + SHMe(Et)$. Thus, methyl phenyldithiocarbazinate and hydrazine hydrate yield *phenylthiocarbohydrazide* (I, R=Ph, R'=H), m. p. 149—150° (*hydrochloride*, m. p. 181°); *ethyl* m-*tolyldithiocarbazinate*, m. p. 99°, prepared by successive treatment of *m*-tolylhydrazine with carbon disulphide and potassium hydroxide solution, and ethyl bromide, gives m-*tolylthiocarbohydrazide*, m. p. 163—164° (decomp.), and *ethyl* 1-*phenyl-1-methyldithiocarbazinate* affords 1-*phenyl-1-methylthiocarbohydrazide* (I, R=Ph, R'=Me), m. p. 228—229° (decomp.). The following *phenylthiocarbohydrazones* are described : benzaldehyde-, m. p. 185° ; p-*nitrobenzaldehyde*-, m. p. 192° ; *cinnamaldehyde*-, m. p. 167—198° (168 ?) ; *salicylaldehyde*-, m. p. 206° (decomp.), and *acetone*-, m. p. 162°. p-*Nitrobenzaldehyde*-m-*tolylthiocarbohydrazone* has m. p. 165—166°. When benzaldehydephenylthiocarbohydrazone is heated with ferric chloride solution there is formed 2-*phenyl-5-phenylhydrazino*-1 : 3 : 4-*thiodiazole*, m. p. 172°. The formation of this compound is explained by an initial isomerisation of the thiocarbohydrazone and subsequent loss of two atoms of hydrogen, viz.,

$$NHPh \cdot NH \cdot C(SH) \vdots N \cdot N \vdots CHR \longrightarrow N \underset{CR \cdot S}{\overset{N=C \cdot NH \cdot NHPh}{<}}.$$
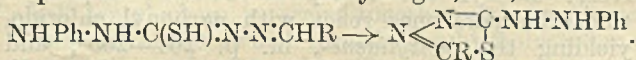
2-*Cinnamyl*- and 2-p-*nitrophenyl-5-phenylhydrazino*-1 : 3 : 4-*thiodiazoles* have m. p. 173° and 263—264°, respectively. Phenylthiocarbohydrazide and o-chlorobenzaldehyde react yielding 2-*phenylhydrazino*-6 : 7-*benzo*-1 : 3 : 4-*heptathiodiazine*,

$$C_6H_4 \underset{S-C \cdot NH \cdot NHPh}{\overset{CH \vdots N}{<}} \quad , \text{ m. p. 195°, formed by}$$
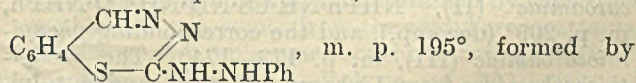
elimination of hydrogen chloride from the intermediate thiocarbohydrazone. The action of phenyl- and m-tolyl-thiocarbohydrazides on phenanthraquinone is to form the *phenylhydrazone*, m. p. above 300°, and m-*tolylhydrazone*, m. p. above 295°, of 2-*keto-5* : 6-*phenanthra*-1:3:4-*oxadiazine*, $(\overset{\cdot C \cdot N \vdots N}{\underset{\cdot C \cdot O \cdot C \vdots N \cdot NHR}{\,}})$, respectively, thus differing from the action of thiocarbohydrazide on benzil (A., 1926, 417). Acenaphthaquinone, phenanthraquinone monoxime, and isatin react with phenylthiocarbohydrazide yielding 2-*keto*-

5 : 6-*acenaphtha*-1 : 3 : 4-*oxadiazine phenylhydrazone*, m. p. above 300°, 2-*keto*-5 : 6-*phenanthra*-1 : 3 : 4 : 7-*heptaoxatriazine phenylhydrazone*, m. p. above 300°, and 2-*keto*-5 : 6-*isatino*-1 : 3 : 4-*thiodiazine*, darkens at 260°, respectively.

Ethyl acetoacetate and phenylthiocarbohydrazide form the corresponding *phenylthiocarbohydrazone*, m. p. 115—116°, which with sodium methoxide eliminates 1 mol. of alcohol giving 1-*thiocarbophenyl-hydrazido*-3-*methyl*-5-*pyrazolone*, m. p. 142° (decomp.). Similarly, acetonylacetone furnishes 5 : 8-*dimethyl*-2-*phenylhydrazino*-1 : 3 : 4-*octathiodiazine*, m. p. 230° (decomp.) ; ω-bromoacetophenone yields 5-*phenyl*-2-*phenylhydrazino*-1 : 3 : 4-*thiodiazole*, m. p. 199°, and ethyl chloroacetate gives the *hydrazone*, m. p. 152—153° (*benzylidene* derivative, m. p. 158°), of 2 : 5-*di-keto*-4-*phenyltetrahydro*-1 : 3 : 4-*thiodiazine*. Salicyl-aldehydephenylthiocarbohydrazone and ethyl chloro-acetate give the *salicylidene* derivative, m. p. 220° [*benzylidene* derivative, m. p. 189° (decomp.)], of 2 : 5-*diketo*-4-*phenyltetrahydro*-1 : 3 : 4-*thiodiazine* 2-*hydrazone* [(*hydrochloride*?), m. p. 247—248° (decomp.)], whilst from ω-bromoacetophenone there is formed the *salicylidene* derivative, m. p. 221°, of 2-*keto*-4 : 5-*diphenyldihydro*-1 : 3 : 4-*thiodiazine* 2-*hydrazone*.

IV. Phenylthiocarbohydrazide is converted by 100% formic acid into 2-*phenylhydrazino*-1 : 3 : 4-*thiodiazole*, m. p. 220°, and by acetic anhydride into its 5-*acetyl* derivative, m. p. 172—173° (decomp.). With potassium ethyl xanthate there is formed 5-*thion*-2-*phenylhydrazino*-1 : 3 : 4-*thiodiazole*, m. p. 127° (decomp.), oxidised by ferric chloride to a *disulphide* (?), $C_{16}H_{14}N_8S_4$, m. p. 237° (decomp.). Carbonyl, acetyl, and benzoyl chlorides convert phenylthiocarbo-hydrazide into its hydrochloride, but phthalyl, malonyl, and thionyl chlorides yield 5-*hydroxy*-8-*keto*-2-*phenylhydrazino*-6 : 7-*benzo*-1 : 3 : 4-*octathiodiazine*, m. p. 206° (decomp.), 5-*hydroxy*-7-*keto*-2-*phenyl-hydrazino*-6 : 7-*dihydro*-1 : 3 : 4-*heptathiodiazine*, m. p. 201—202° (decomp.), and 2-*phenylhydrazino*-1 : 5 : 4 : 3-*dithiodiazole* 5-*oxide*, m. p. 220° (decomp.), respect-ively. Benzylidene- and p-nitrobenzylidene-phenyl-thiocarbohydrazones react with carbonyl chloride, yielding the *benzylidene*-, m. p. 204—205°, and p-*nitrobenzylidene*-, m. p. 258°, derivatives of 2 : 5-*di-keto*-4-*phenyltetrahydro*-1 : 3 : 4-*thiodiazole* 2-*hydrazone*, respectively.

Phenylthiocarbohydrazide reacts with phenylcarb-imide and phenylthiocarbimide to form the *phenyl-carbamide* (II), NHPh·NH·CS·NH·NH·CO·NHPh, m. p. 209° (decomp.), and the corresponding *phenyl-thiocarbamide* (III), m. p. 173—174°. The *phenyl-thiocarbamides* from 1-phenyl-1-methyl- and m-tolyl-thiocarbohydrazides have m. p. 219—220° (decomp.) and 160° (decomp.), respectively. Treatment of (II) with hot 20% potassium hydroxide solution furnishes 5-*keto*-1-*phenyl*-2-*phenylhydrazino*-4 : 5-*dihydro*-1 : 3 : 4-*triazole*, m. p. 244—245°, whilst similar treatment of (III) yields a mixture of 5-*anilino*-2-*phenylhydrazino*-1 : 3 : 4-*thiodiazole* (IV), m. p. 199°, and 5-*thiol*-2-*phenylhydrazino*-1 : 3 : 4-*thiodiazole*, m. p. 258—259° (*triacetyl* derivative, m. p. 206—207°). Oxidation of this last compound with ferric chloride gives the corresponding *disulphide*, m. p. 205° (decomp.).

Treatment of (III) with hot concentrated hydro-chloric acid furnishes 2 : 5-*diketotetrahydro*-1 : 3 : 4-*thiodiazole*, m. p. 222°. Oxidation of (II) with ferric chloride affords a *compound*, $C_{28}H_{28}O_2N_{10}S_2$, m. p. 198—199° (decomp.), whilst (III) yields 2-*anilino*-5-*phenylazo*-1 : 3 : 4-*thiodiazole*,

$$\begin{array}{c} N{:}C{\cdot}NHPh \\ \qquad \qquad >\!S \\ N{:}C{\cdot}N{:}NPh \end{array}, \text{ m. p. } 256—$$

257°, also obtained by oxidation of (IV) with hydrogen peroxide.

When methyl phenyldithiocarbazinate is treated with ethylenediamine and o-phenylenediamine, there are formed 2-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3-*thiazole phenylhydrazone*, m. p. 223°, and 5-*thiol*-1-*phenyl*-2 : 3-*benzodihydro*-1 : 4 : 6-*triazine*, m. p. 292—293° (*acetyl* derivative, m. p. 203—204°), respectively. This last compound is oxidised by ferric chloride to the *disulphide*, $C_{26}H_{20}N_9S_2$, m. p. above 300°.

H. BURTON.

Rhodanine and related compounds. R. ANDREASCH (Monatsh., 1928, **49**, 122—132).—Re-duction of 5-benzylidene-3-phenylrhodanine with zinc dust and alcoholic hydrogen chloride yields 4-*keto*-3-*phenyl*-5-*benzylideneietetrahydrothiazine*,

$$\begin{array}{c} NPh{\cdot}CH_2{\cdot}S \\ CO{-}{-}{-}C{:}CHPh \end{array}, \text{ m. p. } 206°. \text{ 3-Phenylrhodanine}$$

similarly yields 4-*keto*-3-*phenyltetrahydrothiazine*, m. p. 115°, whilst 3-p-tolylrhodanine by reduction with amalgamated zinc yields 4-*keto*-3-p-*tolyltetrahydro-thiazine*, m. p. 243°. When the reduction of rhodanine itself was attempted only the products of hydrolytic fission (thioglycollic acid and ammonia) could be isolated. *Benzylidenediphenylthiohydantoin*, m. p. 206°, is obtained in 86% yield when diphenylthio-hydantoin and benzaldehyde are heated together in acetic acid. Sodium β-bromo-β-phenylpropionate reacts with ammonium phenyldithiocarbamate to yield 2-*thioketo*-3 : 6-*diphenyltetrahydro*-1 : 3-*azthine*,
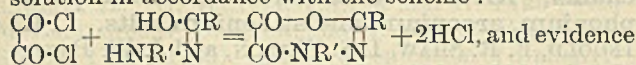
$$\begin{array}{c} NPh{\cdot}CS{\cdot}S \\ CO{\cdot}CH_2{\cdot}CHPh \end{array}, \text{ m. p. } 122°, \text{ which by heating with}$$

alkali is converted into β-phenyl-β-thiolpropionic acid. Similarly, sodium α-bromo-β-phenylpropionate and ammonium phenyldithiocarbamate yield 5-*benzyl*-3-*phenylrhodanine*, m. p. 118—119°. The anilide of thio-glycollic acid when heated with benzaldehyde in acetic acid is converted into the *dianilide* of benzylidene-dithioglycollic acid, CHPh(S·CH$_2$·CO·NHPh)$_2$, m. p. 178°. By the action of sodium hydroxide on a mixture of rhodanine and the hydrogen sulphite compound of isobutaldehyde is obtained 5-iso*propylidenerhodanine*, m. p. 128°. α-Bromoisovaleric acid or its ester reacts with thiocarbamide in alcohol solution to yield iso*propylthiohydantoin*, m. p. 229°. By heating rhod-anine or 3-phenylrhodanine with o-chlorobenzaldehyde in acetic acid are obtained, respectively, 5-o-*chloro-benzylidene*-, m. p. 169°, and 3-*phenyl*-5-o-*chloro-benzylidene*-, m. p. 140—141°, *rhodanines*. The latter is hydrolysed by heating with barium hydroxide to yield α-*thiol*-p-*chlorocinnamic acid*, m. p. 119—120°.

J. W. BAKER.

1 : 3 : 4-Oxadiazines. I. J. VAN ALPHEN (Rec. trav. chim., 1928, **47**, 673—682).—Derivatives of 1 : 3 : 4-oxadiazine are produced by the action of

oxalyl chloride on β-acylphenylhydrazines in benzene solution in accordance with the scheme :

$$\begin{array}{ll} CO \cdot Cl & HO \cdot CR \\ CO \cdot Cl & HNR' \cdot N \end{array} = \begin{array}{l} CO-O-CR \\ CO \cdot NR' \cdot N \end{array} +2HCl, \text{ and evidence}$$

in favour of the structure assigned is adduced. Thus from the appropriate acylphenylhydrazine the following are obtained : Δ²-4-*phenyl-2-methyl*-5 : 6-*diketo*-1 : 3 : 4-*oxdiazine*, m. p. 141°. This is hydrolysed by water in two stages, rupture of the 1 : 6-linking occurring first, followed by the 4 : 5-linking with the regeneration of oxalic acid and β-acetylphenyl-hydrazine. Decomposition with substances of the type NH_2R or $NHR \cdot NH_2$ yields the corresponding substituted amide or hydrazide of oxalic acid, whilst the action of alcohol produces α-*ethoxalyl-β-acetyl-phenylhydrazine*, $CO_2Et \cdot CO \cdot NPh \cdot NHAc$, m. p. 95°, which is synthesised by the action of ethoxalyl chloride on β-acetylphenylhydrazine. Δ²-2 : 4-*Diphenyl*-5 : 6-*diketo*-1 : 3 : 4-*oxdiazine*, m. p. 175°, which by treatment with alcohol yields α-*ethoxalyl-β-benzoylphenyl-hydrazine*, m. p. 157° (synthesised from β-benzoyl-phenylhydrazine) ; Δ²-4-*phenyl*-2-*benzhydryl*-5 : 6-*diketo*-1 : 3 : 4-*oxdiazine*, m. p. 167—168°, which is converted by boiling alcohol into α-*ethoxalyl-β-diphenylacetylphenylhydrazine*, m. p. 189° (also synthesised). J. W. BAKER.

Alkaloids of *Ceanothus Americanus*. II. A. H. CLARK (Amer. J. Pharm., 1928, **100**, 240—242 ; cf. A., 1926, 548).—Various methods have been used for extracting the alkaloids without materially increasing the yield. Fractional extraction with acetone and recrystallisation from butyl alcohol afforded a *compound*, m. p. 260—263°. The *phosphate*, *oxalate*, *sulphate*, *tartrate*, and *chloride* (m. p. 255—260°) have been prepared.

A light petroleum extract furnished a fat, saponification value 136—155, and a non-alkaloidal *substance*, m. p. 175°. A sample of very pure " gallotannic " acid was also obtained. S. COFFEY.

Simplest homologues of codeine. A. E. TSCHITSCHIBABIN and A. V. KIRSSANOV (J. Russ. Phys. Chem. Soc., 1928, **60**, 691—694).—See this vol., 188.

Syntheses in the aporphine group. II. Synthesis of bulbocapnine methyl ether. J. M. GULLAND and R. D. HAWORTH (J.C.S., 1928, 1132—1137).—Condensation of β-piperonylethylamine with 2-nitro-3 : 4-dimethoxyphenylacetyl chloride (Kay and Pictet, J.C.S., 1913, **103**, 952) yields 2′-*nitro*-3′ : 4′ - *dimethoxyphenylaceto* - β - 3 : 4 - *methylenedioxy-phenylethylamide*, m. p. 158°. Treatment of a cold chloroform solution of this substance with phosphorus pentachloride gives a good yield of 2′-*nitro*-3′ : 4′-*di-methoxy*-6 : 7-*methylenedioxy*-1-*benzyl*-3 : 4-*dihydroiso-quinoline*, m. p. 164° [*sulphate* ; *nitrate* ; *hydrochloride*, m. p. 230° (decomp.)]. When the *methiodide*, m. p. 215° (decomp.), of this base is heated with dilute alkali, oxyhydrastinine and 2-nitrohomoveratrole are obtained. Reduction of the methiodide in strongly acid solution with zinc dust gives 2′-*amino*-3′ : 4′-*di-methoxy*-6 : 7-*methylenedioxy*-1-*benzyl*-2-*methyltetra-hydro*isoquinoline (I), isolated as the *dihydrochloride*, m. p. 231° (decomp.). Phenanthrene ring-closure is

effected by diazotisation of the base (I) in a mixture of methyl alcohol and 2N-sulphuric acid. *dl*-Bulbo-capnine methyl ether (*methiodide*, m. p. 243°), isolated as the *hydriodide*, m. p. 250° (decomp.), is thus obtained (cf. Gadamer, A., 1911, i, 1011). M. CLARK.

Alkaloids of some Indian aconites (*A. Balfourii*, *A. deinorrhizum*, and " Chumbi aconite "). T. A. HENRY and T. M. SHARP (J.C.S., 1928, 1105—1121).—ψ-Aconitine, the alkaloid present in *Aconitum Balfourii*, was extracted in quantity from *A. deinorrhizum*, Stapf. The pure substance has m. p. 214° (decomp.), $[\alpha]_D^{20}$ +17·06° in alcohol, +22·75° in chloroform. It forms a *hydrochloride*, m. p. 179—182° (decomp.), $[\alpha]_D^{20}$ −18·1° in water (+4H₂O, +3H₂O), *oxalate*, m. p. 216° (decomp.), *per-chlorate*, m. p. 239° (decomp.), and *picrate*, m. p. 196° (decomp.). From their analytical results, the authors incline to the provisional formula $C_{36}H_{51}O_{12}N$ suggested by Dunstan and Andrews (*ibid.*, 1905, **87**, 1636). ψ-Aconitine, which contains six methoxyl groups, yields on hydrolysis 1 mol. proportion each of acetic and veratric acids and, in addition, ψ-aconine, $C_{25}H_{41}O_8N$, m. p. 93—94°, $[\alpha]_D^{20}$ +38·7° in water (+1Me₂CO), which gives a *tetra-acetyl* deriv-ative, m. p. 228°, $[\alpha]_D^{20}$ −8·1° in alcohol. The two oxygen atoms unaccounted for must therefore be present as hydroxyl groups. The nitrogen is present as a methylimino-group. On oxidation with cold nitric acid, ψ-aconitine yields a pale yellow *substance*, (A), $C_{33}H_{40}O_{16}N_4$, blackening at 260°, decomp. 270°, and a bright yellow *substance* (B), $C_{34}H_{43}O_{17}N_3$, decomp. 195°. Product (A) still contains the acetyl group, but the veratroyl residue has been nitrated in position 6. Five methoxyl groups remain, two belonging to the nitroveratroyl radical. The methyl-imino-group has been converted into a ∶N·NO group, since the compound gives Liebermann's nitrosoamine reaction. The remaining nitrogen atom is probably present as a nitro-group, indicating the presence of a benzene ring in the nucleus. When (A) is treated with acetyl chloride at 100° under pressure, nitrosyl chloride, obtained by the conversion of the ∶N·NO group into a *N*-acetyl group, is formed together with a *substance*, m. p. 227—230°, which furnishes on hydrolysis 3 mol. proportions of acetic acid. Two of these are obtained by alkaline hydrolysis, arising (1) from the acetyl group originally present in ψ-aconitine and persist-ing in (A) and (2) from an acetyl group formed in the reaction by acetylation of a hydroxyl group in A. The third mol. of acetic acid, obtained by subsequent acid hydrolysis, comes from the acetyl group attached to nitrogen by replacement of the nitroso-group in the reaction. Alkaline hydrolysis of (A) gives, in addition, 6-nitroveratric acid and a *substance* (C), $C_{22}H_{31}O_{10}N_3$, m. p. 215°, $[\alpha]_D$ +30·9° in alcohol. The function of the unaccounted-for oxygen atom in (A) is demonstrated by the behaviour of (C) on being dissolved in methyl alcohol containing sodium methoxide, when a *sodium* salt, $C_{22}H_{32}O_{11}N_3Na$, is produced by addition of the elements of sodium hydroxide, showing the presence of a lactin group in the hydrolytic product and also in A. ψ-Aconitine, therefore, probably contains a group such as NMe·CH·OH, oxidised by nitric acid to ·N(NO)·CO.

Acetylation of (C) gives a *substance*, $(C_{26}H_{35}O_{12}N_3?)$, m. p. 257° (decomp.), and a small amount of a *substance*, decomp. 322°. The nitric acid oxidation product, (B), gives on hydrolysis acetic and 6-nitroveratric acids and an amorphous nitrogenous product. It contains 5 methoxyl groups, of which 2 are in the nitroveratroyl residue, and a nitroso-group eliminated on treatment with acetyl chloride as in the case of (A). On oxidation with permanganate, ψ-aconitine yields acetaldehyde and a complex mixture of solid products (cf. Carr, J.C.S., 1912, **101**, 2243). Oxidation with chromic acid yields a neutral *substance*, $C_{34}H_{45}O_{11}N$, decomp. 255°, $[\alpha]_D^{20}$ +67·95° (*hydrochloride*, decomp. 180°, $[\alpha]_D^{20}$ +39·5° in alcohol; *picrate*, m. p. 229—230°; *chloroaurate*, $4C_{34}H_{45}O_{11}N,3HAuCl_4$, sintering 175°, decomp. 185°), containing 5 methoxyl groups and retaining intact the methylimino-group. On hydrolysis by alkalis, this substance gives acetic and veratric acids and a *compound*, $(C_{23}H_{35}O_7N?)$, m. p. 175—177°.

The alkaloid from the "Chumbi aconite," collected on the pass between Sikkim and the Chumbi valley in Tibet, resembles aconitine rather than japaconitine (Dunstan and Read, J.C.S., 1900, **77**, 45). It has m. p. 203° (decomp.), $[\alpha]_D^{20}$ +16·3° in chloroform. It yielded a hydrobromide, m. p. 175°, $[\alpha]_D^{20}$ −34·8° in water (contaminated with a minute quantity of a *substance*, m. p. 199°), *hydrochloride*, m. p. 174°, $[\alpha]_D^{20}$ −35·9° in water, *hydriodide*, m. p. 225°, and *chloroaurate*, m. p. 152°. Hydrolysis and subsequent acetylation of the alkaloid residues after extraction of the crystalline material, gave a *substance*, m. p. 241°, $[\alpha]_D^{20}$ −32·5° in chloroform.   M. Clark.

Grignard's reaction. Preparation of tetraphenylphosphonium salts. J. Dodonov and H. Medox (Ber., 1928, **61**, [B], 907—911).—The production of tetraphenylphosphonium bromide, m. p. 287° (also *dihydrate*), during the action of an ethereal solution of magnesium phenyl bromide on triphenylphosphine is due to atmospheric oxidation : the yield of the compound attains 72% if a brisk current of oxygen is passed through the reaction mixture. Triphenylphosphine oxide does not appear to react under any conditions with an ethereal solution of magnesium phenyl bromide. An explanation of the course of the reaction is afforded, based on the views of Meisenheimer and Casper (A., 1921, i, 654). When treated in aqueous solution with precipitated silver oxide at the ordinary temperature, the bromide gives a strongly alkaline solution of tetraphenylphosphonium hydroxide, which readily loses benzene when concentrated even in a vacuum and yields a residue of triphenylphosphine oxide, m. p. 154·5—155°, and tetraphenylphosphonium carbonate. Treatment of the dilute aqueous solution of tetraphenylphosphonium hydroxide with the requisite acid yields the following salts : *chloride*, m. p. 265°, and its *pentahydrate*; normal *sulphate*, m. p. indef. (also $+18H_2O$). The *nitrate*, m. p. 284° (decomp.), and *iodide*, m. p. 333°, are described. A modification of Pfeiffer's method (A., 1905, i, 164) for the preparation of triphenylphosphine from phosphorus trichloride and magnesium phenyl bromide gives the compound in 76% yield.
                                                      H. Wren.

Nature of the alternating effect in carbon chains. XXVII. Nitration of aromatic phosphonium, arsonium, and stibonium salts. C. K. Ingold, F. R. Shaw, I. S. Wilson, and J. W. Baker (J.C.S., 1928, **1280**—1286).—Investigation of the nitration of phenyltrimethyl-phosphonium, -arsonium, and -stibonium picrates and of benzyltrimethylphosphonium and -arsonium picrates shows that the proportion of *m*-substitution of quaternary salts of the same general type diminishes with the increasing atomic number of the central positively-charged atom. The possible causes of this effect are discussed. The following are described : *Phenyltrimethylphosphonium picrate*, m. p. 132—133° (m-*nitro*-derivative, m. p. 166—167°); *benzyltrimethylphosphonium picrate*, m. p. 173° (o-*nitro*-derivative, m. p. 152—153°; m-*nitro*-derivative, m. p. 171—172°; p-*nitro*-derivative, m. p. 188—189°); *benzyltrimethylarsonium picrate*, m. p. 175—176° (p-*nitro*-derivative, m. p. 166—168°); *phenyltrimethylstibonium picrate*, m. p. 153° (m-*nitro*-derivative, m. p. 203°); m-*nitrophenyltrimethylarsonium picrate*.   M. Clark.

Aliphatic-aromatic arseno-compounds. II. β - Hydroxyethylarsinic acid and some aryl β-arsenoethyl alcohols. R. H. Edee (J. Amer. Chem. Soc., 1928, **50**, 1394—1399; cf. A., 1927, 579).—Orange-yellow, amorphous arylarsenoethyl alcohols, $C_6H_4R·[As]_n·CH_2·CH_2·OH$, are formed by reducing a solution of β-hydroxyethylarsinic acid, m. p. 157—159° (also $+H_2O$; cf. Quick and Adams, A., 1922, i, 600), and the appropriate arylarsinic acid in hydrochloric acid with hypophosphorous acid at a low temperature. In this way p-*hydroxyphenylarsenoethyl alcohol*, p-*aminophenylarsenoethyl alcohol* (*hydrochloride*), 3 - amino - 4 - hydroxyphenyltetra-arsenoethyl alcohol, and p-*carboxymethylaminophenyltetra-arsenoethyl alcohol* are prepared. A mixture of *p*-acetoxyphenylarsinic acid and β-hydroxyethylarsinic acid is reduced at the ordinary temperature to p-*acetoxyphenylarsenoethyl alcohol* and at 60° to (?) p-*acetoxyphenyltriarsenoethyl alcohol*, $C_{10}H_{12}O_4As_3$.
                                            H. E. F. Notton.

Conversion of diaminodiphenylarsinic acid into diphenylarsinic acid. V. V. Nekrassov (J. Russ. Phys. Chem. Soc., 1927, **59**, 877—880).—The possibility of obtaining diphenylarsinic acid by the diazotisation and subsequent reduction of diaminodiphenylarsinic acid, which is a waste by-product of arsanilic acid manufacture, was studied. Since the reduction by means of alcohol or alkaline stannite was impossible, excess of hypophosphite was used; the yields of diphenylarsinic acid, however, were low (38·5%) even with five times the theoretical quantity of the salt. Addition of a small amount of copper sulphate raised the yield to 60%, and increased the rate of reduction.   M. Zvegintzov.

Diphenylamine-p-arsinic acid. C. S. Gibson and J. D. A. Johnson (J.C.S., 1928, 1286—1288).—A corrected m. p., 295—297° (decomp.) after darkening at 287°, is recorded for diphenylamine-*p*-arsinic acid [*hydrochloride*, m. p. 153—155° (decomp.)] (cf. Burton and Gibson, A., 1926, 419; Lieb and Wintersteiner, this vol., 312). *N*-Acetyl-*p*-aminodiphenylamine has m. p. 127—128°.   M. Clark.

Diphenylamine- and triphenylamine-arsinic acids. II. O. WINTERSTEINER and H. LIEB [with M. BASILIOUS, F. SEELICH, and H. MAYER (Ber., 1928, 61, [B], 1126—1135).—Direct arsenication of diphenylamine gives diphenylamine-*p*-arsinic acid in only very modest yield (cf. this vol., 312) and the reaction is less successful when applied to the nitro- and amino-diphenylamines. *p*-Arsanilic acid does not react with bromobenzene according to Ullmann's method in boiling nitrobenzene or amyl alcohol, whereas reaction occurs readily with *o*-arsanilic and bromobenzene or its derivatives; amyl alcohol is generally a suitable solvent, since decomposition frequently takes place at the temperature of boiling nitrobenzene. Thus *o*-arsanilic acid, bromobenzene, potassium carbonate, copper powder, and cuprous iodide at 130—140° afford *diphenylamine-o-arsinic acid*, m. p. 162° (*disodium* salt ($+6H_2O$)]. If the temperature of the reacting mixture is raised to 160—170°, the main product is *o-diphenylaminophenylarsinic acid*, $NPh_2 \cdot C_6H_4 \cdot AsO_3N_2$, decomp. 150°. Similarly, *o-acetamidophenylarsinic acid*, m. p. 215°, is readily converted into *o-acetanilidophenylarsinic acid*, $NPhAc \cdot C_6H_4 \cdot AsO_3H_2$, decomp. 158°. *o*-Arsanilic acid and *p*-dibromobenzene at 130—140° yield *op'-bromophenylaminophenylarsinic acid*, m. p. 80°, and at 150—160° afford *o-di-p'-bromophenylaminophenylarsinic acid*, $(C_6H_4Br)_2N \cdot C_6H_4 \cdot AsO_3H_2$, m. p. 215°. The three isomeric bromobenzoic acids condense analogously with *o*-arsanilic acid yielding, respectively, *oo'-carboxyphenylaminophenylarsinic acid*, decomp. 237° (hydrated *monosodium* salt), *om'-carboxyphenylaminophenylarsinic acid*, decomp. 238° (cf. Burton and Gibson, A., 1927, 1098), and *op'-carboxyphenylaminophenylarsinic acid*, decomp. 210°; in the last case the action appears to follow a different course if cuprous iodide is used in place of potassium iodide in the condensation. The yield is quantitative with the *o*-bromobenzoic acid, good and mediocre, respectively, with the corresponding *m*- and *p*-compounds. The isomeric bromonitrobenzenes yield *oo'-nitrophenylaminophenylarsinic acid*, decomp. 245° (temperature of condensation 110°), *om'-nitrophenylaminophenylarsinic acid*, decomp. 205—210°, and *op'-nitrophenylaminophenylarsinic acid*, decomp. 245—250°. Formation of triphenylamine-arsinic acids is not observed with the bromonitrobenzenes or bromobenzoic acids.

Direct action of arsenic acid on *m*-nitrodiphenylamine at 140—150° gives *pm'-nitrophenylaminophenylarsinic acid*, decomp. above 330° (*trihydrated disodium* salt), in 10% yield. Analogously, *po'-nitrophenylaminophenylarsinic acid*, decomp. 342° (*hexahydrated disodium* salt), and *pp'-nitrophenylaminophenylarsinic acid*, decomp. above 320°, are obtained in very poor yield. The three acids are reduced by hypophosphorous acid to the corresponding arsenobenzenes. H. WREN.

Preparation of organo-mercury compounds of phenols, phenol ethers, and aromatic amines. P. NEOGI and M. P. CHATTERJI (J. Indian Chem. Soc., 1928, 5, 221—229).—Mercury derivatives of aromatic compounds can be prepared by the action of mercuric chloride and sodium hydrogen carbonate solution in presence of glycerol (cf. A., 1927, 214). In this way phenol gives *o*- and *p*-hydroxyphenylmercuric chlorides, but pyrocatechol, resorcinol, orcinol, guaiacol, phloroglucinol, and quinol yield derivatives in which each ·OH group is replaced by ·OHgCl. These mercurated derivatives are insoluble in, and are decomposed by sodium hydroxide solution. When alcoholic solutions of primary and secondary amines are treated with sodium hydrogen carbonate and mercuric chloride, the amino-hydrogen atoms are replaced by the ·HgCl grouping. Under similar conditions dimethylaniline gives *p*-mercurodiphenylenetetramethylmercurodiammonium chloride (cf. Pesci, A., 1894, i, 248). H. BURTON.

Position occupied by acetatomercuri(Hg·OAc')-groups in anilines containing in the nucleus a halogen group or a hydrocarbon residue. III. L. VECCHIOTTI (Gazzetta, 1928, 58, 231—239; cf. this vol., 655).—*p*-Bromoaniline reacts with 1 mol. of mercuric acetate in alcoholic solution to give *4-bromo-2-acetatomercurianiline*, m. p. 194° (*acetyl* derivative, m. p. 204°), from which the corresponding *2-hydroxymercuri*-, m. p. 180°, and *2-bromidomercuri*-, decomp. 194°, derivatives are prepared, and 2 : 2'-*mercury bis-*(4-bromoaniline), m. p. 220°. The position of the acetatomercuri-group is shown by the action of bromine in acetic acid, which yields 2 : 4-dibromoacetanilide.

It is observed that anilides *p*-substituted by halogen or a hydrocarbon residue do not (except *p*-nitroaniline) take up more than one acetatomercuri-group, which enters in the *o*-position to the amino-group. E. W. WIGNALL.

Action of mercuric acetate on *o*-bromoaniline. L. VECCHIOTTI (Gazzetta, 1928, 58, 239—244).—The action of mercuric acetate in aqueous solution, slightly acidified with acetic acid, on an equimolecular proportion of *o*-bromoaniline yields *2-bromo-4-acetatomercurianiline*, (I), m. p. 152—153°, (*acetyl* derivative, m. p. 220—221°), of which the corresponding *4-hydroxymercuri*-, m. p. 253—254°, and *4-bromidomercuri*-, m. p. 213—214°, derivatives are prepared. The action of sodium thiosulphate solution on (I) yields 4 : 4'-*mercury bis-o-bromoaniline*, m. p. 125°.

The structure of (I) is shown by the action of bromine, sodium bromide, and acetic acid on the acetyl derivative, which yields 2 : 4-dibromoacetanilide, with an unidentified substance, m. p. 183—184°. E. W. WIGNALL.

Mol. wt. of hæmocyanin. T. SVEDBERG and E. CHIRNOAGA (J. Amer. Chem. Soc., 1928, 50, 1399—1411).—The partial specific vol. of hæmocyanin from *Helix pomatia* is approx. 0·734 at p_H 3·8—7·0 and 0·754 at p_H 8·0. Its ultra-violet and visible absorption spectrum is unchanged from p_H 8·0 to p_H 4·7, but at p_H 3·8 the maximum is displaced towards the red on account of partial molecular disintegration. The diffusion coefficient, unlike that of other proteins, approaches a constant value only in 0·1% or more dilute solutions, decreasing rapidly at higher concentrations, probably as a result of intermolecular frictional forces. Using low concentrations near the isoelectric point, the mol. wt. determined from the sedimentation velocity (cf. A., 1927, 716; this vol., 191) is $4·93 \times 10^6$, and

from the sedimentation equilibrium, which is attained only with small centrifugal forces, 5.08×10^6. The good agreement indicates that the particles are approximately spherical ($r = 12.2 \times 10^{-7}$ cm.), and the results of both experiments together with the sharp differentiation between solvent and solution produced by high-speed centrifuging show that they are of uniform size. H. E. F. NOTTON.

Action of alkalis, acids, and enzymes on proteins and allied substances. III. E. ABDERHALDEN and H. MAHN (Z. physiol. Chem., 1928, **174**, 47—75).—The effect of the following reagents on gelatin, dispersed in 12.5% lithium bromide solution, has been investigated : (1) N-hydrochloric acid at 18°, 38°, 50—55°, 70—75° ; (2) $0.5N$-sodium hydroxide at 18° ; (3) N-sodium hydroxide at 18°, 38°, 50—55° ; (4) a borate buffer of p_H 8.3 at 38° ; (5) pepsin–hydrochloric acid at 38° ; (6) trypsin at p_H 7.6—8 and 38°. Measured by the rate of increase in amino-nitrogen the order of increasing activity of the acid or alkali is as follows : N-hydrochloric acid at 38°, N-sodium hydroxide at 18°, N-hydrochloric acid at 50—55°, N-sodium hydroxide at 38°, N-hydrochloric acid at 70—75°, N-sodium hydroxide at 50—55°. There is no constant relationship between the alteration in the optical rotation of these reaction mixtures with time and the increase in amino-nitrogen. At p_H 8.3 in absence of enzyme there is a slow change in the rotation of a gelatin solution, but no increase in the amino-nitrogen. If gelatin or elastin is digested for 3 days with trypsin, subsequent treatment with N-sodium hydroxide brings about a further slow hydrolysis, but treatment with pepsin–hydrochloric acid or with $0.1N$-hydrochloric acid has little if any further effect. The relationship of the experimental findings to the possible structure of proteins is discussed at some length. H. D. KAY.

Apparatus for the determination of carbon by the baryta method. P. DICKENS (Chem. Fabr., 1928, 293—294).—The barium hydroxide is contained in an absorption tube with a glass filter plate at the bottom above the gas inlet. The restriction on the passage of the gas causes the combustion tube to be under pressure during operation, whilst the apparatus is previously swept out with pure oxygen. Above the tube is a filter and flask so arranged that after combustion the apparatus may be inverted and the barium carbonate filtered and washed with water free from carbon dioxide. The excess of barium hydroxide is titrated and the precipitated barium carbonate weighed as sulphate. The method gives results accurate to $\pm 0.001\%$. C. IRWIN.

Analysis of mixtures of ethyl alcohol, ethyl acetate, acetic acid, and water. S. POZNANSKI (J. Amer. Chem. Soc., 1928, **50**, 981—988, and Rocz. Chem., 1928, 8, 152—164, 229—241).—Alcohol in the absence of esters may be accurately determined by a modification of the Bourcart–Kuriloff method (A., 1897, ii, 352) ; in the presence of esters, the alcohol is boiled with a known excess of acetic anhydride, excess of water is added, and the acetic acid produced determined by titration. Ethyl acetate is determined by hydrolysing at 60—65° with excess of barium hydroxide solution. The micro-titration of acetic acid in a modified Pilch apparatus is described. The methods are applied successfully to the analysis of a mixture of the four substances.
S. K. TWEEDY.

Furfuraldehyde–sulphuric acid reaction. O. COQUELET (Compt. rend. Soc. Biol., 1927, 97, 747—748; Chem. Zentr., 1928, i, 386—387).—The optimal conditions for the detection and determination of bile acids and cholesterol are described.
A. A. ELDRIDGE.

Colorimetric determination of histidine. K. SUZUKI and Y. KAISHIO (Bull. Agric. Chem. Soc. Japan, 1927, 3, 33—34).—The yellow colour developed when excess of a 2% solution of sulphanilic acid in 10% sulphuric acid, and concentrated acid to produce a 11—15% solution, are added to an aqueous solution of histidine, the mixture shaken and rendered alkaline with sodium hydroxide, is compared with that of $0.01N$-potassium dichromate solution.
CHEMICAL ABSTRACTS.

Measurement of quantities of chloroplast pigments. H. B. SPRAGUE (Science, 1928, 67, 167—169).—The chlorophylls a and b are obtained as aqueous solutions of the chlorophyllins, which are green by transmitted light. The comparison solution for the chlorophyllins from maize was prepared by diluting 0.3 c.c. of 0.5% aqueous malachite-green and 11.2 c.c. of 0.5% aqueous naphthol-yellow to 5500 c.c. with distilled water. The colour is equivalent to that of 10.708 mg. of chlorophyll hydrolysed to chlorophyllins and diluted to 1 litre. The carotin standard (equivalent to 1.890 mg. of carotin per litre of light petroleum) is made by adding 3.5 c.c. of 0.5% aqueous naphthol-yellow and 0.5 c.c. of 0.5% aqueous orange-G to 1 litre of distilled water. The xanthophyll standard (equivalent to 1.537 mg. of xanthophyll per litre of light petroleum) is made by adding 2.8 c.c. of 0.5% aqueous naphthol-yellow to 1 litre of distilled water. A Duboscq colorimeter is employed. A. A. ELDRIDGE.

Biochemistry.

Oxygen-carrying ability of the blood. K. YABUKI (Acta Schol. Med. Univ. Imp. Kyoto, 1927, **10**, 25—32).—Replacement of blood-serum by isotonic salt solution decreases the oxygen-carrying capacity of the red blood-corpuscles, but the effect of Locke's solution is less marked. Gum-arabic is without influence, but the presence of sodium hydrogen carbonate tends to increase the oxygen-carrying capacity. W. O. KERMACK.

Combination of hæmoglobin with oxygen. I. Aggregation of hæmoglobin molecules in the blood studied from the oxygen dissociation curve. K. YABUKI (J. Biochem. Japan, 1927, 8,

107—133).—The value of n in Hill's formula $y/100 = Kx^n/(1+Kx^n)$ is variable. Log K is a linear function of p_H, but the angle of inclination is 60°.

CHEMICAL ABSTRACTS.

Influence of reduced atmospheric pressure on the hæmoglobin concentration of the blood-corpuscles and on the action of the spleen on blood regeneration. L. DRASTICH (Biochem. Z., 1928, **195**, 189—205).—An apparatus provided with an animal container and suitable for continuous use with pressures reduced to 300 mm. mercury, is described. The hæmoglobin concentration (g. of hæmoglobin/100 c.c. of corpuscles by hæmatocrit) of the corpuscles of an animal after living under reduced pressure for some time is below normal but later increases. In splenectomised animals the blood regenerates under reduced pressure more slowly than in non-operated animals. Under reduced pressure, as in pernicious anæmia, the erythrocytes increase in size. Injection of spleen pulp favours the formation of corpuscles. P. W. CLUTTERBUCK.

Respiratory proteins of the blood. III. Acid-combining capacity and dibasic amino-acid content of hæmocyanin of *Limulus polyphemus*. A. C. REDFIELD and E. D. MASON (J. Biol. Chem., 1928, **77**, 451—457).—The hæmocyanin of *Limulus polyphemus* reacts as a univalent base with pK 3·3; it is able to bind 160×10^{-5} mol. of acid per g. as determined by titration, whilst calculation from the content of dibasic amino-acids leads to a combining capacity for acid of $155·5 \times 10^{-5}$ mol. per g. C. R. HARINGTON.

Vapour pressure of dog's blood at body temperature. A. GROLLMAN (J. Gen. Physiol., 1928, **11**, 495—506).—The vapour pressures of dog's plasma and whole blood measured by the dynamic method at 37·5° are both equal to 48·10 mm. of mercury, corresponding with an osmotic pressure of about 8·2 atm. The vapour pressure of the ultrafiltrate of the plasma is but slightly lower than that of the plasma itself by an amount corresponding with an osmotic pressure of 0·06 atm. for the plasma-colloids. W. O. KERMACK.

Molecules and ions in plasma. R. KELLER (Biochem. Z., 1928, **195**, 14—19).—A theoretical discussion of the effect of recent work on conceptions of the mobility of ions in plant and animal tissues and fluids. P. W. CLUTTERBUCK.

Electrodialysis of serum. G. ETTISCH and W. EWIG (Biochem. Z., 1928, **195**, 175—188).—The conditions are outlined for fractionation of serum-globulin by electrodialysis and compared with those of other authors. The best results are obtained with quick fractionation of undiluted serum, care being taken to avoid any considerable change of p_H and the temperature being maintained within physiological limits. An albumin–collodion membrane is described and used as anodic membrane together with a parchment membrane. This membrane cannot be replaced by a pure collodion membrane. Under the conditions described, the globulin of about 40 c.c. of serum is completely precipitated in about 1 hr. P. W. CLUTTERBUCK.

Phosphates in blood and the urinary excretion of phosphates. R. T. BRAIN, H. D. KAY, and P. G. MARSHALL (Biochem. J., 1928, **22**, 628—648).—The acid-soluble phosphorus in the plasma consists of inorganic phosphate, of which at least 80% is ultra-filtrable and dialysable, and of organically combined (ester) phosphoric acid. The latter is about 10% of the former. The amount of inorganic phosphate is less than the amount expected from the Donnan equilibrium between corpuscles and plasma. The very low concentration of ester phosphorus in the plasma cannot be raised by taking phosphoric esters by mouth, but can be raised temporarily by intravenous injection of these compounds. Doubling the plasma concentration of inorganic phosphate in the rabbit by intravenous injection results in about tenfold increase of excretion of the compound in the urine. When sodium glycerophosphate or fermentation sodium hexosediphosphate is injected there is a rapid rise of organic phosphorus in the plasma, which is followed by a fairly rapid fall. At the same time the inorganic phosphate in the plasma increases. This is reflected by an immediate increased excretion of inorganic phosphate in the urine, which reaches its maximum in the second hour after the injection, when the phosphoric ester content of the plasma has almost returned to its normal value. Similar results were obtained by injecting intravenously sodium glycerophosphate in human subjects. There appears to be a renal threshold for phosphate excretion. Within wide limits there is no relationship between the amount of urinary phosphate and the urinary volume. The various theories of the origin of urinary phosphate are critically discussed. S. S. ZILVA.

Colorimetric determination of iron and hæmoglobin in blood. II. S. Y. WONG (J. Biol. Chem., 1928, **77**, 409—412).—The blood is treated with concentrated sulphuric acid and potassium persulphate in the cold, the mixture is diluted and treated with sodium tungstate; iron is determined in an aliquot portion of the filtrate by the author's colorimetric method (A., 1923, ii, 435). C. R. HARINGTON.

Effects of congestion and heat on the composition of venous blood samples. Indirect determination of iron and chlorine in blood-corpuscles. F. H. SMIRK (Biochem. J., 1928, **22**, 739—744).—The errors in the determinations of corpuscular blood-chloride are due to incomplete separation of plasma from the corpuscles and not to the chemical analysis. Congestion of the arm causes a concentration of iron and increased venosity in samples from the median basilic vein. This is associated with a reduced percentage of chlorine in the plasma and an increased percentage in the corpuscles. Heating the arm renders the venous sample more arterial in appearance and this is associated with a transference of chlorine ions from corpuscles to plasma. The iron content of the blood may be raised. Venous samples should be taken with a minimum of congestion and should be thoroughly shaken with atmospheric or alveolar air if they are to form a trustworthy index of changes in the plasma-chlorides of the general circulation. S. S. ZILVA.

Determination of chloride in blood-serum. D. RAQUET (J. Pharm. Chim., 1928, [viii], 7, 487—489). —A protein-free filtrate is prepared by precipitating the proteins with zinc ferrocyanide and chloride is then determined by Volhard's method.

W. O. KERMACK.

Uric acid. I. Comparison of the direct and isolation methods for determining uric acid in blood filtrate, and a modification of Folin's method. R. E. WIENER and H. J. WIENER (J. Lab. Clin. Med., 1926, 11, 1035—1045).—Preliminary isolation of the uric acid is recommended in the determination of uric acid in the filtrate obtained by Folin's method. Silver lactate (5% in 5% lactic acid, 5 c.c.) is added to the filtrate (10—20 c.c.), the mixture being centrifuged for 5—7 min., after keeping in the dark for 5 min. The supernatant liquid is stirred with 10% lithium chloride solution (3 c.c.) and with water (8—10 c.c.), immediately centrifuged for 8—10 min., 15% sodium cyanide solution (2 c.c.) added, then 1 c.c. of reagent, and the colour allowed to develop for 20—30 min. The method is also applicable to the determination of uric acid in urine, details for which are given. Phenol, resorcinol, and tyrosine intensify the blue colour developed by uric acid and Benedict's reagent; phenol and resorcinol react less markedly, and tyrosine only slightly, with Folin's reagent. CHEMICAL ABSTRACTS.

Determination of urea in serum and whole blood. L. BALLIF, A. RESNIC, and I. LUNEVSKY (Compt. rend. Soc. Biol., 1927, 97, 1026—1027; Chem. Zentr., 1928, i, 386).—The statement of Pagel (A., 1924, ii, 575) and of Péchon (A., 1926, 763) that the first quantities of blood removed are richest in urea is not confirmed. A. A. ELDRIDGE.

Micro-method for the colorimetric determination of urea in blood. (MISS) F. BEATTIE (Biochem. J., 1928, 22, 711—719).—The method is based on the precipitation of urea as dixanthylcarbamide from deproteinised serum by the addition of an alcoholic solution of xanthhydrol. The results are in good agreement with those obtained by the urease method. S. S. ZILVA.

Lipochromes. III. Determination of carotin in blood and tissues. C. L. CONNOR (J. Biol. Chem., 1928, 77, 619—626).—Blood-plasma is treated with an equal volume of 95% alcohol, the excess of the latter poured off, and the residue shaken with light petroleum; tissues are hydrolysed with aqueous-alcoholic potassium hydroxide, water is removed from the hydrolysate with calcium sulphate, and the whole is then extracted with light petroleum; further extraction with 85% alcohol removes xanthophyll; the carotin in the light petroleum extracts is determined colorimetrically by comparison with a solution of potassium dichromate. Figures are given for the carotin content of human blood and of various animal tissues. C. R. HARINGTON.

Colorimetric determination of lipoid phosphorus in blood. A. R. HARNES (J. Biol. Chem., 1928, 77, 405—407).—Dried blood is extracted with chloroform and the phosphorus in the extract determined by the method of Briggs (A., 1922, ii, 718). C. R. HARINGTON.

Determination of blood-sugar. O. FOLIN (J. Biol. Chem., 1928, 77, 421—430).—Blood is freed from protein by treatment with a dilute solution of tungstic acid; an aliquot portion of the filtrate is heated with potassium ferricyanide in presence of sodium cyanide and sodium carbonate; ferric sulphate is then added and the resulting blue colour compared with that resulting from similar treatment of a known solution of dextrose. The method requires only 0·1 c.c. of blood. C. R. HARINGTON.

Mercurial deproteinisation of blood in the determination of dextrose. G. FONTÈS and L. THIVOLLE (Bull. Soc. Chim. biol., 1928, 10, 581—589).—The copper amalgam, produced in the previously described method of deproteinisation (A., 1927, 690), is found to absorb small amounts of dextrose. The amount of this amalgam produced may be reduced to a minimum by the use of potassium hydroxide and tartaric acid in place of sodium hydroxide and acetic acid, respectively.

G. A. C. GOUGH.

Condition of the ("free") sugar in serum. L. F. LOEB and D. KRÜGER (Z. klin. Med., 1927, 106, 354—359; Chem. Zentr., 1928, i, 372).—"Free" blood-sugar consists of the reducing substances, chiefly dextrose, present after the deproteinisation of whole blood, plasma, or serum; "bound" blood-sugar consists of the substances which exhibit reducing properties only after hydrolysis. The latter substance has not yet been identified. The free sugar in normal and diabetic individuals is molecularly disperse. A. A. ELDRIDGE.

Reducing substances in the blood of the dogfish and certain other fishes. F. D. WHITE (J. Biol. Chem., 1928, 77, 655—669).—Figures are given for the sugar content of the blood of various fishes; that of the dogfish is very low immediately after capture, but on keeping the fish for 4 days, under normal or fasting conditions, it rises to a constant level of 55—60 mg. %; in this fish the blood-sugar is almost entirely fermentable by yeast, but in various teleostean fishes there is present 10—12 mg. % of non-fermentable reducing substance. Asphyxiation does not produce hyperglycæmia in the dogfish. C. R. HARINGTON.

Course of glycolysis in the blood of normal and diabetic subjects. S. A. HOLBÖLL (Acta med. scand. Suppl.-Bd., 1926, 16, 509—514; Chem. Zentr., 1928, i, 84).—A discussion; lack of "neoglucose" is indicated. A. A. ELDRIDGE.

Rôle of calcium in the action of the glycolytic enzyme and the phosphatase of blood. A. ROCHE and J. ROCHE (Compt. rend. Soc. Biol., 1927, 97, 804—806; Chem. Zentr., 1928, i, 371).

Determination of succinic acid in blood. P. W. CLUTTERBUCK (Biochem. J., 1928, 22, 745—748).—The amount of succinic acid recovered from tissues by Moyle's method (A., 1924, i, 791) was 86±2% and not as high as that obtained by Moyle in determinations in muscle (95±5%). The method has been modified and adapted to the determination of succinic acid in blood, the amount of acid recorded being 87±3%. S. S. ZILVA.

Serum lipase. Influence of chemical and physical treatment. E. ADLER (Deut. med. Woch., 1927, **53**, 1987—1988; Chem. Zentr., 1928, i, 364).—A study of changes caused by injection of protein, disturbance of mineral metabolism, and so-called specific stimulation.   A. A. ELDRIDGE.

Acid fixation and swelling of fibrin. I. E. VOIT. II. F. SCHULDENZUCKER. III. F. LOCH-MÜLLER.—See this vol., 706.

Physico-chemical properties of the cell membrane. IV. Change in the permeability of red blood-corpuscles [caused] by hæmolytic agents. V. Observations on the hæmolytic process with the ultramicroscope. M. SUZUE (J. Biophys., 1927, **2**, 49—65, 67—80).—IV. Experiments on the conductivity of red blood-cells, subjected to the action of saponin, ethyl alcohol, and high temperature, show that the permeability of the cell membrane increases with increasing application of the agent until hæmolysis takes place, whilst in the cases of hydrochloric acid and ammonia no alteration in permeability is observed until the cell membrane disrupts and hæmolysis occurs.

V. Three types of hæmolysis are distinguished. The first is brought about by acids and bile, the second by bases, high temperature, or hypotonic solutions, and the third by saponin, alcohols, and hypertonic solutions.   W. O. KERMACK.

The erythrocyte as a colloidal chemical system. II. Isoelectric zone of erythrocytes. A. P. KONIKOV (Zhur. exp. Biol. Med., 1927, **6**, 406—418).—The acid agglutination of erythrocytes in an 8% sucrose solution occurs within a definite p_H range in each series, and the degree of agglutination varies in each species. The acid hæmolysis and agglutination reactions are reciprocally related.
CHEMICAL ABSTRACTS.

Poison of the water snake (*Tropidonotus natrix*). I. Action of the water snake blood on the isolated cold-blooded heart. O. GESSNER (Arch. exp. Path. Pharm., 1928, **130**, 375—383).—The substance present in blood-serum or -plasma of the water snake acting on the isolated heart of the frog or toad is probably not related to digitonin but from its pharmacological action appears to be of a saponin nature.   W. O. KERMACK.

Inorganic composition of human and animal tissues. L. LEMATTE, G. BOINOT, and E. KAHANE (Bull. Soc. Chim. biol., 1928, **10**, 553—567).—Detailed determinations of the inorganic components of various organs of man and animals are given and special precautions are taken to avoid analytical errors. Although human brain contains more phosphorus than the liver or the spleen, in animals the testes and the thymus gland often possess higher phosphorus contents. In all cases examined the spleen has the highest iron value and nearly all the iodine of the body is concentrated in the thyroid gland. The sulphur and nitrogen values for the same organs in different animals show wide variations.
G. A. C. GOUGH.

Animal nutrition. VI. Distribution of the mineral elements in the animal body as influenced by age and condition. A. G. HOGAN and J. L. NIERMAN (Mo. Agric. Exp. Sta. Res. Bull., 1927, [107], 1—45).—Determinations of the composition of the ash of cattle indicate that the mineral content of the lean and fat, or of the hide and hair is unaffected by age or condition, but the total mineral content of the internal organs decreases with age. The blood-sodium tends to decrease with age. The skeletal calcium, phosphorus, and magnesium contents increase with age.   CHEMICAL ABSTRACTS.

Iodine as a biogenic element. XV. Animal organs and products and their iodine content. XVI. Occurrence of iodine in fodders and manures. K. SCHARRER and J. SCHWAIBOLD (Biochem. Z., 1928, **195**, 228—232, 233—237; cf. A., 1926, 638; 1927, 372, 798, 903).—XV. The iodine content of pig's heart, liver, lung, kidney, and spleen is subject to considerable variation, but is always low (5·5—40 γ-%) and after continued peroral administration of iodide only the liver, kidney, and spleen show any increase, the kidney reaching 66 γ-%. The iodine content of the milk of cows fed on marshy pasture or on hay obtained therefrom, is only 50% higher than normal, whereas milk of cows fed on pastures after flooding with sea-water contained 300—800% more iodine than that of Swiss cows.

XVI. Tables indicate the iodine contents of different types of fodder, artificial manures, and of a variety of samples of Chile saltpetre. The last-named contains almost all its iodine as iodate.
P. W. CLUTTERBUCK.

Determination of iodine in the thyroid gland. K. WINTERFELD and H. ROEDERER (Apoth. Ztg., 1928, **43**, 132).—The dry material (0·5 g.) is fused with borax (1·5 g.) and sodium potassium carbonate (1 g.), the cool mass extracted with warm dilute sulphuric acid (7 c.c.) and water, filtered, and the filtrate shaken in a glass-stoppered flask with bromine water. After 10 min., 2—5 drops of liquefied phenol are added, and after mixing and keeping for several minutes, 0·1 g. of potassium iodide and 5 c.c. of 25% phosphoric acid are added, the liberated iodine being titrated with thiosulphate solution.
CHEMICAL ABSTRACTS.

Embryonic metabolism. I. Isolation of four pentose nucleotides from chicken embryos. II. Isolation of a hexose nucleic acid. H. O. CALVERY (J. Biol. Chem., 1928, **77**, 489—495, 497—503).—I. There was isolated from chicken embryos a β-nucleoprotein, similar in properties to that of Hammarsten (A., 1894, i, 310), which yielded, on hydrolysis, the same four pentose nucleotides as are obtained by hydrolysis of yeast nucleic acid. It is proposed to substitute the terms hexose nucleic acid and pentose nucleic acid for the thymus nucleic acid and yeast nucleic acid at present employed.

II. In addition to the above-described β-nucleoprotein, chicken embryos contain a hexose nucleic acid which is apparently identical with the nucleic acid obtainable from other animal tissues.
C. R. HARINGTON.

Rapid formation of adipocere during cadaveric putrefaction. E. BARRAL (J. Pharm. Chim., 1928, [viii], **7**, 486—487).—More than twice the normal

amount of fat has been found in a cadaver three months after death.　　　　　　　　　　W. O. KERMACK.

Hydrolysis of keratin for tryptic digestion. III. Z. STARY (Z. physiol. Chem., 1928, **175**, 178—236; cf. A., 1924, i, 1007; 1925, i, 847).—Keratin is converted by the action of bromine, chlorine, or by weak oxidising agents into products which are almost as complex as and physically similar to the original substance, but are readily hydrolysed by trypsin, and it is considered that long-chain polypeptides are formed by the bromination or oxidation. Hydrolysis of keratin by acids or alkalis gives products, however, which are resistant to trypsin. Thus by the action of bromine and acetic acid on human hair, fractions containing bromine are obtained which have the properties of peptones or even higher proteins; these fractions differ in composition, precipitation reactions, and solubilities, but they are all digested by trypsin. It is concluded that keratin consists of substances which, on oxidation by this method, yield polypeptides and that this change cannot be produced, except perhaps to a slight extent, by the partial hydrolysis of hair. Fractionation, purification, or drying of these fractions results in a loss of digestibility by trypsin and a decrease in solubility. Possible explanations of the resistance of keratin to tryptic digestion are discussed. Examination of the values given by other workers for the amounts of the different amino-acids present in various proteins leads to the conclusion that a relatively large amount of the original protein (never less than 20%) is unaccounted for as carbon, nitrogen, oxygen, hydrogen, and sulphur of these amino-acids and the term protein " residue " is applied to this remainder. This " residue " contains a much higher percentage of oxygen than the original protein and this excess of oxygen cannot be attributed to imperfect determinations of the hydroxy-amino-acids. The protein " residues " from various animal proteins are of fairly constant composition, but the " residues " from the alcohol-soluble vegetable proteins (zein, gliadin, hordein, and rye-prolamin) contain rather less oxygen. Scleroproteins (fibroin, koilin, ovokeratin, and elastin) give figures which are in general agreement with those for the other proteins, although greater individual variations occur here. The possible nature of the substances or groups containing oxygen is discussed.　　A. WORMALL.

Determination of carbamide and amino-acid nitrogen in animal tissues. V. C. KIECH and J. M. LUCK (J Biol. Chem., 1928, **77**, 723—731).—The tissue is minced, frozen with liquid air, and pulverised; a weighed sample is suspended in ice-water and treated with tungstic acid; aliquot portions of the filtrate are employed for the determination of carbamide by the xanthhydrol method and of amino-acid nitrogen by the Van Slyke method; in the latter case ammonia is removed by boiling with sodium hydroxide.　　　　　　C. R. HARINGTON.

Thiol titrations with iodine–starch and sodium nitroprusside. R. BIERICH and K. KALLE (Z. physiol. Chem., 1928, **175**, 115—134).—These two methods for the determination of the thiol content of tissues have various sources of error and different dilution factors. If corrections are applied to the nitroprusside drop method, the values obtained are nearer the theoretical value than are those given by the iodine–starch method. Both methods give results which are too high for tissue extracts and with more dilute solutions the error is still greater. The dilution factors are specific for each of the methods, but the factors are not affected appreciably by acids (concentrations of 0·5—8·0% hydrochloric acid) or by the presence of trichloro-acetic acid. If the titration is carried out at a higher temperature, the iodine requirement of a tissue extract increases, whilst the effect of dilution on the titration value is less pronounced at low temperatures. The iodine value for a trichloroacetic acid extract of tissues (liver, muscle, or yeast) decreases if the extract is exposed to the air. This decrease is attributed to the oxidation of the thiol group, and in an atmosphere of oxygen the decrease is five times as large as that in air. Determinations on tissues which have been exposed to the air for some hours and then extracted show that the iodine requirement rises with increased exposure. The total sulphur in the extracts is approximately constant and the increase in the thiol value is attributed to the cleavage of cysteine from complexes containing the thiol group. Yeast does not show this increase in iodine requirement on keeping. To reduce the errors obtained by both methods it is suggested that the tissues should be " fixed " as quickly as possible by means of trichloroacetic acid, or if necessary kept on ice, and that the filtrates should be as concentrated as possible and be titrated at a low temperature ($-15°$).　　　　　　　　　　A. WORMALL.

Determination of total chloride and loosely combined chloride in gastric juice. D. RAQUET and M. PAGET (J. Pharm. Chim., 1928, [viii], **7**, 489—492).—Total chlorides in gastric juice are determined by precipitating the organic matter by means of zinc ferrocyanide and determining the chloride in the filtrate by Volhard's method. The loosely combined hydrochloric acid and the inorganic chlorides are determined in a similar way after expelling the free hydrochloric acid by heat.
　　　　　　　　　　W. O. KERMACK.

Metabolism of the bile. I. Determination of bile acids in blood. M. ALDRICH and M. S. BLEDSOE (J. Biol. Chem., 1928, **77**, 519—537).—Blood is treated with alcohol and filtered; the filtrate is decolorised with charcoal and an aliquot portion is treated with barium hydroxide and evaporated to dryness; the residue is extracted with ether and the insoluble portion, containing the bile acids as barium salts, is treated with sucrose and sulphuric acid; the resulting solution, after removal of barium sulphate, is compared colorimetrically with one obtained by subjecting a known solution of sodium glycocholate to the Pettenkofer reaction under similar conditions. The method is applicable to 5 c.c. of blood; when applied to mixtures of bile salts it gives results in agreement with those obtained by the method of Schmidt and Dart (A., 1921, ii, 284).
　　　　　　　　　　C. R. HARINGTON.

Origin of bile acids. I. Determination of bile acid, cholesterol, and the other unsaponifiable

constituents in dog's bile. M. JENKE. II. Cholesterol-bile-acid balance in a dog with complete bile fistula. III. Steric configuration of sterols and their influence on the formation of bile acids. E. ENDERLEN, S. J. THANNHAUSER, and M. JENKE (Arch. exp. Path. Pharm., 1928, 130, 280—291, 292—307, 308—318).—I. The bile is freed from mucin by addition of alcohol and the bile acids and cholesterol are liberated by hydrolysis with potassium hydroxide solution. The cholesterol is separated by extracting the alkaline solution with ether. From this extract the cholesterol is precipitated by means of digitonin and the unsaponifiable materials left after separation of the cholesterol are determined gravimetrically. The bile acids and fatty acids are extracted with a mixture of ether and light petroleum, and the bile acids are then determined from polarimetric observations. In dogs with bile fistula free cholic acid is eliminated in the bile as well as conjugated acids, and bile acids administered by the mouth are quantitatively excreted in the bile. A titration method for the determination of bile acids is given.

II. Evidence is adduced that the bile acids are not formed from cholesterol in the animal body.

III. When administered intravenously, coprosterol and *allo*cholesterol, which are stereochemically closely related to cholic acid, increase the output of bile acids. It is not certain whether coprosterol and *allo*cholesterol are converted into bile acid or whether they exert some specific action on the synthesis or excretion. W. O. KERMACK.

Determination of pancreatic secretion. S. OKADA, E. SAKURAI, T. IMAZU, and K. KURAMOCHI (Proc. Imp. Acad. Tokyo, 1928, 4, 131—133).—The contents of the duodenum are collected, by means of a duodenal tube, for a period of 3 hrs. and the trypsin, amylase, and lipase contents are then determined. The total enzymic efficiency is not markedly affected by the addition of stimulants, is somewhat less for subjects above 40 years of age, and is low in females. J. STEWART.

Diffusion of carbamide in various body fluids. C. T. RIETTI (Compt. rend. Soc. Biol., 1927, 97, 1038—1039; Chem. Zentr., 1928, i, 373).—In a dog the kidneys of which had been excluded from the circulation, carbamide injected into the blood was found first in the saliva, in the cerebrospinal fluid, fairly soon in the pancreatic juice, in the bile, and very soon in the lymph. A. A. ELDRIDGE.

Determination of carbamide in urine. M. HOPF (Biochem. Z., 1928, 195, 206—209).—Laubender's method (A., 1927, 896) for the microdetermination of carbamide is very trustworthy provided the directions are rigidly followed. The urease method is equally good provided that the action of the urease is carried out by Pincussen's or Laubender's method, that distillation of ammonia proceeds for 50 min., and that the temperature never rises above 45°. P. W. CLUTTERBUCK.

Determination of hippuric acid and free benzoic acid in the urine of cattle. F. J. WARTH and N. C. D. GUPTA (Biochem. J., 1928, 22, 621—627).—After alkaline hydrolysis the liquid is acidified and

shaken with a definite volume of petroleum. The liberated benzoic acid is determined with the aid of a partition coefficient. The method when applied to unhydrolysed urine gives some indication that titratable impurities are likely to be determined with the free benzoic acid. The partition coefficient of benzoic acid between water and different solvents has been determined. S. S. ZILVA.

Indican in urine analysis. E. SCHLECHT (Pharm. Ztg., 1928, 73, 567).—Polemical, maintaining that urine containing indican reduces Nylander's solution. S. COFFEY.

Indican in urine analysis. C. OTTO (Pharm. Ztg., 1928, 73, 567; cf. preceding abstract).—A sample of horse urine containing indican no longer reduced Fehling's or Nylander's solutions when freed from protein. Potassium indoxylsulphonate has no reducing action on the above reagents either alone or when mixed with urine containing comparatively small or large amounts of indican, provided the latter has been freed completely from other reducing substances (cf. Jolles, this vol., 662). S. COFFEY.

Detection of albumin in urine. A. JOLLES (Deut. med. Woch., 1927, 53, 1906—1907; Chem. Zentr., 1928, i, 99).—The usual methods are critically discussed; the Spiegler–Jolles reagent is modified. A. A. ELDRIDGE.

Determination of urobilin in urine and fæces. E. GREPPI (Folia clin. chim. micros., 1926, 1, 61—67; Chem. Zentr., 1928, i, 99).—In Terwen's method, a second reduction after neutralisation is recommended. A. A. ELDRIDGE.

Determination of silicic acid in urine and fæces. B. KINDT (Z. physiol. Chem., 1928, 174, 28—39).—The urine (300—500 c.c.) or fæces (40—50 g.) is carefully oxidised with 100 c.c. of concentrated nitric acid, the mixture evaporated almost to dryness, the residue mixed with a little water and incinerated, the ash warmed with hydrochloric acid for 15 min., and the mixture evaporated to dryness and heated at 140° for 1 hr. Dilute hydrochloric acid is again added and the process repeated twice. The residue is finally boiled with hydrochloric acid and filtered through a special paper. Some silicic acid remains unprecipitated in the first filtrate, and may be recovered by evaporating to dryness and treating three times with dilute hydrochloric acid followed by evaporation and heating at 140°, as before. The second precipitate is collected on a second paper. Both precipitates are dried in a platinum dish, ashed, and weighed. Hydrofluoric acid and a few drops of sulphuric acid are added, and the dish is again heated to constant weight. The difference in weight represents the weight of silica. For the latter stages of the analysis an alternative precipitation method in which mercury ammonium carbonate is used is also described, but the first method is recommended for most purposes. H. D. KAY.

Silicic acid excretion in man after ingestion of sodium silicate. O. RIESSER and B. KINDT (Z. physiol. Chem., 1928, 174, 40—46).—After a diet relatively rich in silicic acid (bread containing 1·28 g. per day of SiO_2 added as sodium silicate) there is an

increase of silicic acid both in the urine and in the fæces. In two subjects, at least 34% of the ingested silicic acid is absorbed from the intestine, and both the urinary and fæcal excretion of this substance increase. A portion (22—34%) is not excreted during the 24 hrs. following the ingestion. H. D. KAY.

Nature of material in liver effective in pernicious anæmia. II. E. J. COHN, G. R. MINOT, G. A. ALLES, and W. T. SALTER (J. Biol. Chem., 1928, 77, 325—358; cf. ibid., 1927, 74, lxix).—Fresh minced liver was brought to p_H 5·0 by addition of sulphuric acid and the water-soluble substances were thoroughly extracted; coagulable protein was removed from the extract by heating at 70°, and the filtrate concentrated under diminished pressure. The solution was treated with alcohol to make a 70% concentration of the latter, the precipitate was rejected, the filtrate was again concentrated, and poured into enough alcohol to make a final concentration of 95%; the aqueous solution of the resulting precipitate was cleared with basic lead acetate, and, after removal of excess of lead, was treated with phosphotungstic acid. The solution obtained on recovery from the phosphotungstates was rich in the active substance; of the best preparations doses of 0·6 g. per day (calculated as ash-free organic matter) exercised a definite physiological effect. These preparations contained, on an ash-free basis, about 19% of nitrogen; they were free from carbohydrate and from iron. The active substance is precipitated by mercuric acetate in neutral solution; the possibility of its identity with vitamin-B is excluded. The physiological assay of the active substance is discussed.
C. R. HARINGTON.

Iron in nutrition. V. Availability of rat for studies in anæmia. J. WADDELL, H. STEENBOCK, C. A. ELVEHJEM, and E. B. HART. VI. Iron salts and iron-containing ash extracts in correction of anæmia. J. WADDELL, C. A. ELVEHJEM, H. STEENBOCK, and E. B. HART. VII. Copper as supplement to iron for hæmoglobin formation in the rat. E. B. HART, H. STEENBOCK, J. WADDELL, and C. A. ELVEHJEM (J. Biol. Chem., 1928, 77, 769—775, 777—795, 797—812).—V. Young rats weaned at 3—4 weeks and placed on a diet of cow's milk form suitable subjects for the investigation of nutritional anæmia.

VI. Inorganic iron salts (0·5 g. Fe per day) are not effective in curing nutritional anæmia in young rats, whilst the ash of liver, lettuce, and maize containing 0·5 g. of iron, or an acid extract of such ash, is highly effective.

VII. An extract of liver as used for the treatment of pernicious anæmia in man, as also the ash of this preparation, formed, in combination with inorganic iron, a cure for nutritional anæmia in rats. The active portion of the above ash could be concentrated by treatment of a dilute hydrochloric acid extract of the ash with hydrogen sulphide, and the effect of the ash could indeed be imitated by that of small amounts of copper. C. R. HARINGTON.

Detection of homogentisic acid in serum in alkaptonuria. G. KATSCH and E. METZ (Deut. Arch. klin. Med., 1927, 157, 143—157; Chem. Zentr., 1928, i, 386).—In a case of alkaptonuria the serum contained 1 mg.-%. A. A. ELDRIDGE.

Amino-acids of flesh. II. Diamino-acid content of some normal and pathological tissues. J. L. ROSEDALE (Biochem. J., 1928, 22, 826—829).—The diamino-acid contents of the tissues of different animals and of different parts of a normal animal are similar. There is a low content of lysine in carcinoma and in chickens which have derived the whole of their food protein from maize. No marked differences were observed between the results obtained by Van Slyke's and by the modified Kossel's method for the determination of diamino-acid. S. S. ZILVA.

Cholesterol content of the blood of infants and children. A. GOLDBLOOM and R. GOTTLIEB (Can. Med. Assoc. J., 1927, 17, 1333—1336).—The cholesterol content of whole blood is the greater, the younger is the individual. The effect of various pathological conditions was investigated.
CHEMICAL ABSTRACTS.

Pancreatic activity in diabetes mellitus. S. OKADA, T. IMAZU, K. KURAMOCHI, K. HORIUCHI, and T. TSUKAHARA (Proc. Imp. Acad. Tokyo, 1928, 4, 134—135).—The disturbance of pancreatic function manifests itself in the diminution of enzymic activity, or of the amount of juice, or of both, the greatest alteration in enzymic efficiency and activity being in the proteolytic and lipolytic enzymes. There may be disturbance either of the internal or of the external secretion of the pancreas, or of both, the severity of the diabetes not necessarily running parallel to the degree of disturbance in the external secretion.
J. STEWART.

Significance of the non-fermentable reducing substances of the blood in diabetes. I. M. RABINOWITCH (Biochem. J., 1928, 22, 751—757).—The non-fermentable reducing substances of the blood vary between 16 and 31 mg. per 100 c.c. (as dextrose) and are fairly constant for the individual. There are no significant differences between normal and diabetic bloods. Blood-sugar curves after the administration of dextrose show no significant differences in the amounts of these substances between normal and diabetic subjects. Arterial and venous blood-sugar-time curves obtained simultaneously are identical in normal and diabetic subjects as far as variations of non-fermentable reducing substances are concerned. The amounts of non-fermentable reducing substances are not influenced in the blood of the diabetic by insulin administration. The metabolism of non-fermentable substances is therefore not disturbed in diabetes. S. S. ZILVA.

Plasma lipoids. I. Fatty acids of blood-plasma in diabetes and nephrosis. S. M. LING and S. H. LIU (Chinese J. Physiol., 1928, 2, 157—161). —The fatty acids of normal plasma are highly unsaturated, with an average iodine value of 156·6. In diabetes mellitus and in nephrosis they are much less unsaturated, and their iodine value is lower, being 45—98 in the former and 59—87 in the latter disease.
H. D. KAY.

Iodine and exophthalmic goitre. W. H. JANSEN and F. ROBERT (Deut. Arch. klin. Med., 1927, 157, 224—246; Chem. Zentr., 1928, i, 539).—The

iodine content of the normal human thyroid gland is 2·2—4·58 (average 3·3) mg. Values in exophthalmic goitre are recorded. A. A. ELDRIDGE.

Lactic acid content of the blood in hepatic disease. A. ADLER and H. LANGE (Deut. Arch. klin. Med., 1927, **157**, 129—142; Chem. Zentr., 1928, i, 371).—The normal blood-lactic acid value is 7—13 mg.-%. In hepatic disease the value is raised.
A. A. ELDRIDGE.

Esterification of serum-cholesterol in hepatic disease. M. BURGER and H. HABS (Klin. Woch., 1927, **6**, 2221—2223; Chem. Zentr., 1928, i, 376).— A study of the relation of free and esterified serum-cholesterol values to various pathological conditions of the liver. A. A. ELDRIDGE.

Protein metabolism and phosphorus content in experimental hæmolytic and stasis icterus. T. HATAKEYAMA (J. Biochem. Japan, 1927, **8**, 261—273). CHEMICAL ABSTRACTS.

Composition of blood in lipæmia after hæmorrhage. E. H. FISHBERG and A. M. FISHBERG (Biochem. Z., 1928, **195**, 20—27).—In rabbits, from which 35 c.c. of blood were removed daily, lipæmia developed, the increase in blood-fat and -cholesterol being due to loss of serum-proteins, particularly albumin, this loss causing a compensatory mobilisation of fat in order to maintain the colloid osmotic pressure at its normal level. P. W. CLUTTERBUCK.

Acid–base equilibrium in the plasma in malaria. S. H. LIU (Chinese J. Physiol., 1928, **2**, 151—156).—The equilibrium has been studied in 13 cases of malaria. All the values found (for p_H, total base, hydrogen carbonate, chloride, and protein) lie within normal limits. During the feverish stage the p_H remains unchanged, but there is a slight increase of total base and a slight decrease in hydrogen carbonate and chloride. The excess of residual base in fever is bound by organic acids of undetermined nature. The above effects are not a specific result of bacterial infection but are due to the fever.
H. D. KAY.

Sugar and chloride content of the cerebrospinal fluid with special reference to neurosyphilis. S. W. BECKER (J. Lab. Clin. Med., 1926, **12**, 43—52).—In neurosyphilis there was a small, variable decrease in the reducing substances of the cerebrospinal fluid. There is a slight normal variation in the sugar content. Alimentary hyperglycæmia produced no increase of sugar in the cerebrospinal fluid. The variation in chloride content is not so great as for blood-chloride; in neurosyphilis the chloride content of the cerebrospinal fluid was normal. CHEMICAL ABSTRACTS.

Avitaminosis. VII. Influence of experimental scurvy on the synthesis of hippuric acid. A. PALLADIN and D. ZUWERKALOW (Biochem. Z., 1928, **195**, 8—13).—In guinea-pigs, the power to synthesise hippuric acid is decreased in proportion to the extent of development of scurvy.
P. W. CLUTTERBUCK.

Experimental tetany. C. I. URECHIA and G. POPOVICIU (Compt. rend. Soc. Biol., 1927, **97**, 1012—1015; Chem. Zentr., 1928, i, 373).—Thyro-parathyroid-ectomised dogs show in the pre-tetanic period an increase in phosphorus content and a reduction in that of calcium. Rigidity and convulsions are accompanied by a reduction of the phosphorus, but scarcely of the calcium, content. The phosphorus content immediately before death is extremely large.
A. A. ELDRIDGE.

State of plasma-calcium in parathyroidectomised dogs. C. I. REED (J. Biol. Chem., 1928, **77**, 547—554).—Acute tetany following parathyroidectomy develops when the Ca : P ratio falls to unity or less; in some animals, however, a condition of "latent" tetany occurs in which such low Ca : P ratios are observed without accompanying symptoms. After parathyroidectomy there is a tendency towards both relative and absolute diminution of the diffusible fraction of the plasma-calcium, but this result is not constant. C. R. HARINGTON.

Hydrogen-ion concentration and carbon dioxide content of the blood of dogs after removal of the accessory thyroid. W. F. WENNER and E. MUNTWYLER (Proc. Soc. Exp. Biol. Med., 1927, **24**, 480—482; Chem. Zentr., 1928, i, 84).—Neither in manifest nor in latent tetany was alkalosis observed, even when the carbon dioxide content was reduced. In one case, production of lactic acid caused a change of p_H from 7·29 to 7·09. A. A. ELDRIDGE.

Oxygen consumption by various tissues and by muscle of various animals. K. TSUNEYOSHI (J. Biochem. Japan, 1927, **7**, 227—233).—The oxygen-consuming power of various tissues and muscle is compared. CHEMICAL ABSTRACTS.

Effect of lipin and allied substances on the oxidative activity of tissues. K. TSUNEYOSHI (J. Biochem. Japan, 1927, **7**, 235—258).—Lecithin increases, whilst cholesterol diminishes, the consumption of oxygen by tissue powder and the oxidation of amino-acids on charcoal; kephalin, cuorin, cholesterol esters, hydrogenated or hydrolysed lecithin show no effect. CHEMICAL ABSTRACTS.

Significance of lipins in the oxygen-consuming activity of tissues. I. Oxygen-consuming activity of tissue and the mitochondrial structure. S. KAKINCHI (J. Biochem. Japan, 1927, **7**, 263—265).— The oxygen consumption of dry ox-heart muscle powder was studied in the untreated material and after treatment with alcohol, ether, acetone, and acetic acid. In every case it was found that treatment which destroyed the mitochondrial mechanism (alcohol, acetic acid) also practically abolished the oxidative process. CHEMICAL ABSTRACTS.

Respiration of fat tissue. M. N. SHATERNIKOV, O. P. MOLCHANOVA, and M. T. TONIME (Zhur. exp. Biol. Med., 1927, **7**, 375—382).—Sheep's fat tissue consumes more oxygen than corresponds with the production of carbon dioxide: a conversion of fat into carbohydrate is assumed. CHEMICAL ABSTRACTS.

Sulphur-fixing and -oxidising function of the liver. M. LOEPER, J. DECOURT, and R. GARCIN (Presse med., 1927, **35**, 321—323; Chem. Zentr., 1928, i, 88).—A discussion. A. A. ELDRIDGE.

Acceleration of growth rates by dietary modifications. A. G. HOGAN, J. E. HUNTER, and H. L.

KEMPSTER (J. Biol. Chem., 1928, **77**, 431—436).— A diet is described which yields rates of growth in chicks and turkeys above those hitherto considered to be normal, the results being analogous with those obtained by Osborne and Mendel (A., 1926, 1180) with rats.   C. R. HARINGTON.

Growth of rats on vegetarian diets. H. WU and D. V. WU (Chinese J. Physiol., 1928, **2**, 173—194).— Rats do not grow well on exclusively vegetarian diets, although when the "small cabbage" (a Chinese vegetable) is added practically normal growth is obtained. The vitamin-*D* content of spinach is low.
                                                 H. D. KAY.

Relative utilisation of different calcium compounds in the production of eggs. G. B. BUCKNER, J. H. MARTIN, and A. M. PETER (J. Agric. Res., 1928, **36**, 263—268).—A comparison has been made between the effects of calcium in the form of carbonate, sulphate, chloride, phosphate, and lactate on the rate of egg production of hens fed on a basal diet of wheat, yellow maize, skim milk, and fresh vegetables. Calcium carbonate produced a greater egg yield than either calcium sulphate or lactate; calcium chloride was not consumed by the hens, and calcium phosphate, although consumed, did not affect the rate of egg production.   E. A. LUNT.

Sulphur metabolism and partition of sulphur in the urine of fasting dogs. S. MORGULIS (J. Biol. Chem., 1928, **77**, 627—645).—In dogs the N : S ratio in the urine varies from 16·1 to 29·7 and is not generally altered during starvation, so that it appears to be a peculiarity of the individual dog rather than of the metabolic condition. No relationship could be observed between the N : S ratio of the food and that of the urine, nor did the latter indicate the nature of the body-tissues being broken down during starvation. The inorganic sulphate and neutral sulphur show irregular variations during fasting, the proportion of the former being characteristic of the individual dog, and that of the latter being apparently unconnected with diminished oxidative processes. The variations in the excretion of the ethereal sulphates indicate that the latter are largely endogenous in origin.
                                 C. R. HARINGTON.

Selective absorption of iodine compounds by the hyperplastic thyroid gland. H. B. VAN DYKE (Arch. Int. Med., 1928, **41**, 615—621).—The rate of iodine absorption by the hyperplastic thyroid gland of the dog diminishes along the sequence of the following substances : potassium iodide, potassium iodate, iodine in sodium chloride solution, and thyroxine. The rate of absorption of the iodine in the last substance is extremely slow. Bilateral ligation of the suprarenal glands 6 hrs. before iodine administration does not affect its absorption. E. A. LUNT.

Increase in the weight, volume, and total nitrogen content of the liver with a diet rich in nitrogen. C. GAUTIER and H. P. THIERS (Bull. Soc. Chim. biol., 1928, **10**, 537—552).—The right lobes of the livers of starved frogs were removed and compared with the remaining portions of the livers of the same animals after feeding for some weeks on a variety of cheese. The remaining portions, although greatly increased in weight, contained actually less nitrogen

and water than the removed portions. Control experiments with intact animals were in agreement with these results.   G. A. C. GOUGH.

Muscular exercise and nitrogenous metabolism of dogs. W. H. CHAMBERS and A. T. MILHORAT (J. Biol. Chem., 1928, **77**, 603—618).— Muscular work in fasting dogs produced an increase of 50—100% in the nitrogenous metabolism; this increase was entirely prevented by the previous ingestion of carbohydrate, except after very prolonged fasting. It is thought that the extra nitrogen excreted under these conditions originated from a limited store in the body, and did not arise from the breakdown of tissue protein.   C. R. HARINGTON.

Biological degradation of uric acid to allantoin. H. BRÜNIG, F. EINECKE, F. PETERS, R. RABL, and K. VIEHL (Z. physiol. Chem., 1928, **174**, 94—111).— The 4 : 5-glycol of uric acid, the 4 : 5-dimethyl ether of this glycol, and *spiro*-4 : 5-dihydantoin, all possible intermediate substances in the metabolism of uric acid, are not oxidised to allantoin by the intact dog or by the surviving liver of this animal. Allantoin is found in the urine when any one of the four (1-, 3-, 7-, 9-) monomethyluric acids is administered to a dog. The methyluric acids are precipitable as silver salts, and give a colour similar to that produced by uric acid with Folin's reagent. Methylallantoin may be separated from allantoin by precipitation of the latter with Wiechowski's reagent at p_H 6·2. Carbamide interferes with the precipitation both of allantoin and of methylallantoin with this reagent.   H. D. KAY.

Ammonia production on illumination of the retina. H. RÖSCH and W. T. KAMP (Z. physiol. Chem., 1928, **175**, 158—177).—The retina of the frog kept for 10 min. in the dark contains varying amounts of ammonia (0·9—3·4 mg. in 12 experiments), but good agreement is obtained when those of the two eyes of one frog are compared; the differences in the latter case are usually less than 10% and the maximum difference obtained is 13%. If one retina is exposed to a strong light for 10 min. there is a marked increase in the ammonia production, the increase being between 74% and 582% of the values for the unexposed retina. Fresh ox retina pulp kept in 2% sodium hydrogen carbonate solution at 40° gives rise to the production of ammonia, thus confirming Warburg, Posener, and Negelein (Biochem. Z., 1924, **152**, 309). This enzymic production of ammonia appears to be rapid and is complete in less than 2 hrs. Addition of guanosinephosphoric acid to the retina pulp in sodium hydrogen carbonate solution does not increase the ammonia production appreciably, although a slight increase is noted on occasions; urea also leads to no marked increase. With adenosinephosphoric acid, however, there is a marked increase in ammonia formation, representing a yield of up to 90% of the amino-group. The precursor of ammonia in the retina is not adenosinephosphoric acid, however, since after treatment of the pulp with 1% hydrochloric acid, treatment which destroys the ammonia-producing enzyme, no ammonia formation can be effected by adding an extract of muscle which has a powerful action on adenosinephosphoric acid.
                                          A. WORMALL.

Bile acids. III. Effect of bile acids on the protein metabolism of the rabbit. Antiseptic effect of bile acids in the rabbit intestine. R. Kaziro (J. Biochem. Japan, 1927, **7**, 293—310).—Rabbits fed on deoxycholates, and particularly cholates, exhibit increased urinary elimination of total nitrogen and inorganic sulphate; larger doses are toxic. Choleinic acid and the conjugated bile acids are less effective. Chemical Abstracts.

Behaviour of pyridine, quinoline, and nicotinic acid in the Eck-fistula dog. T. Kamel (J. Biochem. Japan, 1927, **7**, 197—210).—Pyridine, quinoline, and nicotinic acid when administered to Eck-fistula dogs appear to a much smaller degree than in normal dogs as methylated derivatives in the urine. The liver is thus regarded as the important seat of the methylation reaction. Chemical Abstracts.

Intracellular oxidation–reduction. I. Reduction potentials of *Amoeba dubia* by micro-injection of indicators. B. Cohen, R. Chambers, and P. Reznikoff (J. Gen. Physiol., 1928, **11**, 585—612).—*A. proteus* and *A. dubia* have been injected by the micro-technique with 25 different oxidation–reduction indicators, both in the reduced and in the oxidised forms, under definite conditions as regards oxygen tension. The observations made allow conclusions to be reached both as to the toxicity of the indicators and as to the oxidation–reduction potentials of the protoplasms of the organisms. In discussing the results it is pointed out that the reduction intensity, the reducing capacity, and the rate factor must be distinguished from one another. W. O. Kermack.

Micrurgical studies in cell physiology. VI. Calcium ions in living protoplasm. H. Pollack (J. Gen. Physiol., 1928, **11**, 539—545).—The injection by micro-methods into living cells (*Amoeba dubia* or *A. proteus*) of the sodium salt of alizarinsulphonic acid, the calcium salt of which is relatively insoluble in water, produces quiescence of the cell and certain other pathological changes. Subsequent injection of small quantities of calcium chloride neutralises these effects. The abnormal behaviour of the amoebæ observed after the reduction of calcium ions, following the injection of sodium alizarinsulphonate, is also seen when the ions are reduced by injection of oxalate, tartrate, citrate, and phosphate or when the sodium- or potassium-ion concentration is increased. W. O. Kermack.

Does methylene-blue penetrate living cells ? M. Irwin (Nature, 1928, **121**, 939).—Polemical. A. A. Eldridge.

Significance of changes in the composition of the blood and urine after ingestion of dextrose. I. Katayama (J. Lab. Clin. Med., 1926, **11**, 1024—1034).—Ingestion of dextrose causes a slight fall in the inorganic phosphorus of the blood, and increased elimination in the urine; blood-chloride varied inconstantly, but urine-chloride was diminished. Variable changes in the blood non-protein nitrogen and the urine-nitrogen, and increase in blood-lactic acid were observed. Chemical Abstracts.

Disappearance of intravenously injected α-, β-, and αβ-glucose from the blood. E. N. Allott (Biochem. J., 1928, **22**, 773—776).—No definite difference was found between the behaviour of α-, β-, and αβ-glucose when injected intravenously into rabbits. S. S. Zilva.

Assimilation of lævulose. S. J. Steinberg (Pflüger's Archiv, 1927, **217**, 686—695; Chem. Zentr., 1928, i, 821).—Lævulose is not consumed by the heart, pancreas, or small intestine. It is consumed as readily as dextrose by the skeletal muscle and kidneys, less readily by the salivary gland, and more readily by the liver and lungs. A. A. Eldridge.

Variations of blood-phosphorus in dextrose tolerance tests. H. C. Chang (Chinese J. Physiol., 1928, **2**, 195—202).—The inorganic phosphate of the blood diminishes in the normal subject after ingestion of 150 g. of dextrose. There is also a corresponding fall in the inorganic phosphate of the urine. In mild diabetes the fall is still to be observed, but is less marked and longer delayed. In severe diabetes the fall in inorganic phosphate is inappreciable. H. D. Kay.

Function of the cells of the reticulo-endothelial apparatus. Problem of permeability. N. Okunev (Biochem. Z., 1928, **195**, 28—39).—Various colloidal substances, *e.g.* trypan-blue, carmine, cholesterol, Indian ink, colloidal silver and iron, erythrocytes, and bacteria, which are known to be absorbed by the cells of the reticulo-endothelial system, also possess the power of decreasing the surface tension at the limiting surface of water and benzene and of water and olive oil. The results are discussed in relation to absorption and phagocytosis. P. W. Clutterbuck.

Rôle of aluminium compounds in animal and plant physiology. E. V. McCollum, O. R. Rask, and J. E. Becker (J. Biol. Chem., 1928, **77**, 753—768).—From spectrographic observations it appears that aluminium is not a normal constituent of plant or animal matter. Amounts of aluminium up to 0·6% of the diet exercise no toxic effects on rats, and, indeed, aluminium given by the mouth seems not to be absorbed from the alimentary tract. C. R. Harington.

Effect of metallic salts on the glycolysis and respiration of tissues. M. Jowett and J. Brooks (Biochem. J., 1928, **22**, 720—738).—Measurements made on the glycolysis and respiration of various tissues agree in the main with those of other workers. No aërobic glycolysis of liver was found. The toxicity of metallic salts to glycolysis is in the order HgI_2, $HgCl_2 > Cu\cdot\cdot > Zn\cdot\cdot > Cd\cdot\cdot > Ca\cdot\cdot$. Lead ion at low concentrations accelerates slightly the glycolysis of malignant tissue and at much higher concentrations its respiration. With normal tissues its effects are smaller. The glycolysis of malignant tissue is more sensitive to metallic poisons than that of normal tissues. Glycolysis appears to be more sensitive than respiration to heavy metals in the case of malignant tissue. For normal tissues the converse is the case. A mechanism of the action of mercuric halides on glycolysis and respiration is suggested. S. S. Zilva.

Chemical and biological relationships between thallium and lead. A. Buschke and L. Berman

(Klin. Woch., 1927, **6**, 2428—2429; Chem. Zentr., 1928, i, 543).—Similarities between the toxic effects of lead and thallium salts on rats and mice were observed.   A. A. ELDRIDGE.

Convulsant action of acid and neutral salts of acid fuchsin. J. E. THOMAS (J. Pharm. Exp. Ther., 1928, **33**, 1—19).—Comparative results are given of the time which elapses in the frog between the injection of acid and alkaline solutions of fuchsin either by perfusion of the blood-vessels or by injection into the bloodless aorta and the consequent occurrence of convulsions. Solutions of the acid salts of fuchsin cause convulsions in less time and with greater regularity than solutions of the neutral salts.
                                          E. A. LUNT.

Influence of ingestion of methylxanthines on excretion of uric acid. V. C. MYERS and E. L. WARDELL (J. Biol. Chem., 1928, **77**, 697—722).—Ingestion of caffeine in human subjects is followed by an immediate increase in excretion of uric acid, which increase is not, however, maintained during prolonged administration of caffeine. Theobromine causes no increased excretion of uric acid but theophylline causes a marked increase. Since certain methyl derivatives of uric acid, *e.g.*, 1-methyl- and 1 : 3-dimethyl-uric acids, react with the colorimetric reagent employed in the above determinations, whilst others, *e.g.*, 3 : 7-dimethyluric acid, do not, it is possible that the above methylxanthines appear, partly at least, in the urine as the corresponding methyluric acids and not as uric acid itself.   C. R. HARINGTON.

Influence of ultra-violet light on the oxidation quotient of urine. J. SPIRT (Biochem. Z., 1928, **195**, 142—148).—Müller's oxidation quotient (cf. A., 1927, 996), viz., nitrogen content : "oxygen requirement," is obtained and inverted for comparison with the C : N ratio. The quotient is obtained constant for a dog by feeding on a diet containing excess nitrogen and only varies from 0·5 to 0·6 in different dogs, daily variations being very small. The quotient varies with the intensity of irradiation, the variations being caused by alterations of oxygen requirement and not of nitrogen content. Irradiation for $\frac{1}{2}$ hr. at a distance of 80 cm. causes an increased quotient and an inhibition of oxidation, and irradiation for 1 hr. at a distance of 60 cm. a decreased quotient and an increased oxidation.   P. W. CLUTTERBUCK.

Action of gallic acid on the sugar and cholesterol content of the blood. C. LANG and H. JUNGMANN (Klin. Woch., 1927, **6**, 2241—2242; Chem. Zentr., 1928, i, 371).—Injection of gallic acid, as of cholic, glycocholic, or taurocholic acid, causes a fall in the blood-sugar of fasting animals.
                                          A. A. ELDRIDGE.

Effect of acetylcholine chloride and pilocarpine on the threshold of sugar elimination. G. EDA (J. Biochem. Japan, 1927, **7**, 319—331).—Diminution of sugar assimilation and rise of the threshold of sugar excretion are caused frequently in mild diabetics by subcutaneous injection of acetylcholine chloride, and invariably in rabbits by injection of pilocarpine.
                                    CHEMICAL ABSTRACTS.

Effect of atropine and scopolamine on the sugar excretion threshold. G. EDA (J. Biochem. Japan,

1927, **7**, 345—360).—In rabbits atropine invariably causes an increase in the sugar-excretion threshold, but the assimilation of sugar is practically unaffected. In patients with Parkinson's disease scopolamine always brought about a rise in the excretion threshold values and an improvement in the power of assimilation. In diabetics the effect of scopolamine varies, causing a rise in some and a lowering in others of the excretory threshold, and the diminution in assimilation corresponding with an increase in threshold is generally not observed.   CHEMICAL ABSTRACTS.

Effect of atropine on alimentary hyperglycæmia. S. TERASHIMA (J. Biochem. Japan, 1927, **7**, 489—503).—In diabetics a mild and brief, but not a more marked, hyperglycæmia is inhibited by atropine. The power to increase sugar assimilation attributed to atropine was not observed either in man or in the rabbit.   CHEMICAL ABSTRACTS.

Value of iron salts in counteracting toxic effects of gossypol. W. D. GALLUP (J. Biol. Chem., 1928, **77**, 437—449).—Administration of ferric citrate or of ferrous ammonium sulphate, but not of ferric oxide, counteracted the toxic effects of gossypol in rats on a diet containing a large proportion of cotton seed, provided that the ratio of iron to gossypol was not less than 3 : 1. Iron forms an insoluble compound with gossypol of apparently constant composition.
                                          C. R. HARINGTON.

Mechanism of the action of synthalin. G. HETÉNYI (Klin. Woch., 1927, **6**, 2194; Chem. Zentr., 1928, i, 85—86).—Continuous administration of synthalin leads to a progressive reduction of sugar in the organism, no premortal storage of sugar in the liver being observed.   A. A. ELDRIDGE.

Similarity of "glukhorment" and synthalin. F. BISCHOFF, N. R. BLATHERWICK, and M. SAHYUN (J. Biol. Chem., 1928, **77**, 467—471).—Glukhorment contains a considerable amount of a guanidine derivative apparently identical with synthalin (cf. Dale and Dudley, Brit. Med. J., 1927, (ii), 1027).
                                          C. R. HARINGTON.

Respiratory exchange, temperature, and blood-sugar of anæsthetised animals. E. T. CONYBEARE, H. B. A. R. DENSHAM, M. MAIZELS, and M. S. PEMBREY (J. Physiol., 1927, **64**, Proc. Physiol. Soc., xix—xx).—Urethane anæsthesia causes a rise in the blood-sugar; in ethylene anæsthesia the values vary.   A. A. ELDRIDGE.

Effect of anæsthesia on recovery process in mammalian skeletal muscles. C. N. H. LONG (J. Biol. Chem., 1928, **77**, 563—579).—Stimulation of muscles in animals under general (amytal) anæsthesia was followed by normal breakdown of glycogen to lactic acid, but the recovery phase, as indicated by restoration of the muscle glycogen to its normal level, was almost entirely inhibited; at the same time the lactic acid disappeared from the muscles. This phenomenon may be of practical importance in connexion with the condition of those muscles which are essential to life during anæsthesia.
                                          C. R. HARINGTON.

Hypnotics of barbituric acid series. N. B. EDDY (J. Pharm. Exp. Ther., 1928, **33**, 43—68).—When administered orally to cats in 10% gum-acacia

solution the average fatal dose per kg. body-weight of diethylbarbituric acid is 280 mg., of ethyl*iso*amylbarbituric acid 100 mg., of calcium ethyl*iso*propylbarbiturate 140 mg., of ethyl *n*-butylbarbituric acid 84 mg., and of *cyclo*hexenylethylbarbituric acid 120 mg. As a hypnotic *cyclo*hexenylethylbarbituric acid is the most desirable of this group. E. A. LUNT.

Relation between chemical constitution and germicidal activity of alcohols and phenols. J. M. SCHAEFFER and F. W. TILLEY (J. Bact., 1927, **14**, 259—273).—Isomeric alcohols having the longest straight chains, and isomeric phenols having the longest straight chains in the *para*-position to the hydroxyl group are most efficient germicides. The coefficients of *cyclo*hexanol and the methyl*cyclo*hexanols are about half as great as those of phenol and the corresponding cresols.
CHEMICAL ABSTRACTS.

Chemical constitution of the respiratory enzyme. O. WARBURG (Naturwiss., 1928, **16**, 345—350).—A close similarity exists between the processes of respiration and fermentation. The principal facts concerning hæmin are : its widespread distribution in nature, the reversible reactions of its iron atom with oxygen and carbon monoxide, the precisely definable distribution of hæmin between the two gases, and also the fact that the carbon monoxide compound dissociates on irradiation. The respiratory enzyme of yeast shows the same properties, but hæmoglobin is not essentially a catalyst and it retains carbon monoxide more strongly than the enzyme. Whilst hæmoglobin, hæmopyridine, and hæmonicotine, like the respiratory enzyme, will react, in the reduced state, with oxygen and carbon monoxide, cytochrome will not do so, at least under 1 atm. pressure. Cytochrome and the respiratory enzyme must therefore be different substances. In the living cell there may be present hæmin belonging to the enzyme and hæmin independent of the respiration process. In order to discriminate between such conditions, the respiration has been hindered by the formation of the carbon monoxide complex. The increased respiration induced by light has been utilised as follows : irradiation by monochromatic light of different wave-lengths but equal intensities results in a measurable increase in respiration; by plotting this effect against wave-length a curve is obtained which indicates the absorption of light by the hæmin belonging to the enzyme. Curves of this type reproduce the absorption spectra of compounds of the type carbon monoxide–hæmonicotine. Using yeast cells it is found that the spectrum of the respiratory enzyme is almost exactly similar in shape to the absorption curve (measured photometrically and bolometrically) of the carbon monoxide compound of reduced hæmin. The maximum of the latter curve is, however, at 408 $\mu\mu$, whereas the respiratory enzyme shows a maximum at 436 $\mu\mu$. This discrepancy is interpreted by assuming that the respiratory enzyme exists in the solid state, adsorbed on the surface of the cells, whilst the absorption spectrum of the hæmin compound is measured in solution. The shift in the entire absorption curve is consistent with this explanation (cf. A., 1926, 1277; 1927, 1221). R. A. MORTON.

Action of neutral salts in enzymic processes. Effect of bromides on salivary amylase. K. C. SEN (J. Indian Chem. Soc., 1928, **5**, 245—249).—The optimum p_H for the amyloclastic action of salivary amylase is about 6·7. Addition of sodium chloride accelerates enzyme action but sodium and potassium bromides in small concentration retard it (cf. Thomas, A., 1917, i, 598). H. BURTON.

Digestion of crude starch by saliva. E. POZERSKI (Compt. rend. Soc. Biol., 1927, **97**, 1592—1594; Chem. Zentr., 1928, i, 818).—Pulverised starch is readily attacked, but some, although not all, kinds of potato starch are practically unattacked in the crude state. The grinding produces reducing substances.
A. A. ELDRIDGE.

Polarised light and starch hydrolysis. J. W. M. BUNKER and E. G. E. ANDERSON (J. Biol. Chem., 1928, **77**, 473—488).—No evidence could be obtained of acceleration of the enzymic hydrolysis of starch by illumination with polarised light.
C. R. HARINGTON.

Enzymes and light. L. PINCUSSEN. **X. Diastase. V.** S. KUMANOMIDOH. **XI. Pepsin. I.** K. UEHARA. **XII. Lipase. I.** S. HAYASHI (Biochem. Z., 1928, **195**, 79—86, 87—95, 96—102).—X. The effect of the presence of a series of chlorides on the inactivation of salivary-, malt-, and takadiastase by heat and by irradiation is investigated. With all three enzymes, potassium has a much greater inactivating effect than calcium. With salivary diastase, magnesium is intermediate, and with malt diastase the effect is in the following order : Mg> K,Na>Li,Rb>Ca. With malt-diastase the effect of these ions on heat inactivation is in the following order : Mg>Ca>Li>Rb>K,Na. Potassium, whilst increasing injury by the action of light, decreases injury by heat, and the reverse is true of calcium (cf. A., 1927, 482).

XI. The greatest injury of the action of pepsin, when reacting with fibrin from the blood of different animals in various buffer solutions, on irradiation with ultra-violet light is obtained at p_H 1·14, and this must therefore be the optimal p_H for the action of this enzyme. The optimum is placed in the literature at from 1·4 to 2·0.

XII. The lipase action of the serum of rabbits is considerably injured by irradiation. Removal of part of the proteins (which have a protective action) causes the injury to be increased. With guinea-pig's serum, the injury by light is greatest in faintly acid solution. P. W. CLUTTERBUCK.

Structure and enzyme reactions. IV. The system glycogen–amylase–lipoids. R. TRUSZKOWSKI (Biochem. J., 1928, **22**, 765—772; cf. Przylecki and others, A., 1927, 1113; this vol., 328). —Amylase is adsorbed on lipoids to about 67% of the quantity present in solution. Adsorbed amylase is quantitatively eluted by narcotics, partly by glycogen, and scarcely at all by water. Glycogen is not adsorbed on lipoids. The addition of lipoids to the system glycogen–amylase causes retardation of hydrolysis and the enzyme is in consequence inactivated. Its activity can, however, be restored by elution.
S. S. ZILVA.

Structure and enzyme reactions. V and VI. The systems dextrose-enzyme and ester-catalyst. S. J. PRZYLECKI, W. GIEDROYĆ, and E. A. SYM (Biochem. J., 1928, **22**, 811—825).—During the first stage (3—7 days) of the reaction in the system dextrose–maltose–maltase the presence of an adsorbent such as charcoal has no appreciable effect on the velocity of the reaction of synthesis. On the other hand, after a lapse of 2—5 months there is a considerable difference between the amounts of disaccharide synthesis in the presence or absence of charcoal. Thus whilst in the latter case 1·4% of biose is found after 2 months and 1·67% after 5 months, in the presence of charcoal there is 2·03 and 2·42% after 2 and 5 months, respectively. This is due to the fact that the product of synthesis (maltose), by being adsorbed to a greater extent than the substrate, is removed from the reacting medium.

The introduction of charcoal into the system glycerol–butyric acid–catalyst increases the equilibrium constant in favour of hydrolysis. In the case of the system ethyl alcohol–acetic acid–catalyst the reaction of hydrolysis does not proceed as far in the presence as in the absence of an adsorbent, the equilibrium constant remaining unaffected in the dispersing medium. There is an increase in the synthesis of ethyl acetate, as a result of the addition of charcoal. The mechanism of reversible reactions in the presence of adsorbents is discussed.

S. S. ZILVA.

Glycerophosphatase. H. KOBAYASHI (J. Biochem. Japan, 1927, **8**, 205—223).—Kaolin adsorbs glycerophosphatase completely at p_H 4·1; alumina shows maximal adsorption at p_H 4·7, and none at p_H 7·0. The adsorbed enzyme can be completely leached out of the kaolin at p_H 5·6; the optimal reaction is p_H 5·45, but a substance X which passes through collodion membranes and is precipitable with lead acetate is present. The pure enzyme has optimal activity at p_H 3—4; it can be freed from substance X by adsorption on kaolin and subsequent leaching or by shaking the enzyme with alumina at p_H 7·0. CHEMICAL ABSTRACTS.

Phosphatases of mammalian tissues. H. D. KAY (Biochem. J., 1928, **22**, 855—866).—The distribution of phosphatases in the tissues of the rabbit, of the cat, and of man has been quantitatively determined. They appear to function at an optimum p_H between 8·8 and 9·3, although the character of the substrate influences this optimum. The distribution is similar to that of ereptase described by Vernon. In the presence of excess of the alcohol concerned, inorganic phosphate can be esterified through the agency of the phosphatases. Thus glycerophosphoric acid, isolated as the barium salt, has been synthesised and several other alcohols have been shown to combine with inorganic phosphate. This reversible reaction catalysed by the enzymes has been studied in the esterification of glycerol. S. S. ZILVA.

Glyoxals. Formation of methylglyoxal from hexosephosphate in presence of living tissues. N. ARIYAMA (J. Biol. Chem., 1928, **77**, 359—394, 395—404).—Glyoxals may be determined colorimetrically, in presence of sodium cyanide and sodium carbonate, by means of the arsenophosphotungstic acid reagent of Benedict (A., 1922, ii, 405). Glyoxals are stable in neutral aqueous solution; at reactions more alkaline than p_H 8·0 methylglyoxal disappears from the solution, being converted partly into an unknown substance and partly into lactic acid, unless the p_H be greater than 12·0, when conversion into lactic acid is quantitative. Glyoxalase is most active at p_H 7·0; it is not affected by the presence of fluoride or of toluene (cf. Dakin and Dudley, A., 1913, i, 665, 1267); figures are given for the relative concentrations of the enzyme in different tissues. Insulin is without effect on glyoxalase; the antiglyoxalase of pancreas (Dakin and Dudley, *loc. cit.*) apparently acts directly on glyoxalase (cf. Foster, A., 1925, i, 1495) but is only partly destroyed by heating at 120° for 30 min., and may therefore not be enzymic in character. In presence of cyanide, especially at alkaline reactions, methylglyoxal disappears rapidly from solution, but not with production of lactic acid unless the p_H be greater than 12·0 (cf. Meyerhof, A., 1925, i, 1507); at less strongly alkaline reactions a reducing substance is produced which makes possible the above-mentioned colorimetric determination.

Muscle-tissue which has been freed from glyoxalase by incubation for 24 hrs. at 37° is able to convert hexosediphosphate into methylglyoxal to the extent of about 10%; this suggests the presence in the tissue of an enzyme which converts the hexosediphosphate into methylglyoxal as a stage in the formation of lactic acid. C. R. HARINGTON.

Lactacidogen. Influence of salts on muscle hexosephosphatase. Y. ODA (J. Biochem. Japan, 1927, **8**, 45—55).—Muscle phosphatase causes practically complete hydrolysis of lactacidogen. The reaction is inhibited by sodium fluoride or calcium chloride. CHEMICAL ABSTRACTS.

Lactic acid formation in muscle extracts. I. Relationship between phosphoric ester accumulation and phosphoric ester breakdown and lactic acid formation from glycogen. II. Effect of sodium hexosediphosphate on the rate of ester accumulation during the incubation of glycogen in certain types of extracts. III. Glycolysis in sterile cell-free extracts of muscle. D. STIVEN (Biochem. J., 1928, **22**, 867—873, 874—881, 882—888).—I. Phosphoric ester accumulation is not an essential accompaniment of lactic acid formation from glycogen. When ester accumulation does occur there is no definite constant ratio of the molar amount of lactic acid produced to the molar amount of phosphorus that accumulates as ester. In the second period, when the ester that accumulates in the first period is broken down, the molar ratio of lactic acid produced to phosphorus set free is also very variable. An extract of cat muscle was used in these experiments. It was prepared by extracting in the cold the finely-ground tissue with a solution of sodium hydrogen carbonate and sodium chloride.

II. In a mixture of zymophosphate and glycogen in certain concentrations there is less lactic acid produced than in the corresponding glycogen concentration in the absence of the ester. This is associated, not invariably but very frequently, with an increased

accumulation of phosphoric ester in the mixture as compared with the corresponding glycogen experiment. The "extra ester accumulation" due to the presence of zymophosphate is also associated with a more rapid loss of glycogen in addition to the above-mentioned inhibition of the lactic acid formation.

III. There is glycolysis in sterile extracts of perfused muscle after filtration through Berkefeld filters (cf. Brunton and Rhodes, Proc. Roy. Soc., 1901, 68, 417). S. S. ZILVA.

Rate of reaction between enzyme and substrate. J. BERKSON and L. B. FLEXNER (J. Gen. Physiol., 1928, 11, 433—457).—Determinations have been made of the rate of hydrolysis of gelatin by commercial pancreatin using the method of Northrop (A., 1923, ii, 271) in which the progress of the reaction is followed by measuring the viscosity of the protein solution at various times. The results are found to fit the equation $v_t - v_w = (v_f - v_w)/\{1 - (v_0 - v_f)/(v_0 - v_w)e^{-rt}\}$, where v_t is the time of flow of the reaction mixture through the viscosimeter, v_w that for water, v_f that of the mixture when proteolysis is complete, v_0 the time of flow at the beginning of the experiment, t the time of observation, and r a constant. An analogous equation fits the data collected from the literature referring to the rate of action of various enzymes on their substrates. The equation may be derived theoretically by assuming a bimolecular reaction between enzyme and substrate following the law of mass action. W. O. KERMACK.

Proteolytic activity of pancreatic juice and the rôle of enterokinase. V. LOMBROSO (Arch. Int. Physiol., 1927, 29, 213—226; Chem. Zentr., 1928, i, 364).—A defence of the author's views. Pancreatic juice causes fission of gliadin, fibrin, and zein, which are not attacked by intestinal juice. Calcium chloride has a small inconstant effect. Egg-albumin undergoes fission only in presence of enterokinase, which cannot be substituted by calcium chloride.
A. A. ELDRIDGE.

Effect of various substances of the quinine group on the enzymic functions of the organism. VIII. Digestion of edestin by pepsin in presence of quinine hydrochloride. J. A. SMORODINCEV (Biochem. Z., 1928, 195, 1—7).—0.2% Quinine hydrochloride, under the conditions of the determination of pepsin by the edestin method, has no effect on digestion, but 0.5% often shows inhibition due to the slight shift of p_H to the alkaline side which this amount causes. In more strongly acid medium (p_H 1.7), the inhibition is not obtained (cf. A., 1927, 591). P. W. CLUTTERBUCK.

Fermentation by dried yeast preparations. II. A. HARDEN and M. G. MACFARLANE (Biochem. J., 1928, 22, 786—789).—The addition of various organic and inorganic salts to zymin in a large volume of sugar solution appreciably reduces the period of induction normally occurring before the onset of rapid fermentation. Sodium arsenate is an exception to this general salt effect in that it prolongs the induction period without toxic effect on the fermentation. S. S. ZILVA.

Potentially unlimited multiplication of yeast with constant environment, and the limiting of growth by changing environment. O. W. RICHARDS (J. Gen. Physiol., 1928, 11, 525—538).—The decrease in the rate of growth of yeast on culture medium is the result of the presence of toxic products produced by the yeast during its growth and of these, alcohol appears to be the most important.
W. O. KERMACK.

***Schizosaccharomyces hominis,* nov. sp.** T. BENEDEK (Zentr. Bakt. Par., 1927, I, 104, 291—303; Chem. Zentr., 1928, i, 368).—A *Schizosaccharomyces* isolated from eczematous human skin decomposed dextrose, galactose, lævulose, sucrose, maltose, lactose, dextrin, inulin, starch, mannitol, and glycerol, but not dulcitol. A. A. ELDRIDGE.

Lactic acid fermentation. V. A. I. VIRTANEN and H. KARSTRÖM (Z. physiol. Chem., 1928, 174, 1—27).—Fermentation of dextrose with dried preparations of *B. casei* ε proceeds quite well in the presence of toluene, and takes place independently of the presence of living cells. The fermentative power of a killed, dried preparation of *B. casei* ε is about 3.7% of that of an equal number of living cells. The dried preparation is most active at p_H 5.6—6.2, with a flat optimum just below 6. It is inactive on the acid side of p_H 4.7, and very slow on the alkaline side of p_H 7.0. With living bacteria the optimum lies a little more toward the alkaline than with the dried preparation, and the rate does not fall so rapidly in either more acid or more alkaline media. For dextrose fermentation there is an optimal phosphate concentration at 0.14M with the living cells, at 0.5M with the dried preparation.

Half the dextrose that disappears during fermentation with dried *B. casei* ε does not reappear as lactic acid, and so far has not been accounted for. Aëration of a suspension of bacteria containing lactic acid leaves the amount of the latter unchanged. Insulin (several preparations) cannot replace the co-enzyme of *B. casei* ε fermentation. H. D. KAY.

Symbiotic fermentation. A. CASTELLANI (Ann. Inst. Pasteur, 1928, 42, 461—474).—Numerous examples are given of the micro-organisms which do not cause fermentation except in mixed cultures or in mixtures of pure cultures of two organisms. This symbiotic phenomenon may be employed for the identification of certain sugars and bacteria.
E. A. LUNT.

Fermentation of substituted carbohydrates by bacteria of the *B. coli* and *B. lactis aërogenes* groups. H. HEES and C. TROPP (Zentr. Bakt. Par., 1926, 100, 273—284; Chem. Zentr., 1928, i, 367).

Metabolic regulation of bacteria. E. ZIMMERMANN (Zentr. Bakt. Par., 1927, I, 104, 451—456; Chem. Zentr., 1928, i, 366—367).—The consumption of sugar by *Bacillus coli* and *B. suipestifer* in a synthetic medium depends only on the demand. "Resting" bacteria (*coli*) in aqueous sugar solution do not consume any sugar. A. A. ELDRIDGE.

Properties of the dehydrogenating enzymes of bacteria. J. H. QUASTEL and W. R. WOOLDRIDGE (Biochem. J., 1928, 22, 689—702).—The enzyme (or active centre) of *B. coli* which activates lactic acid as a hydrogen donator has the property of specifically adsorbing compounds having a particular structure

which seems to be ·CO·C(OH*)· or ·CH(OH)·C(OH*)·, where H* is mobile, the compound having acidic properties. The specificity of adsorption is very marked. The enzyme (or active centre) which activates succinic acid has also the property of adsorbing compounds having a particular structure which seems to be ·C·CH·CO₂H or ·C·CH₂·CO₂H. The formic acid enzyme is independent of the lower fatty acids other than formic acid itself and of all the substances so far investigated. The activity of dextrose as a hydrogen donator is not perceptibly inhibited by the presence of oxalic acid or of hydroxy-malonic acid. The reduction of methylene-blue by dextrose in presence of bacteria is independent, therefore, of the intermediate production of lactic acid. The action of toluene on *B. coli* is to eliminate the activity of the organism to many substances which can still be shown to be adsorbed at an active centre. Toluene appears also to affect the adsorption coefficient of the active centre towards substrates.

S. S. ZILVA.

Rate of reduction of methylene-blue by *Bacillus coli*. G. S. EADIE (J. Gen. Physiol., 1928, **11**, 459—468).—The rate of reduction of methylene-blue in presence of "resting" *B. coli* with succinic acid as hydrogen donator conforms to the equation $v = a + b \log c$ (v=rate of reduction, c=concentration of succinic acid, a and b are constants) as found by Quastel and Whetham (A., 1925, i, 1015). When dextrose is substituted for succinic acid the same equation holds over a wide range of concentration but fails if the concentration of dextrose is too low. The influence of p_H and of temperature on the rates of reduction has been investigated as well as the result of substituting other oxidation–reduction indicators in the place of methylene-blue. The mechanism of reduction is probably dependent on adsorption.

W. O. KERMACK.

Synthesis of acyloins by the enzymes of acetic acid bacteria. T. KITASATO (Biochem. Z., 1928, **195**, 118—127).—After fermentation by acetic acid bacteria of acetaldehyde, ethyl alcohol, and pyruvic acid, in spite of the powerfully oxidising character of these organisms, only acetylmethylcarbinol was obtained, diacetyl and butylene glycol never being detected.

P. W. CLUTTERBUCK.

Action of *K*-rays of aluminium on certain micro-organisms. A. LACASSAGNE (Compt. rend., 1928, **186**, 1316—1317).—Agar inoculated with cultures of *B. pyocyaneus*, *B. prodigiosus*, *Staphylococcus*, and *Enterococcus* was exposed at a range of 3 mm. to *K*-rays of aluminium for 1—600 sec. before incubation. The four species differed in their sensitivity to the rays, but in all cases exposure for a few seconds visibly affected the subsequent growth of the bacteria. A longer exposure caused irregular growth in isolated patches, and a surprisingly greater length of exposure (*e.g.*, 40—300 sec.) was necessary to ensure complete sterilisation (cf. following abstract).

B. W. ANDERSON.

Interpretation in terms of energy of the action of *K*-rays of aluminium on micro-organisms. F. HOLWECK (Compt. rend., 1928, **186**, 1318—1319). —An explanation of the long interval between partial and complete extinction of bacteria exposed to *K*-rays of aluminium (cf. preceding abstract). The same mean quantity of energy is capable of producing different effects on different individual bacteria, since the number of quanta each receives and the region in the micro-organism where consequent ionisation takes place may vary considerably. It is calculated in the case of *B. pyocyaneus* that on the average 300 ionised molecules per individual modify growth, 6000 prove fatal to most, but 45,000 are necessary to sterilise them all.

B. W. ANDERSON.

Precipitable substances derived from *Bacillus typhosus* and *B. paratyphosus* B. J. FÜRTH and K. LANDSTEINER (J. Exp. Med., 1928, **47**, 171—183).—Specific substances soluble in ether were not obtained from *B. typhosus*; two serologically active protein substances and one non-protein were separated. One of the proteins is soluble in 75% ethyl alcohol. Specific substances similar to this non-protein, and containing much carbohydrate, were prepared from *B. paratyphosus* B, *B. enteritidis*, and *Proteus* HX 19 and OX 19.

CHEMICAL ABSTRACTS.

Oxygen consumption of luminous bacteria. E. N. HARVEY (J. Gen. Physiol., 1928, **11**, 469—475).—At 21·5° the average value of oxygen consumption by *Photobacterium phosphorescens* is $4·26 \times 10^{-11}$ mg. per bacterium or $2·5 \times 10^4$ mg. per kg. (cf. *ibid.*, 1926, **8**, 89).

W. O. KERMACK.

Hydrogen-ion concentration of the gastro-intestinal tract and its relation to chemical bacteriology. L. ARNOLD (Chem. Bull. [Chicago], 1928, **15**, 5—6, 30).—A discussion of the p_H in the lumen of the gastro-intestinal tract as influenced by the addition of the various digestive secretions, by the presence of the bacterial flora, and by the character of the food ingested.

CHEMICAL ABSTRACTS.

Circulatory hormone. II. H. KRAUT, E. K. FREY, and E. BAUER (Z. physiol. Chem., 1928, **175**, 97—114).—The constituent of the urine (cf. Frey and Kraut, A., 1926, 1168) which has a marked action on the heart, producing an increase in the amplitude and usually an increase in rhythm, has been investigated further. This hormone is also present in blood (dog, human, and horse), but the preparations obtained contain a large amount of impurity. The addition of serum to a preparation of the hormone from urine or blood inactivates the hormone, and this "inactivator" of serum, which does not appear to be of high mol. wt., is destroyed by heat, by the addition of alcohol, or by mild acidification of the serum. This "inactivator" does not destroy the hormone, but an inactive compound is formed from which the active hormone can be regenerated. It is considered that blood contains the hormone as this inactive compound, and by digestion of the proteins of defibrinated blood by papain at p_H 5 with dialysis against running water, a solution with a powerful action on the heart and circulation is obtained. The preparation from blood is not as pure as that from urine, but the two preparations appear to be identical; both are destroyed by heat, and are inactivated by the addition of serum, whilst they differ in several respects from histamine.

The increase in the activity of the heart and the lowering of the blood pressure are due to the same substance in all these preparations. A. WORMALL.

Production of alcohol in the animal body. IV. Influence of adrenaline on the amount of blood-alcohol. M. AOKI (J. Biochem. Japan, 1927, 7, 405—409).—An injection of adrenaline causes an increase in the alcohol content of the blood of animals. CHEMICAL ABSTRACTS.

Changes in the glycogen content of the heart and brain, and the lactic acid and lactacidogen content of the muscle in adrenalectomised rats. B. A. HOUSSAY and P. MAZZOCCO (Compt. rend. Soc. Biol., 1927, 97, 1252—1253; Chem. Zentr., 1928, i, 542).—The glycogen content for normal and adrenalectomised rats was : heart 0·066, 0·069%, brain 0·128, 0·156%; the lactic acid in the muscle was 0·185, 0·169%. A. A. ELDRIDGE.

Causes of the increase of insulin content of venous pancreatic blood after intravenous administration of adrenaline. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1927, 97, 917—919; Chem. Zentr., 1928, i, 370).—Injection of adrenaline into the atropinised blood donor in transfusion experiments causes hyperinsulinæmia, whilst the glycæmia of the other animal falls after transfusion. The injection of adrenaline appears to be the direct cause of the secretion of insulin.
A. A. ELDRIDGE.

Effect of insulin on protein metabolism. A. T. MILHORAT and W. H. CHAMBERS (J. Biol. Chem., 1928, 77, 595—602).—After a short period of fasting in the dog injection of insulin causes an increase in the urinary output of nitrogen; no such increase is observed after prolonged fasting unless carbohydrate be administered at intervals, thus producing a nitrogen-sparing effect. C. R. HARINGTON.

Autodigestion. III. Antitrypsin and insulin. H. NECHELES (Chinese J. Physiol., 1928, 2, 229—230).—Insulin in physiological concentrations does not affect the antitryptic titre of dog's blood.
H. D. KAY.

Effect of intraperitoneal injections of insulin on the blood-sugar of well-fed rabbits. M. SAHYUN and N. R. BLATHERWICK (J. Biol. Chem., 1928, 77, 459—466).—Whilst the first intraperitoneal injection of insulin into well-fed rabbits may fail to produce hypoglycæmia, subsequent similar injections produce the usual insulin effect, and insulin is more effective when given intraperitoneally than intravenously (cf. Hoskins and Snyder, A., 1927, 1222).
C. R. HARINGTON.

Insulin hypoglycæmia, shock, and leucocytosis in man. O. KLEIN and H. HOLZER (Z. Klin. Med., 1927, 106, 360—385; Chem. Zentr., 1928, i, 370).

Antiketogenic influence of insulin in diabetes mellitus. J. A. KILLIAN (J. Lab. Clin. Med., 1926, 11, 1132—1139).—The ketone substances of the blood and urine are immediately decreased, and the alkali reserve of the blood-plasma rises. The rise in carbon dioxide capacity is associated with a proportional rise in the $p_{\rm H}$ of the blood-plasma. The antiketogenic

influence of insulin is apparently due to its stimulation of the oxidation of the carbohydrates.
CHEMICAL ABSTRACTS.

Physiological variations of the internal secretion of the pancreas. I. Demonstration of a physiological insulinæmia. II. The pneumogastric, a nerve causing insulin secretion. III. Rôle of the nervous system in the regulation of physiological insulinæmia. IV. Hyperinsulinæmia following hyperglycæmia provoked by the injection of dextrose. V. Hyperinsulinæmia following the injection of adrenaline. J. LA BARRE (Arch. Int. Physiol., 1927, 29, 227—238).—Normal insulinæmia can be demonstrated in the blood from the superior pancreatic vein. Hyperglycæmia produced by the intravenous injection of dextrose increases the insulin secretion into the pancreatic vein; the hyperinsulinæmia is prevented by atropinisation and vagotomy. Increase of the insulin content of the pancreatic vein caused by intravenous injection of adrenaline is not so prevented. CHEMICAL ABSTRACTS.

Glycæmin and insulin. O. LOEWI (Klin. Woch., 1927, 6, 2169—2176; Chem. Zentr., 1928, i, 83).—The mechanism of the fixation of dextrose by insulin and its conversion into lactic acid is discussed. Diabetic plasma contains an inhibitant, " glycæmin." This antagonistic substance is dialysable, is not decomposed when the dialysate is dried, and is soluble in absolute alcohol. Diabetic hyperglycæmia is ascribed to an increased secretion of glycæmin, and a deficient secretion of insulin.
A. A. ELDRIDGE.

Biological standardisation of insulin. R. WERNICKE, F. MODERN, and C. M. SCOTTI (Anal. Asoc. Quim. Argentina, 1927, 15, 324—336).—Details are given of a method, based on that given in Publications of the League of Nations, III, Health, 1926, III, 7, of standardising insulin by a preliminary determination with white mice, followed by exact determination with rabbits. The insulin solution is diluted until a subcutaneous injection of 0·5 c.c. per 20 g. causes the same proportion of mice to show symptoms of hypoglycæmia under standard conditions as controls injected with an equal quantity of standard solution containing 0·025 clinical unit per c.c. The final standardisation is carried out by injecting different groups of rabbits with standard insulin (0·5 clinical unit in 1 c.c. per kg.) and the sample in similar amount. From analysis of samples of blood from each group the initial and mean final blood-sugar levels are determined. The percentage decrease is proportional to the activity of the preparation. Data are given of the variation of sensitivity of rabbits and mice to insulin injections.
R. K. CALLOW.

Effect of pituitary extracts on blood-sugar. G. FRITZ (Magyar Orvosi Arch., 1928, 29, 8—15).—Intramuscular injection of pituitary extracts causes a rise in the blood-sugar of normal, but not of adrenalectomised, rabbits, guinea-pigs, and rats.
CHEMICAL ABSTRACTS.

Pituitary and urinary excretion of phosphate, sulphate, and chloride. P. C. TUNG, H. C.

CHANG, and S. M. LING (Chinese J. Physiol., 1928, 2, 231—246).—After extirpation of the pituitary in dogs there is a fall in chloride output. The phosphate excretion usually shows a slight rise, followed by a fall up to the 4th or 5th hr. Later a secondary rise, the recovery phase, occurs. In animals surviving the operation from 1 to 16 weeks, phosphate excretion continued uninterruptedly. The authors therefore disagree with the suggestion of Brull and Eichholtz (A., 1926, 88) that removal of pituitary control abolishes inorganic phosphate excretion.

H. D. KAY.

Adsorbability of the active substances of the posterior lobe of the pituitary on animal charcoal. G. SATO (Arch. exp. Path. Pharm., 1928, 130, 323—325).—The adsorption on animal charcoal of the pituitary active principles acting on the uterus and on the melanophores of the frog and of the corresponding principles present in the cerebrospinal fluid has been investigated. The conclusion of Houssay and Ungar (Bol. Soc. biol. Argentina, 1924) that the melanophore-expanding substance in the cerebrospinal fluid is different from that of the posterior lobe because of its apparent non-adsorbability on animal charcoal is not considered well founded. W. O. KERMACK.

Fat metabolism and œstrus hormone of the corpus luteum. C. KAUFMANN and W. DUNKEL (Klin. Woch., 1927, 6, 2228—2229; Chem. Zentr., 1928, i, 369).

Secretin. I—II. Hypoglycæmic action of secretin in animals, man, and in diabetes. L. TAKÁCS (Z. ges. exp. Med., 1927, 57, 527—531, 532—536; Chem. Zentr., 1928, i, 83—84).—With rabbits and dogs, secretin from the mucous membrane of the small intestine causes a 50—60% reduction of blood-sugar, the maximum effect occurring in 4—5 hrs. Similar results were obtained in normal and diabetic man. A. A. ELDRIDGE.

Effect of thyroid gland preparation, ovariotomy, and removal of testes on the sugar-excretion threshold. S. KAWASHIMA (J. Biochem. Japan, 1927, 7, 361—369, 371—377, 379—387).—Administration of " thyroidin " or removal of testes (rabbits) causes a rise in the sugar-excretion threshold; ovariotomy (non-pregnant dogs) had no effect on the assimilation or excretion threshold.

CHEMICAL ABSTRACTS.

Colour tests for sterols and vitamin-*A*. I. Sterol tests. F. WOKES (Biochem. J., 1928, 22, 830—835).—Pure cholesterol freed from ergosterol gives with concentrated sulphuric acid, arsenic or antimony trichloride red colours persisting for many hours. Similar results are obtained with cholesteryl acetate and chloride, α-cholesterylene, and ψ-cholestene, but with the last two more time may be required for the colour to develop. Cholesterol, cholesteryl acetate or chloride, cholestene, and ψ-cholestene in chloroform solution left in contact with concentrated sulphuric acid for some hours and then diluted with more chloroform give a purple or violet colour. Similar colours can be obtained by removal of the chloroform solution from the acid after less than a minute's contact and addition to the former of a drop of formalin. Irradiation of sterol derivatives generally has the effect of rendering the colours more transient. In the case of cholesterol, however, irradiation under certain conditions may develop the property of producing with the " vitamin " reagents blue colours changing to red on keeping for some hours. Activation with other reagents such as acetic anhydride, benzoyl peroxide, or formaldehyde may lead to blue or purple colours being obtained on addition of the " vitamin " reagents. Cholestenone gives transient red colours with these reagents and negative results with all other tests. The other oxidation products of cholesterol which have been tested give negative results in all cases. Antimony pentachloride gives the colour sequence red →blue → red with all cholesterol derivatives examined except the oxidation products. Of these dicholesteryl ether gives both red and blue, cholestenone and hydroxycholesterylene give red only, and β-hydroxycholestenol acetate gives negative results. Introduction of sulphur into the side-chain as in cholesteryl methylxanthate retards the development of the colours but does not necessarily prevent it after the liberation of sulphur compounds has taken place. The " vitamin " reagents give with ordinary concentrations of ergosterol the usual red colour, but if a higher initial concentration be employed the red colour given by arsenic or antimony trichloride changes to purple or blue on diluting with more reagent after a few moments. Sitosterol gives similar results to cholesterol but more slowly.

S. S. ZILVA.

Dual nature of water-soluble vitamin-*B*. II. The effect on young rats of vitamin-*B_2* deficiency. Biological assay of vitamin-*B_2*. H. CHICK and M. H. ROSCOE (Biochem. J., 1928, 22, 790—799).—The caseinogen in the basal diet is purified by extraction with acid water and acid alcohol, thus removing vitamin-B_2. Rats about 4 weeks old are kept on the diet free from vitamins-B_1 and -B_2 for about 2 weeks, after which time B_1 is administered in the form of Peter's antineuritic concentrate. After 3—4 weeks from the beginning of the experimental period the substance to be tested is administered. The minimum dose which gives an average weekly increase of 10—12 g. is suggested as a standard. A description is given of the effects observed in growing rats when they are fed on diets deficient only in vitamin-B_2. Further evidence in support of the composite nature of vitamin-B is also produced. S. S. ZILVA.

Effect of inanition and vitamin-*B* deficiency on the adrenal glands of the pigeon. G. F. MARRIAN (Biochem. J., 1928, 22, 836—844; cf. Marrian and others, this vol., 91).—The adrenal hypertrophy occurring in the vitamin-B-deficient pigeons seems to be mainly due to vitamin-B deficiency, but vitamin-B_2 deficiency is also a contributory factor. The adrenal glands of both starving and vitamin-B-deficient pigeons are œdematous. This œdema accounts for 19% of the total hypertrophy shown by the vitamin-B-deficient birds and 44% in the case of the starving pigeons. A pigeon forcibly fed on a complete diet has developed acute symptoms resembling those due to vitamin-B deficiency, but the condition was not

curable by the administration of vitamin-*B*. The relation of adrenal hypertrophy to starvation and to vitamin-*B* deficiency is discussed. S. S. ZILVA.

Bios. V. B. SUZUKI and Y. HAMAMURA (Proc. Imp. Acad. Tokyo, 1928, **4**, 158—160).—Treatment of crude bios with sodium hydroxide solution gives in addition to γ-acid (this vol., 177), 2 : 6-dihydroxy-quinoline-4-carboxylic, nicotinic, *p*-hydroxybenzoic, and 4-hydroxy-3-methoxycinnamic acids.
H. BURTON.

Antiscorbutic fraction of lemon juice. VII. S. S. ZILVA (Biochem. J., 1928, **22**, 779—785; cf. A., 1927, 702).—When phenolindophenol is added to decitrated lemon juice until the indicator is no longer reduced and the solution is adjusted immediately to p_H 7, the antiscorbutic activity disappears within 24 hrs. Purified antiscorbutic fractions from lemon juice lose their activity much more rapidly than does decitrated lemon juice of similar activity. Decitrated lemon juice dialysed in collodion thimbles of a permeability which leaves the solution inactive after 3 days loses the capacity for reducing phenolindophenol. This reducing capacity is retained to a great extent by the juice when dialysed in thimbles of a permeability which yields an active juice at the end of the dialysis. Acidity retards deterioration on storage of the antiscorbutic activity in anaërobically autoclaved decitrated lemon juice. On storage at p_H 3, however, the deteriorating effect of autoclaving is scarcely perceptible. Lemon juice autoclaved anaërobically, even in a very acid medium, deteriorates much more rapidly at p_H 7 on storage than similar solutions which have not been autoclaved. Comparatively little loss occurs in decitrated lemon juice which has been autoclaved at 40 lb. pressure for 1 hr. under strictly anaërobic conditions. S. S. ZILVA.

Specificity of ergosterol as parent substance of vitamin-*D*. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1928, **22**, 762—766).—Sphingosine, oxycholesterylene, *iso*ergosterol, and digitaligenin cannot be activated by irradiation. The last-named shows only one band with a maximum at 340 μμ extending from 270 to 390 μμ. In addition, there is general absorption and possibly secondary bands in the region below 250 μμ. The broad absorption band of digitaligenin remains practically unchanged after 2 hrs.' irradiation. The above lends further support to the specificity of ergosterol as the parent substance of vitamin-*D*. The discrepancy between results obtained by Windaus and Holtz (Nachr. Ges. Wiss. Göttingen, 1927, 217) and the authors concerning the antirachitic activity of irradiated digitaligenin is discussed. S. S. ZILVA.

Vitamin-*D* in adults. Its effect on the calcium and inorganic phosphate of the blood. R. E. HAVARD and J. C. HOYLE (Biochem. J., 1928, **22**, 713—716).—Neither addition of 8 mg. per day of irradiated ergosterol to the diet of a healthy adult human subject for 21 days nor irradiation for 16 days during the winter caused any significant change in the blood inorganic phosphate or serum-calcium.
S. S. ZILVA.

Correlation between electromotive series and oxidation potentials and plant and animal

nutrition. H. P. COOPER and J. K. WILSON (Science, 1927, **66**, 629—631). CHEMICAL ABSTRACTS.

Vitamin-like substances in plant nutrition. J. F. BREAZEALE (Ariz. Agric. Exp. Sta. Tech. Bull., 1927, **16**, 401—417).—Certain plants, when decomposing, develop compounds which stimulate the growth of other plants. Many plants require for normal growth the presence of small quantities of organic compounds not usually regarded as plant foods. The stimulating property of manure is largely associated with the soluble organic matter.
CHEMICAL ABSTRACTS.

Significance of anthocyanins in plants. T. LIPPMAA (Ber. deut. bot. Ges., 1928, **46**, 267—277).—The occurrence of anthocyanins in the leaves of a large number of plants has been investigated with reference to age of leaf, natural habitat, and climatic factors. From the results obtained the author is unable to support Noack's theory that the function of anthocyanins in the leaves of plants is concerned with the assimilation of carbon dioxide.
E. A. LUNT.

Narcosis of carbon dioxide assimilation and the bubbling method. T. SCHMUCKER (Biochem. Z., 1928, **195**, 149—160).—The bubbling method in assimilation experiments is critically examined with shoots of *Cabomba caroliniana*, modified, and used to investigate the sensitivity of the assimilation of carbon dioxide to various narcotics. Faint stimulation is obtained with ether at 0·1% and ethyl alcohol at 0·3—1%. Reversible inhibition is obtained with chloroform between 0·025 and 0·1 vol.-%, with ether between 0·2 and 2·5%, and with ethyl alcohol between 1 and 3%. The lethal dose with chloroform is only slightly higher than 0·1 vol.-%. Stimulation with acetaldehyde was not obtained.
P. W. CLUTTERBUCK.

Effect of increased atmospheric carbon dioxide on the growth of plants. I. B. D. BOLAS and F. Y. HENDERSON (Ann. Bot., 1928, **42**, 509—523).—An open type apparatus for observing the effect on the growth of plants of air enriched with carbon dioxide is described. In the case of the cucumber, atmospheres containing 0·258—0·424% of carbon dioxide result in a large increase in the dry weight of the plant. E. A. LUNT.

Vegetable assimilation and respiration. XIX. Effect of variations of carbon dioxide supply on the rate of assimilation of submerged water plants. W. O. JAMES (Proc. Roy. Soc., 1928, B, **103**, 1—42).—Carbon dioxide and sodium hydrogen carbonate solutions have been used as source of carbon dioxide in the determination of the rate of assimilation of submerged aquatic plants as a function of carbon dioxide concentration and light intensity. For carbon dioxide, the rate of assimilation increases with the rate of flow of solution; for sodium hydrogen carbonate it is constant. For the same rates of flow when no other factor is limiting, sodium hydrogen carbonate gives a higher rate of assimilation than a solution of carbon dioxide of equal partial pressure.
E. A. LUNT.

Physiology of apples. IX. Chemical composition of mature and developing apples and its

relationship to environment and to the rate of chemical change in store. H. K. Archbold (Ann. Bot., 1928, **42**, 541—566).—Determinations have been made of the nitrogen, acid, sugar, and starch contents of Bramley's Seedlings as a function of time from the setting of the fruit till maturity. Subsequent losses in the cold store are shown to vary with the initial composition of the mature apple and may in some cases determine the length of storage life.
E. A. Lunt.

Temperature in relation to chemical composition in the apple. J. S. Caldwell (J. Agric. Res., 1928, **36**, 367—389).—The theory that every variety of apple has an optimum mean summer temperature at which it attains its best development is confuted. It is concluded that seasonal amount of sunlight is more potent in the determination of the quality of any given crop than the mean summer temperature at which it is grown whatever is the relation that this temperature bears to the optimum mean summer temperature of the variety. E. A. Lunt.

Effect of climatic conditions on the chemical composition of apple juice. J. S. Caldwell (J. Agric. Res., 1928, **36**, 289—365).—The annual variations in total astringency, sugar, and free acid contents in the expressed juice of apples of 216 varieties have been determined over a period of 6 years in order to relate such variations with the annual variation in rainfall, sunshine, and temperature. Amount of sunshine is the most potent factor and amount of rainfall the least potent factor in the determination of the acid–astringency–sugar ratio of the juice of any given crop. A high annual average for sunshine and temperature produces increased sugar and acid contents and decreased astringency. E. A. Lunt.

Reduction of picric acid by plants. E. Barral (Compt. rend. Soc. Biol., 1927, **97**, 753—755; Chem. Zentr., 1928, i, 365).—The plants were killed by high concentrations of picric acid, but when low concentrations (0·10—0·1%) were employed, the flowers were coloured yellow and contained (chiefly in the ovaries) picramic acid. A. A. Eldridge.

Presence of sodium in plants. G. Bertrand and [Mme.] M. Rosenblatt (Bull. Soc. chim., 1928, [iv], **43**, 368—371).—See this vol., 334.

Manganese in the mulberry leaf. S. Bito (Bull. Agric. Chem. Soc. Japan, 1927, **3**, 67—68).— More manganese is present in the mesophyll than in the vein and petiole; it increases with growth and varies with species. The flower contains the same amount. Chemical Abstracts.

Search for elements essential in only small amounts for plant growth. A. L. Sommer (Science, 1927, **66**, 482—484).—Zinc is necessary for the growth of barley, sunflowers, wheat, buckwheat, broad beans, and red kidney beans; "pyrex" containers in culture experiments do not yield traces of all necessary nutrients. A. A. Eldridge.

Development of calcium oxalate cells with particular reference to medicinal plants. D. Brunzema (Arch. Pharm., 1928, **266**, 86—103).— Histological. W. A. Silvester.

Calcium oxalate deposition in grafted plants. L. Daniel (Compt. rend., 1928, **186**, 1143—1144).— The deposition of these crystals in certain plants is greatest at those parts of the grafted junction near the callus where the multiplication of the cells is most rapid. G. A. C. Gough.

Pectin. III. Degree of esterification of pectin in juice of the lemon. A. G. Norman (Biochem. J., 1928, **22**, 749—752; cf. this vol., 559).—In order to prevent partial de-esterification of the pectin, the juice was pressed out by hand and received in 95% alcohol. The precipitate was redissolved and reprecipitated several times in this way. The apparent methoxyl content of such a preparation corresponded with a trimethylated derivative of pectic acid. If, however, a correction for the calcium pectate yield of the preparation is made, the methoxyl content approaches the theoretical value for tetramethylpectic acid. Some other material, probably pectin degradation products, giving a furfuraldehyde yield similar to that of pectin is associated with pectin in this preparation. S. S. Zilva.

Physiological significance of plant constituents with special reference to lignin. M. Rubner (Sitzungsber. preuss. Akad. Wiss., 1928, **11**, 127—145).—The fibrous tissue from various plant sources has been determined quantitatively under the various groups of cellulose, pentosans, lignin, and residual matter and the digestibility of the various fractions has been investigated. E. A. Lunt.

Formation of red anthocyan pigments in the red leaves of *Ampelopsis hederacea.* S. Ionesco (Compt. rend. Soc. Biol., 1927, **97**, 975—977; Chem. Zentr., 1928, i, 365).—The chromogen, *leucoanthocyanidin* (the colour reactions and solubilities of which are described), is converted by warming into a true anthoxycyanidin. When treated with nascent hydrogen or a mixture of barium (or manganese) dioxide and sulphuric acid, or when warmed with 20% hydrochloric acid for 5—10 min. a red pigment is obtained. A. A. Eldridge.

Formation and degradation of starch in vegetable cells. A. Maige (Bull. Soc. Chim. biol., 1928, **10**, 422—429; see also A., 1927, 388).—The suggestion of Brown and Morris (J.C.S., 1893, **63**, 604) that amylase acts both as a hydrolytic and as a synthetic agent is criticised on the following grounds : (*a*) no reversion of the hydrolytic action of amylase is observed *in vitro*; (*b*) the growth of seeds containing large amounts of starch in the presence of dextrose does not inhibit hydrolysis of the starch; (*c*) whilst chloroform or elevation of temperature reduces the formation of starch, the activity of the amylase is unaffected. It is probable that the fall in the amylase content during the production of starch is due to partial cessation of the hydrolysis in the plant-tissues.
G. A. C. Gough.

Physiological significance of pyrocatechol tannins. Michel-Durand (Compt. rend., 1928, **186**, 1145—1147).—The acetone-soluble and insoluble components of the pyrocatechol tannins in the leaves, buds, and wood of *Æsculus hippocastanum* and in the tubers of *Rumex hymenosepalus* are determined. The

acetone-soluble tannin is greater only in the leaves of the former plant, and in the tubers the total tannin content falls more rapidly than the carbohydrate content during early growth. Since tannin consumption decreases when the growth becomes slower, it is suggested that it functions as a reserve food.

G. A. C. GOUGH.

Lævulosans of *Iris*. H. COLIN and A. AUGEM (Bull. Soc. Chim. biol., 1928, **10**, 489—494; see also A., 1927, 1116).—Irisin is best isolated from aqueous extracts of *Iris fœtidissima* (*Iris pseudacorus* and *germanica* contain less irisin) through the *barium* derivative followed by treatment with dilute sulphuric acid. The corresponding *calcium* derivative, which is precipitated from aqueous solutions by alcohol, is more soluble. From *Iris fœtidissima* a non-crystalline carbohydrate, $[\alpha]_D$ −29°, mol. wt. 287—296, is obtained together with irisin by the barium method. This carbohydrate, which is more soluble in water and in 60% alcohol than irisin, yields an insoluble barium derivative, soluble calcium and strontium derivatives, and, like irisin, is not precipitated by salts of the heavy metals. After hydrolysis the carbohydrate does not reduce Fehling's solution and the rotatory power falls to −80°. It is resistant towards the hydrolytic action of emulsin, diastase, and invertase. Whilst the rhizomes of the iris contain only lævulosans and small amounts of sucrose, the leaves contain dextrose and starch in addition. G. A. C. GOUGH.

Seeds of the stone-pine (*Pinus pinea*, L.). A. D. MARANIS (Arch. Pharm., 1928, **262**, 121—122). —The edible seeds of the stone-pine contain water, 4·88%; ash, 1·20%; oil (extracted by carbon disulphide) 51·50%; nitrogenous substances, 37·45%; carbohydrates, 4·80%. The oil has d^{15} 0·92134; setting-point, −21°; Zeiss refractometer value at 40°, 61·0; acid value, 4·19; saponification value (Köttstorfer), 192·22; iodine value (Hübl), 119·0; Hehner value, 96·0; Reichert–Meissl value, 0·22; Polenske value, 0·35; ester value, 188·03. Liquid fatty acids (oleic) and solid fatty acids (stearic) are in the proportion 95 : 5.

W. A. SILVESTER.

Mercury compound of allantoic acid by means of which it may be identified in *Phaseolus vulgaris*. R. FOSSE and A. HIEULLE (Bull. Soc. Chim. biol., 1928, **10**, 310—312).—See A., 1927, 1175.

Determination of allantoic acid as xanthyl-carbamide. Application to analysis of leaves of *Acer pseudoplatanus*. R. FOSSE and V. BOSSUYT (Bull. Soc. Chim. biol., 1928, **10**, 313—315).—See A., 1927, 891.

Identification of allantoic acid in leaves of *Acer pseudoplatanus*. R. FOSSE and A. HIEULLE (Bull. Soc. Chim. biol., 1928, **10**, 308—309).—See A., 1927, 1116.

Difference in physico-chemical properties of various proteins in plant seeds. II. Four kinds of rice protein. T. TADOKORO, T. TSUJI, and S. WATANABE (J. Coll. Agric. Hokkaido Imp. Univ., 1927, **19**, 93—104).—A comparison of the properties of four rice proteins, soluble, respectively, in water, sodium chloride solution, sodium hydroxide solution, and alcohol. CHEMICAL ABSTRACTS.

Influence of caffeine on the germination of seeds. G. B. ZANDA (Arch. Farm. sperim., 1928, **44**, 278—286).—The germination of seeds of *Zinnia elegans*, Jacq., in Sachs' nutrient solution is favoured by 0·01% of free caffeine, larger plants being obtained. The initial germination is accelerated by 0·02—0·03%, but the effect ceases as soon as the seedling forms. With proportions of the base exceeding 0·1% growth is retarded and 0·2—0·3% solutions exert a definite toxic effect. Seeds thus treated grow normally if transferred to caffeine-free nutrient solution.

T. H. POPE.

Enzymes of *Pythiacystis citrophthora*, Sm. and Sm. L. J. KLOTZ (Hilgardia, 1927, **3**, 27—40).— Definite evidence for the presence of diastase, invertase, maltase, emulsin, phloridzinase, asparaginase, urease, peroxidase, catalase, and some of the lower esterases was obtained.

CHEMICAL ABSTRACTS.

Influence of light and of dextrose on the growth of a soil alga. B. M. B. ROACH (Ann. Bot., 1928, **42**, 317—345).—The growth of the soil alga, *Scenedesmus costulatus*, has been realised in liquid media under purely photosynthetic conditions with a light of comparatively strong intensity; addition of dextrose to the medium under these conditions produces no increase in the growth rate. As the photosynthetic growth rate is diminished by diminishing light intensity, increasing dextrose assimilation takes place. The maximum growth rate due to dextrose assimilation alone is less than the maximum photosynthetic rate. E. A. LUNT.

Co-zymase in respiring organs of plants. H. VON EULER and S. STEFFENBURG (Z. physiol. Chem., 1928, **175**, 38—51).—The co-zymase of washed dry yeast is found in a number of higher fungi (*Armillaria melleus*, *Hygrophorus chlor.*, *Clavaria cristata*, *Polyporus ungulatus*, *Lactarius rufus*) and in the leaves of green plants (*Vicia faba*, *Vaccinium vitis idea*), and is essential for the anaërobic part of respiration. There is also present with the co-zymase in the plant organs a heat-resistant, dialysable inhibiting substance. In the flesh of apples either the co-zymase is present in only minute amount, or its activity is prevented by the inhibitor; the respiration (oxygen consumption) here is probably at the expense of plant acids rather than of sugars. C. HOLLINS.

Protoplasm. IV. Plastin of *Myxomycetes* and its alleged ageing. A. KIESEL (Z. physiol. Chem., 1928, **173**, 169—183).—The usual methods for the preparation of plastin (cf. A., 1927, 382, 799) yield a product which contains, besides other impurities, myxoglucosan and glycogen, whilst there is a possibility that the long treatment with $0·5N$-sodium hydroxide produces changes in the native plastin. The preparation of plastin from *Lycogala epidendron*, *Fuligo varians*, and *Reticularia lycoperdon* is described and the analytical results are given; differences are found in the nitrogen content (13·58%, 14·93%, and 15·22% respectively), phosphorus, (0·12%, 0·11%, and 0·12%), and sulphur (0·38%, 0·29%, and 0·15%), whilst slight but significant differences are observed in the nitrogen distribution and the amounts of various amino-acids present

after hydrolysis with acid by the method previously described (A., 1927, 799). In general, however, the agreement between the amounts of the various products of hydrolysis is satisfactory but not sufficient to prove that the different plastins are identical. Physical and possibly chemical changes occur in plastin by treatment with the alkali used for the preparation but no marked decomposition occurs. Plastin preparations from young true plasmodium and from two later stages in the development of *Lycogala epidendron* have been compared. Variations in the nitrogen, phosphorus, and sulphur and in the amounts of various amino-acids present are observed, but the results do not establish the identity of the natural plastins of the plasmodium and of the unripe fruiting bodies.   A. WORMALL.

Mechanism of the degradation of fatty acids by mould fungi. I. T. K. WALKER and P. D. COPPOCK (J.C.S., 1928, 803—809).—Fermentation of calcium propionate by *Aspergillus niger*, in the presence of inorganic salts only, affords lactic acid and finally pyruvic and oxalic acids together with some ethyl alcohol and glyoxylic acid. Acetaldehyde and formic acid are also produced in the earlier stages. In a similar way lactic acid yields ethyl alcohol, oxalic and pyruvic acids, and pyruvic acid yields ethyl alcohol. These results (see also A., 1927, 228, 593) indicate that the fermentation of propionic acid follows the course : lactic acid, pyruvic acid, acetaldehyde, ethyl alcohol and acetic acid; the last-named yields oxalic acid through the stages glycollic and glyoxylic acids (cf. Dakin, A., 1926, 428).
                                          G. A. C. GOUGH.

Energy of growth. XII. Comparative energy yield of different sugars in the development of moulds. L. DE CARO (Bull. Soc. Chim. biol., 1928, **10**, 456—460).—Cultures of *Aspergillus niger* grown on similar media containing different sugars show greater energy yield (A., 1922, i, 706; 1925, i, 1117) for the substances in the order, lævulose, inulin, sucrose, dextrose and maltose, lactose.
                                          G. A. C. GOUGH.

Production of fumaric acid from pyruvic acid by *Rhizopus nigricans*. A. GOTTSCHALK (Z. physiol. Chem., 1927, **172**, 314—316).—Ehrlich and Bender's (this vol., 95) inability to repeat the author's results as to the production of fumaric acid from pyruvic acid by this mould may be due to their having used either a morphologically identical strain having different metabolic powers, or possibly a less viable strain.   H. D. KAY.

Production of fumaric acid from pyruvic acid by *Rhizopus nigricans*. F. EHRLICH and I. BENDER (Z. physiol Chem., 1927, **172**, 317—318).—Polemical; a reply to Gottschalk (cf. preceding abstract). The strain of *R. nigricans* used by the authors and by Gottschalk is the same. Fumaric acid is not produced by this mould from pyruvic acid.
                                          H. D. KAY.

Production of gluconic acid by the *Penicillium luteum-purpurogenum* group. II. Optimal conditions for acid formation. H. T. HERRICK

and O. E. MAY (J. Biol. Chem., 1928, **77**, 185—195).—Production of gluconic acid from dextrose by the above mould is favoured by a temperature of 25° and a concentration of 20—25% of dextrose; the optimal concentrations of salts have also been determined and the composition of the most suitable medium is given.
                                          C. R. HARINGTON.

Spike disease of Sandal (*Santalum album*, Linn.). I. Diastatic activity of the leaves. R. SREENIVASAYA and B. N. SASTRI (J. Indian Inst. Sci., 1928, **11** *A*, 23—29).—Sap was extracted from leaves and stem by freezing in liquid air, grinding at the ordinary temperature, and pressing. Leaf powders were prepared from materials dried in a vacuum over calcium chloride. 2·0 c.c. or 0·25 g. respectively were allowed to act on 25 c.c. of 2% soluble starch for 20 hrs. at the ordinary temperature in presence of toluene. The sugar formed, after clearing the solution with colloidal ferric hydroxide, was determined as maltose by Bertrand's method. The diseased leaves showed markedly higher diastatic activity than healthy leaves, the figures corresponding to those for growing shoots, which have a similar composition to diseased leaves.   F. E. DAY.

Simultaneous determination of minute amounts of oxygen and carbon dioxide. W. O. FENN (Amer. J. Physiol., 1928, **84**, 110—118).—The apparatus and technique have been devised for the purpose of measuring the respiratory exchange of small amounts of tissues *in vitro*. The apparatus consists essentially of a differential volumeter (A., 1927, 583) in which the absorption of oxygen is measured volumetrically. The carbon dioxide produced is determined by means of the change in conductivity of a solution of barium hydroxide enclosed in the volumeter. The calibration of the instrument is described and a number of typical results are reported demonstrating that the respiratory exchange of 0·1 g. of tissue could be determined every ten minutes with a sensitivity of 0·05 mm.^{3}
                                          R. K. CANNAN.

[Pipette for] micro-determination of sugar and chloride in blood. K. SCHUHECKER (Wien. med. Woch., 1927, **77**, 1519—1520; Chem. Zentr., 1928, i, 98—99).—A rinsing pipette is described, the use of which avoids that of the torsion balance.
                                          A. A. ELDRIDGE.

Simple hydrogen electrode for use in biochemistry. A. D. GARRISON, H. O. NICHOLAS, and J. G. PASTERNACK (J. Lab. Clin. Med., 1926, **11**, 1091—1093).—The p_H can be determined with an accuracy of 0·03 in 1 c.c. of liquid.
                                          CHEMICAL ABSTRACTS.

Distilled water for biological purposes. E. CANALS and M. MOUSSERON (Bull. Soc. Chim. biol., 1928, **10**, 472—477).—Water of low conductivity and p_H 5·5—5·6 may be obtained by the use of a pyrex still; that with similar conductivity and higher p_H often contains traces of alkali from the glass. The water maintains its properties better if kept cold and in the presence of platinum-black.
                                          G. A. C. GOUGH.