BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1929.

General, Physical, and Inorganic Chemistry.

Standard solar wave-lengths (3592—7148 Å.). K. BURNS, W. F. MEGGERS, and C. C. KIESS (U.S. Bur. Stand. J. Res., 1928, **1**, 297—317).—The Bureau of Standards and the Allegheny Observatory have co-operated in measuring the wave-lengths in the international system of selected dark lines in the solar spectrum. In the octave 3592·027—7148·159 Å. 729 lines have been measured, the majority having a probable error less than 1 part in 4,500,000 parts. The corrections to be applied to Rowland's table are given.　　　　　　　　　　　　C. J. SMITHELLS.

Spectral intensities of radiation from non-harmonic and aperiodic systems. B. CASSEN (Proc. Nat. Acad. Sci., 1928, **14**, 880—882).—Mathematical. The matrix components of the components of acceleration of a general quantum dynamic system are derived, from which expressions for the spectral intensities and spatial distribution of radiation can be obtained.　　　　　　　　　　A. J. MEE.

Spectrographic investigation of spark discharge. U. NAKAYA and Y. FUJIOKA (Proc. Imp. Acad. Tokyo, 1928, **4**, 464—466).—Four types of spark discharge are distinguished and respectively named three-part spark, short-spark, broken line spark, and flame-like spark.　　W. E. DOWNEY.

Relationships of the hydrogen spectra under various conditions of excitation. I. The spectra in the oscillatory discharge and in the Paschen hollow cathode. Z. BAY and W. STEINER (Z. physikal. Chem., 1928, **B, 1**, 239—252).—At 0·05 mm. pressure the Balmer series, as far as the H_ϵ line, and the complex line spectrum are strongly developed, but the continuous spectrum is relatively weak; as the pressure increases up to 3—7 mm. the continuous spectrum increases in intensity at the expense of the other types. The influence of current density is less characteristic, an increase from 50 to 500 milliamp. resulting in only a strengthening of the α lines of the red Fulcher bands and a simultaneous intensity change in the blue. In the hollow cathode the red Fulcher bands and the region 5700—6000 Å. are considerably weaker than in the Geissler tube, whereas the region 5600—5700 Å. and a region in the neighbourhood of the green Fulcher bands between 5303 and 5434 Å. are somewhat stronger. The distribution of intensities differs throughout the spectrum; the Balmer series are of similar intensities in the two tubes, but the continuous spectrum is appreciably weaker in the hollow cathode. In the oscillatory discharge the whole green region is weakened and the red Fulcher bands, especially 6224 and 6327 Å., are considerably weakened; the α lines in the red are of increased intensity relative to the principal lines, an effect which is noticeable, although to a smaller extent, on increase of pressure in the ordinary tube. Characteristic of the oscillatory discharge spectrum is the strength of a group of lines between 5761 and 5836 Å., and also the relatively slight influence exerted by the walls of the discharge tube on the Balmer series, which are prominently displayed; the continuous spectrum is somewhat weakened. There is but little difference between the oscillatory discharge spectrum in the ordinary tube and in the hollow cathode. The significance of the results is discussed.

H. F. GILLBE.

"Forbidden" hydrogen lines. A. RUBINOWICZ (Physikal. Z., 1928, **29**, 817—823).—A theoretical investigation of forbidden transitions in the simplest case, namely, the Lyman series of hydrogen, using the Schrödinger methods.　　　R. A. MORTON.

Study of the energy relations in the helium spectrum. I. C. CORNOG (Physical Rev., 1928, [ii], **32**, 746—752).—The relations between the lines of the helium spectrum as functions of the accelerating P.D. were investigated, in particular near the critical points of the gas. Photographs of the spectrum produced in an equipotential space using an equipotential cathode were studied photometrically to determine the variation of line intensities on passing the various critical potentials. The 54·2 volt point, at which double ionisation is first possible, is dealt with. Spectra were taken at intervals between 50 and 60 volts, and the plates showed a marked intensity maximum near 54·2 volts for all lines measured.　　N. M. BLIGH.

Helium lines in stellar spectra. O. STRUVE (Nature, 1928, **122**, 995).—Estimates of the intensities of the absorption lines 4472 and 4388 Å. for various stars are recorded. Mean values are 5·2 and 3·2, respectively. It is concluded that whilst the relative abundance of atoms in the mp^3 and mP levels is subject to considerable variations in different stars, the average ratio triplet/singlet in stellar spectra is not very different from that observed in the laboratory under normal pressures.　　　A. A. ELDRIDGE.

Striations in high-frequency discharges [in argon etc.]. S. P. McCALLUM and W. T. PERRY (Nature, 1929, **123**, 48—49).

Structure of the spectrum of ionised argon (A II). T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 771—779).—See this vol., 3.

Zeeman effect of the spectrum of ionised argon (A II). C. J. BAKKER, T. L. DE BRUIN, and P. ZEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 780—799).—See this vol., 3.

New type of low-frequency low-voltage discharge in a neon lamp. G. R. PARANJPE and K. SHESHADRIENGAR (Nature, 1928, **122**, 959—960).

Auroral red line. J. KAPLAN (Proc. Nat. Acad. Sci., 1928, **14**, 882—884).—The red " line " in the spectrum of the aurora borealis, previously supposed to be an unclassified oxygen line, has been re-examined and found to be a band belonging to the first positive group of nitrogen. The green line is probably the only oxygen line in the auroral spectrum.   A. J. MEE.

Quantum explanation of the auroral green line based on measurements of the Zeeman effect. L. A. SOMMER (Z. Physik, 1928, **51**, 451—470).— The magnetic resolution of the auroral green line $5577 \cdot 350 \pm 0 \cdot 005$ Å., due to a field of 6080 gauss produced by a solenoid wound round the discharge tube, has been measured by means of a Fabry–Perot interferometer. The resolution corresponds, within the limits of experimental accuracy, with the normal Zeeman effect. From this it is deduced that the line belongs to the arc spectrum of oxygen, being given by the combination $2^1D_2 - 2^1S_0$, where $^1D_2$ and $^1S_0$ are deep-lying metastable terms. The line is thus explained on the quantum theory as due to a transition of small excitation potential and generally small probability. Analysis of the terms $^1D_2$ and $^1S_0$ indicates the existence of a singlet system in oxygen. This explanation of the green line also accounts for the existence of red and violet oxygen lines in the spectra of the aurora and of the night-sky radiation, these lines being of the same origin as the green line (viz., transition between deep-lying metastable terms).
                                                E. B. ROBERTSON.

Spark spectrum of sulphur, S II, in the Schumann region. P. LACROUTE (Compt. rend., 1928, **187**, 975—976; cf. A., 1928, 1065).—The new lines $1813 \cdot 86$, $1815 \cdot 75$, $1820 \cdot 37$ (?), $1820 \cdot 81$, and $1834 \cdot 76$ Å., forming part of the multiplet $b^4P - a^2P$, are recorded. Combinations between the terms b^4P and $4p^4D$ or a^2D were not detected, and the line $1993 \cdot 37$ Å. corresponding exactly with the notation $b^4P_1 - 4p^4P_3$ is an example of an exception to the rules of selection.   J. GRANT.

Spectra of doubly-ionised arsenic, antimony, and bismuth. R. J. LANG (Physical Rev., 1928, [ii], **32**, 737—745).—These spectra were partly analysed by the use of the irregular doublet law and the Moseley law and the published data for the two preceding elements of each isoelectronic sequence. In As III and Bi III the important terms from the configurations ns^2np, ns^2nd, $ns^2(n+1)s$ were located and, except the quadruplet P terms, those from the $nsnp^2$ configuration. ($n=4$ for As III, 5 for Sb III, and 6 for Bi III). In As III alone the ^2P term of the np^3 configuration was found. The terms of Sb III located consist of some of those for the first three configurations only.   N. M. BLIGH.

Fine structure of the sharp series triplet, $2^3P_{0,1,2} - 2^3S_1$, of optically-excited mercury radiation. E. H. COLLINS (Physical Rev., 1928, [ii], **32**, 753—760).—The possibility of varying fine-structure patterns by changing the method of excitation was investigated. Measurements were made with two Lummer–Gehrcke plates, first with mercury vapour only in the resonance tube, giving excitation by absorption of 4358, and, secondly, with mercury vapour and nitrogen present at 2—4 mm. pressure, giving excitation by absorption of both 4358 and 4047 Å. For the first condition of excitation the wave-length differences are for 5461, 0; for 4358, -157, -107, -20, 0, $+30$, $+46$, $+183$; for 4047, -116, -62, -52, 0. For the second condition, for 5461 they are -235, 0; for 4358, -107, -20, 0, $+30$, $+183$; for 4047, -110, -62, -53, 0. Comparisons under the two conditions and also with the fine structure of the arc show differences making it evident that differences in fine structure exist depending on the method of excitation.   N. M. BLIGH.

Spectra of mercury above the ionisation potential. L. R. MAXWELL (Physical Rev., 1928, [ii], **32**, 715—720).—Experiments were made to separate the effects due to direct impacts and to recombination, and to determine which of these processes contributes the more to the production of the arc lines. Positive ions were withdrawn before they recombined by an electric field perpendicular to the beam of electrons having velocities greater than the ionisation potential. Contrary to the previous explanation of the complete arc spectrum above the ionisation potential, the intensity of the arc lines was found to be independent of the electric field, indicating that recombination contributes very little to the formation of these lines. Hence in addition to simple excitation the arc spectrum can be explained either as due to the return to the 1^1S_0 state by an electron displaced from an inner energy level to a virtual orbit while one of the electrons of the valency group falls in to fill the vacated level, or as due to a special type of recombination called initial recombination. Spark lines due to singly- and doubly-charged ions show a variation of intensity along their length such that it is possible to distinguish them from the arc lines. It is also possible to differentiate between the lines of the first and second spark spectra.
                                                N. M. BLIGH.

Determination of the mean life for the 4797 Å. spark line of doubly-ionised mercury. L. R. MAXWELL (Physical Rev., 1928, [ii], **32**, 721—726; cf. preceding abstract).—The spark line 4797 Å. due to ions moving in a particular direction through a beam of electrons was obtained showing a peculiar variation of intensity. Calculations were made to determine how the intensity of the line should vary with respect to its position across the beam and for different uniform and non-uniform electron current densities of the beam. Comparison with experiment showed that the line is produced at a single electron impact, the average life of the excited state being 4×10^{-7} sec. The mean life for the first order spark lines could not be measured, but was estimated to be less than 1×10^{-7} sec.   N. M. BLIGH.

Wave-length measurements in the arc and spark spectra of hafnium. W. F. MEGGERS (U.S.

Bur. Stand. J. Res., 1928, **1**, 151—187).—Using hafnium salts of the highest available purity, the arc and spark spectra of hafnium were photographed with concave grating and prism spectrographs. The chief impurities encountered were niobium, zirconium, and titanium. Some 1500 lines between 2155·72 and 9250·27 Å. have been measured and ascribed to hafnium. Comparison of these results with the earlier measurements of zirconium spectra proves that hafnium was invariably present as an unrecognised impurity. It is suggested that 4093·17 Å. is the " raie ultime " for neutral hafnium atoms and 2773·37 Å. the one for ionised atoms. The stronger Hf II lines are identified with faint Fraunhofer lines in the sun's spectrum. W. E. DOWNEY.

Some multiplets of doubly-ionised lead. S. SMITH (Proc. Nat. Acad. Sci., 1928, **14**, 878—879).— The spectrum of doubly-ionised lead (Pb III) is investigated, and the lines arising from combinations between triplet terms are identified. A. J. MEE.

Broadening of spectral lines by self-absorption. H. C. BURGER and P. H. VAN CITTERT (Z. Physik, **51**, 1928, 638—651).—A relationship is deduced between the broadening of a line due to self-absorption and the absorption coefficient for the line. Measurements of the widths of some of the strong helium lines have been made with a Fabry–Perot interferometer for various values of the discharge current, and the widths of the lines without absorption found by extrapolation. The broadening of the line for each value of the discharge current is calculated, and hence the absorption coefficient. Helium is particularly suitable for the work on account of the large " Doppler-width " of its lines due to its small atomic weight. For the red line $2^1P—3^1D$ (6678 Å.) the absorption coefficient is very large, as is indicated by theory, only about 0·2% of the light emitted inside a discharge tube 2 mm. wide with a current of 20 milliamp. emerging. Measurements on the triplet lines are rendered difficult by multiplet structure, but resolution can be effected by cooling the discharge tube in liquid air. Most of the work was, however, carried out at the ordinary temperature, and no great accuracy is claimed. For the triplet line 5876 Å. the ratio of the absorption coefficients of the components $P_2—D$ and $P_1—D$ has been found to be about 100 : 50. E. B. ROBERTSON.

Extinction law for various atoms. H. SEYFARTH (Z. Krist., 1928, **67**, 422—429; Chem. Zentr., 1928, ii, 424).—Mathematical. A. A. ELDRIDGE.

Spectrum of aluminium in the extreme ultraviolet. E. EKEFORS (Z. Physik, 1928, **51**, 471—480).—The spectrum of aluminium in the extreme ultra-violet has been examined by means of a 1-metre vacuum spectrograph. Lines due to Al II and Al III have been identified between 480 and 1300 Å. These have been identified with the lines predicted by Paschen, and from them the values of the terms $6s$, $7s$, $6p$, and $7p$ for Al III have been calculated. In the Al II spectrum the triplet $3p_{1,2,3}—5s$, predicted by Paschen, has also been observed. Observations have been extended as far as 320 Å., but in this region the lines are too weak and diffuse to be measured accurately. E. B. ROBERTSON.

Interferometer measurements of wave-lengths in the vacuum arc spectra of titanium and other elements. C. C. KIESS (U.S. Bur. Stand. J. Res., 1928, **1**, 75—90).—More than 300 lines have been measured between 6743 and 2941 Å. for the vacuum arc spectrum of titanium by means of a Fabry–Perot interferometer. W. E. DOWNEY.

Quantitative spectroscopic analysis of alloys. Sensitivity of spectral lines. T. NEGRESCO.—See this vol., 161.

Efficiency of ionisation in hydrogen by positive-ion impact at 7000 volts. R. W. GURNEY (Physical Rev., 1928, [ii], **32**, 795—798).—If ionisation is not accompanied by transfer of kinetic energy, the method used, in which hydrogen at low pressure is bombarded with positive potassium ions, permits a comparison of the ionising efficiency with that of electron impact. It is concluded that either the efficiency is less than 1/150 of that of 50-volt electrons, or that ionisation is accompanied by transfer of kinetic energy. N. M. BLIGH.

Ionisation by collisions of the second kind in mixtures of oxygen with the rare gases. H. D. SMYTH and E. C. G. STUECKELBERG (Physical Rev., 1928, [ii], **32**, 779—783).—An extension of the work of Harnwell (cf. A., 1927, 604, 709). Mixtures of oxygen with argon, neon, and helium and incidental effects of water vapour were studied, and evidence of the following collisions of the second kind was obtained : (1) $A^+ + O_2 \rightarrow O_2^+ + A$. (2) $A^+ + H_2O \rightarrow H_2O^+ + A$ (very strong). (3) $H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$. (4) $Ne^+ + O_2 \rightarrow O^+ + O + Ne$. (5) $He^+ + O_2 \rightarrow O^+ + O + He$. The view is confirmed that the ratio O_2^+/O^+ is independent of the pressure, suggesting that the O^+ is formed directly by electron impact without the need of additional collisions, in contrast to the cases of hydrogen and nitrogen, but the exact value of the first ionising potential is uncertain. N. M. BLIGH.

Ionisation potentials and grating energies of atoms in the solid state. S. C. BISWAS (J. Indian Chem. Soc., 1928, **5**, 561—568).—Following on the assumption of the existence in an atom of a repulsive force varying inversely as some power of the distance, it is deduced that the product of the lattice energy and the fourth root of the compressibility of the elements will be a constant quantity dependent on the lattice type and on the unknown exponent of the repulsive force. The computed values of this product are approximately constant for elements in groups IA, IB, IIA, and IIB, with mean values 10, 7·3, 10, and 10·5, respectively. A method, based on thermochemical data, is given for the calculation of the heat of hydration of gaseous ions, which is independent of the concept of lattice energy. F. G. TRYHORN.

Ionising potentials and far ultra-violet lines of light atoms. L. A. TURNER (Physical Rev., [ii], **32**, 727—736).—Theoretical. An extension and discussion of the work of Millikan and Bowen (cf. A., 1927, 912, 998). By interpolation, the ionising potentials of F and F^+ are found to be 17·4 and 34·5 volts. These values improve the regularity of the values of $(\nu/R)^{\frac{1}{2}}$ corresponding with the ionising

potentials of atoms of the first short period. The energy for removal of a $2s$ electron from each of many of the atoms and ions of these elements (L_{11} levels for an atom) is calculated by use of the s^2p^{n-1}—sp^n lines. The effect of removal of a $2s$ electron on the subsequent removal of a $2p$ electron is found for the boron, fluorine, and neon atoms to be an increase of $(\nu/R)^{\frac{1}{2}}$ by about 0·45. This is used to predict the wave-lengths of missing s^2p^{n-1}—sp^n lines of C, N, N^+, and O. New identifications of the far ultra-violet lines of magnesium are proposed and the third ionising potential is found to be $80·4 \pm 1$ volts. A pair of fluorine lines are tentatively identified as the $2s^2 2p^5 {}^2P$—$2s 2p^6 {}^2S$ lines.   N. M. Bligh.

Critical potentials of light elements for simultaneous transitions. B. B. Ray and R. C. Majumder (Nature, 1929, **123**, 49).—The hypothesis of simultaneous transitions (Ray, A., 1928, 1296) is supported by Moseley curves for elements from iron to copper for such transitions as $2M_1$, $2M_2$, M_1+M_3, M_2+M_3, $M_1+(M_1-M_2)$, $M_2+(M_2-M_3)$, etc.
A. A. Eldridge.

Ionisation processes of iodine interpreted by the mass-spectrograph. T. R. Hogness and R. W. Harkness (Physical Rev., 1928, [ii], **32**, 784—790).—The relative numbers of the ions I^+, I_2^+, and I_3^+ were measured as a function of pressure from 2×10^{-5} to 4×10^{-3} mm. In the primary process of electron collision I^+ and I_2^+ were both formed. I_2^+ was also formed in secondary collision from I^+ by the process $I^+ + I_2 \rightarrow I_2^+ + I$ and I_3^+ was formed from I_2^+ by the process $I_2^+ + I_2 \rightarrow I_3^+ + I$. Evidence and argument against other possibilities are given. The disappearing potentials of I^+ and I_2^+ were both 9·3 volts. Pressure–intensity relationships were determined for the ions I^-, I_2^-, and I_3^- which were found to exist in quantities comparable with those of positive ions. I^- is formed according to $I_2 + E^- \rightarrow I^- + I$. I_2^- and I_3^- are not formed by collision with free electrons, but as a result of secondary collisions of I^- and I_2^-, respectively, with I_2 molecules: $I^- + I_2 \rightarrow I_2^- + I$; $I_2^- + I_2 \rightarrow I_3^- + I$.   N. M. Bligh.

Hydrogen ions as the cause of the occurrence of spectral selectivity in the photo-electric effect for potassium. R. Suhrmann (Physikal. Z., 1928, **29**, 811—815).—Thoroughly purified and dried hydrogen brings about no increase in photo-electric sensitivity when introduced into a potassium cell. Using a specially designed cell, the introduction of H^+ ions is shown to effect an increase in sensitivity from $3·6 \times 10^{-4}$ to about 2×10^{-2} Coul./g.-cal. The maximum photo-electric effect at $440 \, \mu\mu$ is regarded as due to a very loose union between potassium and ionised hydrogen at the metal surface only.
R. A. Morton.

New photo-electric effect. F. M. Penning (Physica, 1928, **8**, 137—140; Chem. Zentr., 1928, ii, 317).—A lecture experiment. The arc potential of a discharge tube containing neon (20 mm.) and argon (0·001%) increases by 50 volts when the gas is exposed to irradiation from another neon tube, thus confirming the theory of ionisation by metastable atoms.   A. A. Eldridge.

Surface layers on tungsten and the activation of nitrogen by electron impact. C. Kenty and L. A. Turner (Physical Rev., 1928, [ii], **32**, 799—811; cf. A., 1927, 913).—Traces of oxygen cause the formation of a layer which renders the tungsten filament insensitive to active nitrogen, whilst traces of hydrogen prevent formation of the nitrogen layer and remove it if already present. The amount of nitrogen adsorbed was shown to be of the order of magnitude necessary to produce a layer of single atoms. Activation of a stream of nitrogen reduces the thermionic emission from a tungsten filament in the stream, similarly to the effect of the active form of nitrogen produced in an arc struck in nitrogen. It seems probable that the activated form is atomic nitrogen.   N. M. Bligh.

Effect of water vapour on the mobility of gaseous ions in air. H. A. Erikson (Physical Rev., 1928, [ii], **32**, 791—794).—Results additional to previous work (cf. A., 1927, 1002) indicate that an H_2O molecule gives up an electron to the final positive air ion and thus forms an H_2O^+ ion of a greater mobility. It is also shown that the reciprocal of the mobility bears a linear relationship to the humidity.
N. M. Bligh.

Directions of emission of photoelectrons. P. Auger (Compt. rend., 1928, **187**, 1141—1142).—The author's experiments (A., 1928, 453) are extended to the $K\alpha$ radiation of molybdenum (0·71 Å.) in hydrogen containing a trace of argon, and the following values (loc. cit.) found: ω_b 77°, cos ω 0·169, ρ 1·9, σ 1·32 (or 1·41 using the value of the K-level of argon).
J. Grant.

Liberation of electrons by means of X-rays. H. Behnken (Physikal. Z., 1928, **29**, 836—837).—The number of electrons liberated from an element under the action of homogeneous X-rays increases in general with increasing atomic number.
R. A. Morton.

Electron counting tube. H. Geiger and W. Müller (Physikal. Z., 1928, **29**, 839—841).—A thin wire evenly covered with a semi-insulating layer is placed axially in a metal tube. At a suitable pressure of gas (e.g., air at 5 cm. of mercury) the electric field between wire and tube can be so regulated that each electron entering the tube at any place can be registered by means of a thread electrometer. The arrangement has the advantage of exposing an area up to 100 cm.^{2} As examples of the use of the apparatus the measurement of potassium β-radiation and of cosmic rays are quoted.   R. A. Morton.

Dosage of cathode-particles from Lenard high-power tubes. R. Thaller (Physikal. Z., 1928, **29**, 841—846).—A convenient condenser method is described for measuring the output from high-power tubes.   R. A. Morton.

Measurements on the ionsation of air by means of electron streams. W. Schmitz (Physikal. Z., 1928, **29**, 847—848).—A new apparatus is described.
R. A. Morton.

Mean life-period of ions in the air above the sea. V. F. Hess (Physikal. Z., 1928, **29**, 849—851). —A preliminary account of recent measurements at Heligoland on the origin of the ionisation of the air above the sea.   R. A. Morton.

Motions of electrons in ethylene. J. BANNON and H. L. BROSE (Phil. Mag., 1928, [vii], 6, 817—824).—The velocity in the direction of the electric force and the velocity of agitation of electrons in ethylene are both dependent only on the ratio of the electric force to the gas pressure. The result is thus similar to those obtained by Townsend and Bailey (A., 1922, ii, 43) in nitrogen and hydrogen, and Brose (Phil. Mag., 1925, [vi], 50, 543) in oxygen. Ethylene undergoes a change, demonstrated only by an increase in the velocities of the electrons, after exposure in the apparatus. It is suggested that this change is due to the action of ultra-violet radiation.
A. E. MITCHELL.

Energy losses of electrons in hydrogen. H. JONES and R. WHIDDINGTON (Phil. Mag., 1928, [vii], 6, 889—910).—Measurements of the energy losses of electrons in hydrogen are described. The most probable effect of a collision between a hydrogen molecule and an electron of velocity 50 volts or greater is the excitation of the C state. The probability of effective collision with 150-volt electrons is 1—2%. At low velocities energy losses of 8—9 volts are observed and it is suggested that these are associated with the dissociation of the molecule and the excitation of the continuous spectrum. The direct stimulation of the B_0 and other low-vibrational B states is considered to be impossible, since no loss of 11·1 volts was found. There is no definite indication that any energy losses are due to direct dissociation.
A. E. MITCHELL.

Spatial distribution of photoelectrons produced by X-rays. E. J. WILLIAMS, J. M. NUTTALL, and H. S. BARLOW (Proc. Roy. Soc., 1928, A, 121, 611—625).—Previous work on the longitudinal asymmetry and dispersion of the photoelectron distribution produced by X-rays is reviewed, with special reference to the demands of modern theory. The possible sources of error in the observation and measurement of photoelectron tracks are discussed : the wavelength of the radiation producing the photoelectrons, the method of examining the photographs, the effect of " choosing " tracks on which measurement is made, and the statistical errors arising from the inaccurate measurement of the directions of individual photoelectrons. The photo-electric emission from oxygen and nitrogen due to the absorption of X-rays of wave-lengths 0·54, 0·61, and 0·71 Å. has been studied experimentally. It is shown that the observed dispersion is adequately expressed by the $\cos^2 \theta$ law, and that the distribution observed indicates a " distortion " of the symmetrical $\cos^2 \theta$ curve corresponding with a value of the asymmetry factor σ of about 1·4.
L. L. BIRCUMSHAW.

Effect of the image force on the emission and reflexion of electrons by metals. L. W. NORDHEIM (Proc. Roy. Soc., 1928, A, 121, 626—639).—It has been shown (A., 1928, 452, 681) that the phenomena of electron emission or reflexion by metals can be dealt with by calculating the emission or reflexion coefficient for the electrons at the surface of the metal and integrating over all incident electrons according to Sommerfeld's conductivity theory; the cold emission in intense electric fields has been treated in the same way. The surface of the metal is considered as a region of sudden variation of potential, which, according to the wave mechanics, produces a reflexion. In the previous papers, R, the reflexion coefficient, and D, the emission coefficient, have been calculated for certain idealised linear forms of the potential steps. In reality the form of the potential is a smooth curve, and in the present paper D and R are calculated for a field which more nearly approaches actual conditions.
L. L. BIRCUMSHAW.

Diffusion of electrons. E. RUPP (Physikal. Z., 1928, 29, 837—839).—See A., 1928, 1068.

Polarisation of light from hydrogen canal rays in an electric field. A. WEIGL (Naturwiss., 1928, 16, 1042).—The polarisation of the light from hydrogen canal rays in an electric field of which the lines of force are perpendicular to the direction of the rays falls to zero as the field strength is increased. For an angle of 45° between field and rays, and for a $P.D.$ of 600 volts, the originally elliptically polarised light becomes almost completely circularly polarised. The observations were made under a pressure of 0·1 mm. of mercury. For the higher pressures and voltages there is linear polarisation in the direction of the lines of force. These results are those which would be expected by Hanle's theory, but Rupp's experiments on this theory, which can explain only the elliptical polarisation of light in oblique fields, are not in agreement.
A. J. MEE.

Attempt to separate the isotopes of cadmium. A. A. SUNIER (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926, 4, 173—177).—After 13 evaporations of cadmium in a vacuum, in each of which half was removed, no difference in at. wt. (densimetric) was observed.
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Separation of the isotopes of chlorine. F. A. JENKINS (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926, 4, 93—98).—Fractionation of hydrogen chloride by diffusion against air at atmospheric pressure through porous pipe stems afforded a fraction in which the chlorine had at. wt. 35·418. By determination of at. wts. from the densities of hydrogen chloride solutions the efficiencies of diffusion apparatus can be compared.
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Isotope effect in the spectrum of chlorine. A. ELLIOTT (Nature, 1928, 122, 997).—Three strong bands and a fourth weaker band in the absorption spectrum of chlorine have been analysed, and the rotation constants for the normal and excited states of the chlorine molecule determined. The first three are due to absorption by $Cl^{35}Cl^{35}$ molecules, and the fourth by $Cl^{35}Cl^{37}$ molecules. The isotopic band due to $Cl^{37}Cl^{37}$ has not been observed. Absolute values of the upper vibration quantum numbers have been calculated.
A. A. ELDRIDGE.

Atomic weight of antimony from different sources. K. R. KRISHNASWAMI (J. Indian Inst. Sci., 1928, 11A, 161—172).—An amplification of a previous paper (A., 1927, 1120).

Ionisation measurements of γ-rays. J. A. CHALMERS (Phil. Mag., 1928, [vii], 6, 745—762).—It is pointed out that the ionisation produced in a

chamber is dependent only on primary γ-rays through the intermediary of the secondary β-rays and may not necessarily indicate a definite property of the γ-rays. The relative ionisations of the Ra-B and Ra-C γ-rays showed marked alterations when the electroscope lining was altered and the γ-ray beam kept the same. The results are in fair agreement with the accepted ideas on the absorption and scattering of β- and γ-rays and demonstrate the importance of an "ionisation function" in γ-ray measurements. It is concluded that ionisation measurements with γ-rays can give only approximate results in the determination of energy quantities.   A. E. MITCHELL.

Heat of β- and γ-radiation of radium. A. DORABIALSKA (Rocz. Chem., 1928, **8**, 475—485).— The heats of β- and of γ-radiation of radium in equilibrium with its degradation products are respectively 9·1 and 12·4% of the total heat of radiation.
R. TRUSZKOWSKI.

γ-Rays and the evolution of heat from radium and mesothorium. D. K. YOVANOVITCH (J. Phys. Radium, 1928, [vi], **9**, 297—306).—The determination of the amount of mesothorium in a mixture containing it and its disintegration products by comparison with a radium standard involves a number of errors. A new calorimetric method is described for the determination which is not accompanied by these difficulties. The heat evolved by a preparation containing mesothorium in disintegrating into radiothorium is measured. The micro-calorimeter used is described. Mme. Curie's relationship for preparations containing radium and mesothorium in unknown proportions, viz., $R = \Delta/I$, where Δ is the ratio of heat evolved by the radium and mesothorium preparation to that evolved by a radium standard, and I is the intensity of the preparation measured in γ-rays in proportion to a radium standard, is verified experimentally. The ratio of mesothorium to radium is deduced for one particular preparation.   A. J. MEE.

Determination of the direction of γ-rays. W. KOLHÖRSTER (Naturwiss., 1928, **16**, 1044—1045).— The method makes use of two Geiger counters one behind the other, which will indicate when one and the same secondary electron traverses both counters. When this coincidence is obtained, the axis of the pair of counters gives the direction of the electrons concerned.   A. J. MEE.

Absorption measurements with secondary β-rays. W. BOTHE and W. KOLHÖRSTER (Naturwiss., 1928, **16**, 1045).—The arrangement of two Geiger counters used for the determination of the direction of γ-rays (cf. preceding abstract) may also be used for measuring the absorption of β-rays by placing a layer of absorbing material between the counters.   A. J. MEE.

Radioactivity of the lighter elements. W. G. GUY (Abstr. Theses Univ. Chicago Sci. Ser., 1925— 1926, **4**, 87—91).—By a method sensitive to 0·003 of the β-radiation from potassium, the elements tantalum, tungsten, lanthanum, selenium, arsenic, tin, antimony, aluminium, and mercury, and compounds of sodium, calcium, barium, strontium, carbon, chlorine, bromine, copper, iron, lead, magnesium, manganese, nickel,

silver, and zinc were found to be non-radioactive. The activities of rubidium and potassium are in the ratio 1·39 : 1. The absorption coefficient in aluminium of the β-rays from potassium chloride under saturation conditions varies from 39·6 to 55·4 with aluminium thicknesses of 0·0135—0·0405 cm.; for rubidium salts it decreases from 593 to 522 with thicknesses of 0·0017—0·0051 cm. Certain organic compounds of potassium are anomalous.
CHEMICAL ABSTRACTS.

Thorium emanation. J. SEBOR (Chem. Listy, 1928, **22**, 521—526).—The value of the disintegration constant for thorium emanation obtained from freshly prepared solutions differs from that for solutions which have been kept for some time, whence it is concluded that the discrepancies between the values obtained by different authors are not due to experimental errors. The constant increases slightly with the period of accumulation of the emanation.
R. TRUSZKOWSKI.

Variation with state of the optical properties of potassium and cæsium. J. B. NATHANSON (J. Opt. Soc. Amer., 1928, **17**, 343—349).—A glass cell containing the alkali mirror was heated by means of a small electric oven enclosing the mirror of metal, and observations were made at temperatures above and below the m. p. of the metals. When the metal changed from the solid to the liquid state, it was found that the angle of azimuth of restored plane polarisation, as well as the phase difference of the components of the light vector parallel and perpendicular to the plane of incidence, changed by only a small amount. After due allowance for the effects of strains in the glass cells, it was concluded that the optical properties of the liquid alkali surface are closely identical with those of the solid alkali surface.
W. E. DOWNEY.

Cosmic radiation and radioactive disintegration. L. R. MAXWELL (Nature, 1928, **122**, 997). —Perrin's view that the disintegration of radioactive elements may be due to their absorption of cosmic radiations is probably incorrect, since the activity of a source of polonium was unchanged when shielded by being placed 1150 ft. below the surface of the earth.   A. A. ELDRIDGE.

Assignment of quantum numbers for electrons in molecules. II. Correlation of molecular and atomic electron states. R. S. MULLIKEN (Physical Rev., 1928, [ii], **32**, 761—772).—Revisions and amplifications are given of various results in a previous paper (cf. A., 1928, 1067). An attempt is made to determine the electronic states of the atomic products which would result by dissociation from each of a number of molecular states previously dealt with. Some suggested new values of the heats of dissociation for the normal states of certain molecules are : N_2, 9·5; N_2^+, 7·1; NO, 7·3; CO^+, 8·3; NO^+, 11·2 volts. The alkali and hydrogen halides are briefly discussed with reference to their electronic states and dissociation products.   N. M. BLIGH.

Proportion of energy radiated by incandescent solids in various spectral regions. L. L. HOLLADAY (J. Opt. Soc. Amer., 1928, **17**, 329—312).— Theoretical. It is shown that from a table of the

proportion of spectral energy emitted from a black-body radiator at a given temperature between wavelengths zero and λ, the proportion of energy ϕ_1 emitted in a given spectral region may be computed for a black-body radiator of any other temperature. Similarly, the energy emitted from the same spectral region by a non-black-body radiator having colour temperature T_c may be computed by multiplying the value of ϕ_1 for a black-body radiator at temperature T_c by a simple factor G. W. E. DOWNEY.

Hydrogen chromosphere. W. H. McCREA (Proc. Camb. Phil. Soc., 1928, **24**, 506—515).—Stratton has found that the intensities of the lines of the Balmer series cannot be accounted for on the assumption of thermodynamic equilibrium for the hydrogen in the chromosphere. The extent of departure from thermodynamic equilibrium is calculated, the gas being supposed to be in radiative equilibrium with black-body radiation incident on it from one side only, mechanical equilibrium being assumed possible. It is found that this state could scarcely be distinguished from thermodynamic equilibrium, although it would be characteristic of a temperature slightly lower than that of the incident radiation. A. J. MEE.

Group-theory of the reciprocal action of atoms. W. HEITLER (Z. Physik, 1928, **51**, 805—816).—Theoretical aspects of the chemical linking in polyatomic molecules are considered. R. A. MORTON.

Vector-framework of the atom according to quantum mechanics. E. FUES (Z. Physik, 1928, **51**, 817—827).—Mathematical. R. A. MORTON.

Explanation of some properties of spectra in terms of the quantum mechanics of the spinning electron. J. VON NEUMANN and E. WIGNER (Z. Physik, 1928, **51**, 844—858).—A first approximation has been made to a solution of the Schrödinger differential equation, taking into account the electron spin. Connexions with Landé's g-formula and the Burger–Dorgelo summation rules have been established. R. A. MORTON.

Scattering power of a bare nucleus according to wave mechanics. G. TEMPLE (Proc. Roy. Soc., 1928, **A, 121**, 673—675).—The scattering power of a nucleus is defined as the volume density of electricity in the scattered wave when the volume density of the incident wave is unity around the nucleus. The investigation of the scattering of an infinite plane wave by a bare nucleus (Mott, *ibid.*, **A, 118**, 542) involves the behaviour of a power series near its circle of convergence, and Mott's result is now obtained by a simpler and more direct method.
L. L. BIRCUMSHAW.

Wiedemann–Franz law. E. GRÜNEISEN (Z. physikal. Chem., 1928, **B, 1**, 379—383).—Polemical against Eucken (A., 1928, 825). M. S. BURR.

Evolution of the odd-numbered elements. W. V. HOWARD (J. Physical Chem., 1928, **32**, 1725—1742).—Theoretical. Certain peculiarities in the mass numbers of the elements are pointed out and rules similar to those of Russell (A., 1923, ii, 748) are given for relations between the elements (cf. also Harkins, A., 1923, ii, 479). The first elements to form were those of even number between carbon and nickel together with hydrogen and helium, after which evolution continued in three ways by the formation of (i) the higher even-numbered elements, (ii) those of odd numbers, and (iii) the elements between nitrogen and lithium. The lower isotopes of any element are shown to be less stable than the higher, which fact determines their abundance. The odd-numbered elements formed by a disintegration process of those of even number whereby one or both of the lowest (less stable) isotopes lost a positive charge from the nucleus and one electron. The formation of gold from mercury, the disintegration experiments of Rutherford and Chadwick, the composition of meteorites, and the formation of magmas are discussed in relation to this hypothesis. L. S. THEOBALD.

Transmutation of elements. L. THOMASSEN (Metall-Wirts., 1928, **7**, 703—708; Chem. Zentr., 1928, ii, 520).—Negative and inconclusive experiments designed to detect transmutation in an X-ray tube are described. A. A. ELDRIDGE.

Average life period of an atom. J. H. J. POOLE (Nature, 1928, **122**, 960—961).—The life of a terrestrial atom is at least 10^{21} years. A. A. ELDRIDGE.

Average life period of an atom. H. JEFFREYS (Nature, 1929, **123**, 87).—A polemical note. (cf. Poole, preceding). A. A. ELDRIDGE.

Sub-atomic energy. A. S. EDDINGTON (Mem. Manchester Phil. Soc., 1927—1928, **72**, 101—117).—A lecture.

Electrical conductivity of stellar matter. S. CHAPMAN (Month. Not. Roy. Astron. Soc., 1928, **89**, 54—57).

Viscosity in the stars. S. ROSSELAND (Month. Not. Roy. Astron. Soc., 1928, **89**, 49—53).

Some difficulties in the spontaneous emission of radiation. L. GOLDSTEIN (Compt. rend., 1928, **187**, 1285—1286).—The incompatibility which appears to exist between the two fundamental notions of the stationary state (Bohr–Sommerfeld) and the spontaneous change of configuration of the atom is discussed in the light of the Broglie–Schrödinger and Dirac analyses of undulatory mechanics. It is concluded that existing atomic structures provide no real physical reason for the possibility of the spontaneous emission of radiation. J. GRANT.

Structure of diatomic molecule spectra according to the quantum mechanics. E. WIGNER and E. E. WITMER (Z. Physik, 1928, **51**, 859—888).—The method of the theory of groups has been applied to the deduction of the characteristics of a rotation band, and to electron terms in molecules.
R. A. MORTON.

Interpretation of spectra of molecules. IV. F. HUND (Z. Physik, 1928, **51**, 759—795).—An attempt is made to systematise molecular spectra on the basis of electron terms for molecules, analogous to those in use for atomic spectra (cf. A., 1927, 183, 495, 809). R. A. MORTON.

Visible radiation characteristics of incandescent oxides. (Miss) M. L. PHILLIPS (Physical Rev., 1928, [ii], **32**, 832—839).—Energy radiated in the visible spectrum of various rare-earth and other oxides

and their mixtures when heated to bright redness between 1400° and 2000° Abs. by cathode-ray bombardment and by gas–air and oxygen–gas flames was measured by an optical pyrometric method. In general, linear relations were found between the logarithm of the reddish-blue intensity ratio and the reciprocal of the brightness temperature, and between the logarithm of the candle power emitted per unit surface area and the logarithm of the brightness temperature. Different modes of heating gave different radiation curves for the same oxide.

N. M. BLIGH.

Origin of the continuous spectrum of the hydrogen molecule. J. G. WINANS and E. C. G. STUECKELBERG (Proc. Nat. Acad. Sci., 1928, **14**, 867—871).—The Rydberg denominators and their differences for the singlet and triplet S-terms of hydrogen and helium are calculated. It is shown that the continuous spectrum of hydrogen extending from the ultra-violet into the visible originates in the transition from any one of the excited triplet levels to the ground state of the system (1^3S).

A. J. MEE.

Continuous spectrum of hydrogen. F. H. NEWMAN (Phil. Mag., 1928, [vii], **6**, 807—811).—The continuous spectrum of hydrogen has been excited in the gas at 10^{-3} mm. pressure by passing an intermittent discharge between two iron electrodes, one of which is maintained at a potential of 200 volts different from a third electrode. The spectrum varies according to the water vapour content of the gas, but in all cases only very few of the lines of the Balmer series appear, all of which have wave-lengths above 4102 Å. In the presence of water vapour the continuous spectrum is absent, being replaced by the water bands and some lines of the Balmer series. The limit of the continuous spectrum on the red side is approximately 4690 Å. The results indicate that the continuous spectrum arises from atomic excitation and not from the aggregation of molecules. By analogy with Franck's explanation (Ann. Physik, 1921, [iv], **44**, 693) of the continuous spectrum of iodine, it is suggested that the continuous character of the spectrum corresponds with the continuous distribution of the initial kinetic energy of the assimilated electrons.

A. E. MITCHELL.

Molecular spectrum of hydrogen with wave-length determinations of 3667 lines between λ4861 and 3314 Å. W. FINKELNBURG (Z. Physik, 1928, **52**, 27—118).—An extensive research into the molecular spectrum of hydrogen between the H_β line (4861 Å.) and the ultra-violet end of the spectrum (3314 Å.). The spectrum was obtained by means of a large Rowland's concave grating, giving on the photographs a dispersion of 1·98 Å. per mm. 3667 Lines were investigated in the above range, the wave-lengths and intensities being recorded in a table. The calculated probable error in the wave-lengths is 0·0035 Å. for the stronger lines, and almost double this value for the weaker ones. More than 2000 lines have been investigated for the first time; 1052 of the lines were classified into three classes on the basis of the intensity differences of the lines with different conditions of excitation.

A. J. MEE.

Band spectrum of chlorine or hydrogen chloride. E. B. LUDLAM (Nature, 1929, **123**, 86—87).—The band spectrum of chlorine burning at a silica jet in hydrogen has been observed. Hydrogen chloride is believed to be the emitter of the bands.

A. A. ELDRIDGE.

Emission band spectrum of chlorine. Y. OTA and Y. UCHIDA (Japan J. Phys., 1928, **5**, 53—58).—The emission spectrum of rarefied chlorine excited by uncondensed discharges was studied with the object of measuring more exactly the wave-lengths of band heads and arranging them in new series schemes. The wave-lengths of 58 band heads between 487 and 392 $\mu\mu$ were measured, and the bands classified into three systems, arranging each in a two-dimensional scheme of vibration quantum numbers. The spectrum radiated by electrically excited chlorine is quite different from the ordinary absorption spectrum.

N. M. BLIGH.

Emission band spectrum of bromine. Y. UCHIDA and Y. OTA (Japan J. Phys., 1928, **5**, 59—66).—Wave-lengths of 80 band heads were measured; the band heads were analysed into two systems of two-dimensional schemes having common final states. The relation between the emission and absorption bands is discussed.

N. M. BLIGH.

New band system of carbon monoxide. R. K. ASUNDI (Nature, 1929, **123**, 47—48).—Bands were observed at 3893·2, 3681·1, 4125·0, and 4380·3 Å.; with the exception of the band at 3681·1 Å., the bands have been analysed. The final state is identical with that of the Ångström bands. The bands are probably due to the transition $3^1S \longrightarrow 2^1P$. The new system has only one n'' progression. Three of the bands are identified with those recorded by Duffendack and Fox (A., 1928, 6).

A. A. ELDRIDGE.

New band system in carbon monoxide. G. HERZBERG (Naturwiss., 1928, **16**, 1027—1028).—Using the electrodeless ring discharge with feeble excitation at 1 mm. pressure of carbon monoxide, the spectrum obtained shows the Ångström a bands very intensely, and also a second group of bands resembling, but not identical with, the Ångström b bands obtained with an ordinary discharge tube. The new system exhibits a constant frequency difference $\Delta \nu = 5004$ cm.$^{-1}$, but the data cannot be harmonised with Birge's classification (A., 1927, 184) of the Ångström bands. The final state in the new bands is the same as the initial state in the fourth positive group of carbon monoxide. A new electron state of the molecule is postulated.

R. A. MORTON.

Band spectrum of lithium. K. WURM (Naturwiss., 1928, **16**, 1028).—Lithium vapour shows two absorption band systems in the visible, one in the red and the other in the blue-green. The fluorescence spectrum obtained by illuminating the vapour at 600—700° by means of white light is identical with the blue-green absorption system, but is better defined. The data are expressed by means of a formula from which the convergence of the levels for the unexcited molecule leads to the value 1·69 volts for the work of dissociation.

R. A. MORTON.

Infra-red spectra of ammonium salts in the transition region. G. HETTNER and F. SIMON (Z. physikal. Chem., 1928, **B, 1**, 293—300).—An apparatus for the measurement of optical absorption at low temperatures is described. It has been used for the examination of the infra-red absorption spectrum of ammonium chloride at wave-lengths 2—8 μ and at temperatures between —160° and 20°. The variation, with temperature, of percentage of light transmitted, or the isochromate, for particular wave-lengths, and also the transmission of different wave-lengths for the same temperature, have been determined. The absorption band at 7·1 μ becomes sharper as the temperature falls and moves a little towards regions of longer wave-length. The band at 5·6 μ also becomes sharper but moves towards regions of shorter wave-length. The band at 3·1 μ does not appear to undergo any change. Sharp breaks are found in the isochromate at about —30°. This corresponds with a similar break in the temperature–molecular heat curve of the salt and is to be ascribed to a change in the nuclear vibration bands due to a rearrangement of the ammonium radical at this temperature. The isochromate of ammonium sulphate for 7·15 μ has a break between —40° and —50°. The specific heat in this region has not been determined.   M. S. BURR.

Near infra-red vibration spectrum of the carbonates. H. H. NIELSEN (Physical Rev., 1928, [ii], **32**, 773—778).—Mathematical. The frequencies and intensities of the near infra-red absorption regions of the carbonate group are investigated theoretically, and the results are found to be in satisfactory agreement with experimental values.
          N. M. BLIGH.

Infra-red absorption spectra of organic carbonates. F. K. BELL (J. Amer. Chem. Soc., 1928, **50**, 2940—2950).—The absorption spectra of methyl, ethyl, propyl, butyl, *iso*butyl, *iso*amyl, and phenyl carbonates were investigated, the last-named being in the molten state. The absorption curves show the same general shape, particularly between 1 and 3 μ, and between 3·6 and 5 μ. Between 8·0 μ and 12·0 μ characteristic differences occur. A band characteristic of the carbonyl linking occurs at 5·75 μ, although intensity observations indicate that this band may really be two superposed bands. A broad band at 7·8 μ may result from a combination of frequencies characteristic of the carbon–hydrogen and carbonyl linkings. The intensity of the band at 3·4 μ increases with increasing mol. wt., but Bonino's empirical formula does not hold (cf. A., 1926, 775). It is suggested that the normal and *iso*-esters are to be regarded as two distinct types of carbonates.
          S. K. TWEEDY.

Characteristic differentiation in the spectra of saturated hydrocarbons. F. S. BRACKETT (Proc. Nat. Acad. Sci., 1928, **14**, 857—864).—The near infra-red spectra of saturated hydrocarbons have been investigated and some differentiation has been observed. The results can be used for the determination of the relative binding forces exerted on the hydrogen atoms when attached to the primary, secondary, and tertiary carbon atoms in a hydro-carbon. There is probably complete identity in the binding forces between the hydrogen atoms and the carbon atoms in benzene, a conclusion which is in accord with the prevailing ideas of organic chemistry. The binding force in benzene is considerably greater than that in saturated hydrocarbons.   A. J. MEE.

Diffuse molecular spectra. B. ROSEN (Z. Physik, 1928, **52**, 16—20).—The spectrum of the sulphur molecule, S_2, has been investigated between the wave-lengths 3000 and 5000 Å. The fading of the bands cannot always be explained on the assumption of inner collisions. Sometimes it is due to the increase in effective cross-section at higher amplitudes of nuclear oscillation. The dissociation energy of the sulphur molecule agrees with that obtained from the convergence limit of the band series. In the work of Henri on the subject both causes of fading of bands were present, viz., external collisions due to higher nuclear amplitude and inner collisions.
          A. J. MEE.

Band spectra of aluminium hydride. E. BENGTSSON (Z. Physik, 1928, **51**, 889—894).—The aluminium arc in hydrogen at atmospheric pressure emits a band system in the visible (4067—4568 Å.), but at low pressures new ultra-violet bands make their appearance. Two bands at 2229 and 2254 Å. have been studied closely. Combination relations and a scheme of levels are applied to the entire band system. Electron terms, the moment of inertia, and the nuclear separation have been calculated.
          R. A. MORTON.

Ultra-violet spectra emitted by a mixture of hydrogen and mercury vapour. H. JEZEWSKI (J. Phys. Radium, 1928, [vi], **9**, 278—296).—Evidence has been obtained for a new system of ultra-violet bands in mercury hydride. These bands were analysed and tabulated, and equations have been calculated giving the line frequencies as a function of the quantum numbers. Changes in the distribution of intensity of the continuous spectrum of hydrogen, caused by the presence of metallic vapours, were attributed to the superposition of the continuous spectrum of hydrogen and the continuous spectra due to the dissociation of metallic hydrides. The high-order lines of the mercury series were investigated.
          N. M. BLIGH.

Measurement of absorption spectra in the visible and ultra-violet regions. H. FROMHERZ (Z. physikal. Chem., 1928, **B, 1**, 301—323).—Calculations have been made of the optical requirements of an apparatus for the photographic measurement of absorption spectra with a rotating sector (cf. Scheibe and others, A., 1924, ii, 712) and a reciprocal light track to obtain a maximum light strength. The apparatus has been tested by measurements of the absorption spectrum of potassium chromate solution. The results are in good agreement with those of other investigators.   M. S. BURR.

Rare earths. XXX. Absorption spectra studies. L. L. QUILL and P. W. SELWOOD [with B. S. HOPKINS] (J. Amer. Chem. Soc., 1928, **50**, 2929—2937).—The absorption spectra of the nitrates of praseodymium, neodymium, samarium, and erbium are specifically influenced by the presence of nitric

acid. The influence exerted on the absorption bands of neodymium nitrate by magnesium nitrate or rare-earth nitrates is similar to the influence exerted by nitric acid itself; hydrochloric acid produces quite a different effect on neodymium chloride. The deviations from Beer's law of neodymium nitrate solutions somewhat resemble the effect of the addition of nitric acid. Delauney's work (A., 1927, 847) cannot be confirmed. Absorption spectra are unsuitable for the qualitative analysis of mixed rare-earth salts, owing to the changes exerted by one salt on the absorption spectra of another. These changes, however, are quite distinct from those recorded by Harris and Hopkins during the concentration of illinium residues (A., 1926, 780, 810). S. K. TWEEDY.

Variation of extinction coefficient with temperature. B. K. MUKERJI, A. K. BHATTACHARJI, and N. R. DHAR (J. Physical Chem., 1928, **32**, 1834—1840).—Measurements of the extinction coefficients for the absorption of light in the visible region of the spectrum have been made for the following solutions : chromic acid; chromic acid and oxalic acid or quinine sulphate in excess of sulphuric acid; eosin; potassium permanganate; copper sulphate; cuprous chloride (in hydrochloric acid); iodine in potassium iodide or alcohol; iodine and potassium or ammonium oxalate or ferrous sulphate; iodine and sodium nitrite or formate both in the presence of sodium acetate; and Rochelle salt and bromine in the presence of sodium acetate. The extinction coefficient increases linearly with a rise in temperature. This is explained by a diminution in the complexity of the solvates with a rise in temperature. It accounts for the increase in quantum yield with temperature frequently observed in photochemical reactions. L. S. THEOBALD.

Fluorescence of benzene and its infra-red absorption. V. POSEJPAL (Compt. rend., 1928, **187**, 1046—1048).—Analogies of the Raman effect exist for fluorescence and phosphorescence spectra. The fluorescence spectra of benzene in the liquid or vapour state lead to the same infra-red absorption bands as those of the Raman spectra, and the calculated and experimental values are in good agreement. J. GRANT.

Polarisation of light emitted by fluorescence. P. SOLEILLET (Compt. rend., 1928, **187**, 976—978).—An attempt is made to express as a function of a number of finite measurable quantities the change in polarisation of fluorescent light following a change in direction of the exciting radiation or of the ray studied. J. GRANT.

Permanent luminescence of certain uranium salts. R. COUSTAL (Compt. rend., 1928, **187**, 1139—1140).—The permanent luminescence of uranium compounds is independent of time, temperature, and the previous insolation. Infra-red radiation is without effect. These results are shown only by crystalline salts in the solid state. The luminescence is most intense when the ultra-violet fluorescence is greatest, and if it is assumed to be a result of the radioactive properties of the salt, then the luminous yield may be shown by calculation to be of the order of 1%. J. GRANT.

Raman effect in aqueous solutions and the polarisation of the Raman lines. A. CARRELLI, P. PRINGSHEIM, and B. ROSEN (Z. Physik, 1928, **51**, 511—519).—The Raman spectra of pure water and of aqueous solutions of nitric acid, sodium nitrate, sodium nitrite, ammonium nitrate, and ammonia on irradiation with a mercury arc have been photographed. The connexion between the frequency differences occurring in these spectra is discussed, and it appears that even apparently optically inactive nuclear vibrations come into action in the Raman effect. Photographs taken with solutions of sodium chloride and hydrochloric acid show, as is to be expected, no displaced lines; probably such lines are produced, even in crystals, only by the nuclear oscillation of the molecule groups and not by the oscillations of the complete ionic lattice which are detected by measurements on residual rays. The polarisation of single lines in the Raman spectra of toluene, benzene, and carbon tetrachloride is not uniform, but appears to possess widely differing values according to the part of the molecular mechanism concerned in the scattering. E. B. ROBERTSON.

Ultra-violet Raman spectrum of water. I. R. RAO (Nature, 1929, **123**, 87).—For every bright line in the mercury arc spectrum there is a Raman band in the spectrum of the light scattered by water. A. A. ELDRIDGE.

Raman effect in X-ray scattering. K. S. KRISHNAN (Nature, 1928, **122**, 961—962).

Critical potentials of molecular hydrogen. E. U. CONDON and H. D. SMYTH (Proc. Nat. Acad. Sci., 1928, **14**, 871—875).—The main experimental observations concerned with the radiation from hydrogen when bombarded by electrons of different speeds are collected and explained theoretically. Curves showing the potential energy as a function of nuclear separation are drawn for five different electronic states of the hydrogen molecule. Below 11 volts the only possible transition which can occur is to the 1^3S state, but the probability of this is small. Hence only a little atomic hydrogen will be produced by electrons of this speed. A little above 11 volts, excitation to the 2^1S state is possible. Return from this state would give radiation which is photo-electrically active. Electrons of greater speeds can (1) excite directly to the 1^3S state, hydrogen atoms of large kinetic energy being formed, (2) excite to the 2^1S state, producing radiation, or (3) excite to the 2^3S state, which would revert to the 1^3S state, giving off a continuous spectrum and forming atomic hydrogen. Some or all of these probably occur in experiments in which a critical potential of 11·5 volts has been noted. For higher speeds the mechanism is uncertain. A. J. MEE.

Magnetic susceptibility of ozone. V. I. VAIDYANATHAN (Indian J. Physics, 1928, **3**, 151—163).—Investigation was made using a retorsional method, with special attention to the elimination of errors due to temperature changes and current fluctuations. It is concluded from the results of a large number of experiments that ozone is diamagnetic. N. M. BLIGH.

Absence of effect of an electric field on the magnetic susceptibilities of hydrogen chloride and nitric oxide. L. M. MOTT-SMITH (Physical Rev., 1928, [ii], **32**, 817—823).—A repetition and extension of the work of Huber (cf. A., 1926, 1189). The susceptibilities investigated both parallel and perpendicular to an electric field of about 8000 volts/cm. were unchanged in every case. Classical theory indicates a 13% change in the susceptibility of nitric oxide measured along the electric field and due to the magneto-electric directive effect. The negative result perpendicular to the field is in agreement with quantum mechanics and favours the new quantum theory. N. M. BLIGH.

Diamagnetism and structure of ethylene. V. I. VAIDYANATHAN (Indian J. Physics, 1928, **3**, 165—174).—Using a torsional method, the magnetic susceptibility of ethylene was investigated, and the gas was found to be diamagnetic with a molecular susceptibility of $15·3 \times 10^6$, in fair agreement with Pascal's additive law. A regularity in the susceptibility of molecular and atomic configurations is observed, and it is found that for nitrogen, sulphur, ethylene, and argon the susceptibility is a linear function of the number of electrons. The structure of the ethylene molecule is discussed from the magnetic and chemical points of view. N. M. BLIGH.

Dielectric cohesion of the rare gases. M. CURIE and A. LEPAPE (Compt. rend., 1928, **187**, 1283—1285).—The dielectric cohesions (a) of the rare gases prepared by Lepape's method (A., 1928, 970) and purified by fractionation over cooled coconut charcoal have been determined at 17° by a modification of the method of Bouty for various pressures and electric fields. In the series neon to xenon a increases, whilst the resonance and ionisation potentials decrease with the atomic number. Helium is an exception to the rule, and the experimental values for argon are considered untrustworthy. J. GRANT.

Refractive indices of a mesomorphic substance in the solid state. (MLLE.) J. ZADOC-KAHN (Compt. rend., 1928, **187**, 1138—1139).—Measurements of the three principal refractive indices of solid *p*-azoxyanisole, crystallised from light petroleum, for λ 0·5893, 0·5780, and 0·5460, have shown that the birefringence is one of the highest known, ($n_g - n_p$) being 0·634, 0·649, and 0·696, respectively. The prism method was used, three prisms being cut with a microtome and arranged so that in the position of minimum deviation each prism furnished two out of the three indices. J. GRANT.

Refraction of helium and argon and its dependence on pressures lower than atmospheric. F. SCHACHERL (Publ. Fac. Sci. Univ. Masaryk, 1928, No. 98, 1—15).—From measurements of the refraction of helium and argon at pressures between 91 and 760 mm., and at 16°, it was found that, for argon, the influence of pressure on refraction was greater than its influence on the density of the gas, with the consequence that the specific refraction of argon, like that of polyatomic gases, increases with pressure. No conclusions could be reached from the results for helium. The refraction of argon, at normal temperature and pressure, and for wave-length 5462·3 Å., is $(n-1) = 282·7 \times 10^{-6}$. The rate of increase with pressure of the specific refraction of oxygen is exactly twice that obtaining in the case of argon. F. G. TRYHORN.

Refractivities of carbon monoxide, nitrogen, and nitrous oxide, and their dependence on pressures lower than atmospheric. F. SCHACHERL (Publ. Fac. Sci. Univ. Masaryk, 1928, No. 99, 1—29).—The refractivity of carbon monoxide, nitrogen, and nitrous oxide has been measured at 16°, and at pressures between 91 and 760 mm. For carbon monoxide and nitrogen the relationship between the displacement of the interference fringes and the pressure is given by $ds/dp = \alpha_1 + \beta_1 p$, whilst for nitrous oxide the same relationship is expressed by $ds/dp = Bp^c$. For light of wave-length 5462·3 Å., the refractivities, expressed as $(n-1) \times 10^6$, are for carbon monoxide, nitrogen, and nitrous oxide, respectively, 336·89, 302·83, and 507·79. For nitrogen, as for all other gases previously measured, the value of $p\beta$, where $\beta = \beta_1/2\alpha_1$, in the equation $n - 1 = Kp(1 + \beta p)$ is constant for pressures up to 1500 mm. For all gases so far investigated the values of β are greater than those of the coefficient β_ρ in the equation $\rho = Kp(1 + \beta_\rho p)$ representing the relationship between pressure and density. The specific refraction of these gases therefore increases with pressure, and with the exception of that of carbon dioxide and of nitrous oxide is proportional to $\log_e p$. The relationship between specific refraction and pressure cannot be expressed as an additive function of the atomic composition of the gas, although an additive relationship holds for gas mixtures. The pairs of isosteres CO_2, N_2O and N, CO show analogous relationships between pressure and their specific refraction. F. G. TRYHORN.

Dipole moments of some methane and ethane derivatives. J. W. WILLIAMS (Z. physikal. Chem., 1928, **138**, 75—84).—The dielectric constants and densities at 25° have been measured of ethylene chloride, bromide, iodide, and cyanide, methyl and ethyl iodide, ethylene glycol, acetonitrile, propionitrile, and benzonitrile in benzene solution. The effect on the dipole moment of a molecule of the introduction of a substituent group is deduced by regarding the dipole moments of the above compounds as due to the substituent groups alone and considering the rest of the molecule as non-polar. Calculations have been made of the angular distortion produced in the tetrahedral symmetry of the carbon atoms by the introduction into the molecule of a given substituent. F. G. TRYHORN.

Optical properties of some artificial minerals. P. GAUBERT (Bull. Soc. Franç. Min., 1927, **50**, 504—515; Chem. Zentr., 1928, ii, 334—335).—Values of n_D for various artificial minerals are: $MgAl_2O_4$ (coloured red by chromium or blue by cobalt) 1·721; gahnite, $ZnAl_2O_4$ (coloured red by chromium), 1·80; corundum, Al_2O_3, w 1·7689, ϵ 1·7609, d 3·988; $3Ca_3(PO_4)_2,CaCl_2$, w 1·642, ϵ 1·637; $3Sr_3(PO_4)_2,SrCl_2$, w 1·658, ϵ 1·664; $3Ba_3(AsO_4)_2,BaCl_2$, w 2·14, ϵ 2·13; monetite, $CaHPO_4$ n_a 1·623, n_γ 1·604, d 2·928 (triclinic); rhombic $SrHPO_4$, n_a 1·625, n_γ 1·608; $BaHPO_4$, n_a 1·635, n_γ 1·617; iron-leucite 1·619, d 2·59; potass-

ium silicoberyllate 1·523, d 2·531; sodium silico-beryllate, $Na_6Be_6Si_{14}O_{37}$, 1·545—1·532, d 2·552; sodium silicotitanate, $Na_4Si_4Ti_5O_{20}$, n_a 1·655, n_γ 1·623, d 2·88.   A. A. ELDRIDGE.

Chemical constitution and rotatory power. M. BETTI and G. B. BONINO (Atti II. Cong. Naz. Chim. pura Appl., 1926, 1244—1247; Chem. Zentr., 1928, ii, 523).—When the fourth root of the optical rotatory power of the condensation products of 1-aminobenzyl-β-naphthol with benzaldehyde and its substitution products is plotted against the negative logarithm of the dissociation constant of the acid corresponding with the aldehyde, analogous structures (e.g., m-derivatives) give values falling on the same curve. The results can be used for determination of dissociation constants of acids.
                    A. A. ELDRIDGE.

Action of heat and loss of water on the optical properties of heulandite. P. GAUBERT (Compt. rend., 1928, **187**, 1057—1059; cf. this vol., 16).—If, as the author's experiments indicate, the rise of temperature of heulandite heated in an inert liquid produces a rotation of the plane of the optical axes and increases their divergence, then the gradual loss of a half-molecule of water brings the axes together again until the crystal is uniaxial, and then causes them to open out perpendicular to the original plane. Consequently, below the temperature (109°) at which water is first evolved, the optical properties depend on the water content. Optical anomalies indicate the presence of sectors or banded structures without changing the sense of the phenomena.   J. GRANT.

Influence of solvents on rotation of optically active compounds. XXVI. Optical activity of malic acid in presence of sodium molybdate. T. S. PATTERSON and C. BUCHANAN (J.C.S., 1928, 3006—3019).—The rotation of malic acid in the presence of sodium molybdate has been examined. Solutions were made up containing a fixed amount of the acid with varying amounts of the salt and the rotation was determined for several colours. With increase in the concentration of the salt the rotation thrice becomes zero and shows two minima and a maximum. The rotation of several solutions was examined at different temperatures. It was found that, in general, the temperature–rotation curves are of the same nature as those obtained with other optically active substances in various solvents. The change in rotation with rise of temperature is, as a rule, similar to that obtained by decreased concen-tration of sodium molybdate. Similar experiments were made with two other concentrations of malic acid; with dilute solutions the rotation at the second minimum has a positive value, whilst with the more concentrated solutions the minimum rotation has a negative value. The rotation of the solid derivative obtained from two molecules of malic acid and one molecule of sodium molybdate was also examined for six colours of light at different temperatures.
                    H. INGLESON.

Rotation dispersion and circular dichroism of caryophyllene nitrosite. S. MITCHELL (J.C.S., 1928, 3258—3260).—The rotatory dispersion of caryo-phyllene nitrosite in benzene has been examined and

found to show the Cotton effect. From measure-ments of the absorption spectra, using both right- and left-handed circularly polarised light, it has been shown that this substance exhibits circular dichroism.
                    J. L. BUCHAN.

Quantum theory of molecule formation. H. LESSHEIM (Z. Physik, 1928, **51**, 828—841).—A revised theory is submitted showing closer agreement with chemical notions, in particular with the position of the rare gases in the periodic table.
                    R. A. MORTON.

Molecular structure and chemical linking. F. HUND (Physikal. Z., 1928, **29**, 851—852).—Prelimin-ary. Two-centre systems are considered using as examples CN, LiH, and He_2 term schemes.
                    R. A. MORTON.

Structure of water. S. PENNYCUICK (J. Physical Chem., 1928, **32**, 1681—1696).—Theoretical. The marked activity of the auxiliary valency fields of both hydrogen and oxygen in water provides a simple explanation of many of the unique properties of this substance. The structure of the water molecule is best represented by the tetrahedron with the electrons in pairs at the tetrahedral corners (cf. Huggins, A., 1926, 458). The resulting polarity enables the water molecules to unite with other molecules solely by means of its own negative electron pairs and its positive hydrogen nuclei.

The difference between true association and the quasi-association (van der Waals, Proc. K. Akad. Wetensch. Amsterdam, 1910, **13**, 107) of normal liquids is discussed, and in conformity with the X-ray structure of ice, it is concluded that the associated molecule in liquid water is the molecule $(H_2O)_6$ and that water is a mixture of relatively stable compound molecules of a benzene-ring structure in a normal solvent. The view that water is a mixture of $(H_2O)_3$, $(H_2O)_2$, and H_2O molecules is untenable.

Evidence derived from the effect of pressure on aqueous systems, the maximum density, the latent heat, the dielectric constant, and other properties of water is discussed and is shown to favour ring associ-ation, and the abnormal activity of the auxiliary fields of the oxygen and hydrogen atoms.
   L. S. THEOBALD.

Size of ions and its influence on the properties of salt-like compounds. L. PAULING (Z. Krist., 1928, **67**, 377—404; Chem. Zentr., 1928, ii, 318).—The forces operating between ions are discussed from the point of view of quantum mechanics and a simple approximate expression is given for these forces as a function of the size of ions. The derivation of interionic distances to a first approximation by neglect of deviations from additivity is discussed. The influence of radius relationships on physical properties of the alkali halides, and on the axial ratios of crystals of the rutile type and of anatase, is dis-cussed, together with the question of the relative stabilities of the various crystal structures.
                    A. A. ELDRIDGE.

Constitution of the polythionic acids. J. A. CHRISTIANSEN (Förh. III nord. Kemistmötet, 1928, 177—179).—The existing formulæ for tetra- and penta-thionic acids are criticised. The reactions of these acids are best explained by the assumption

that they contain a six-membered ring, and the formulæ I and II are proposed; The fact that the
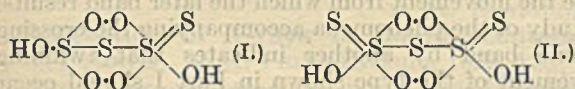
vapour of sulphur trioxide is bimolecular lends support to these views. H. F. HARWOOD.

Constitution of the boron hydrides. F. EPHRAIM (Helv. Chim. Acta, 1928, **11**, 1094—1097).— It is shown that the formation of the boron hydrides may be explained satisfactorily on the octet theory of distribution of the outer electrons.

R. N. KERR.

Effective cross-section of neutral molecules of gases with respect to slow electrons. C. RAMSAUER (Physikal. Z., 1928, **29**, 823—830).—A summary of recent work. R. A. MORTON.

Effective cross-section and molecular structure. E. BRÜCHE (Physikal. Z., 1928, **29**, 831—834).—A review (cf. A., 1927, 4, 181, 492, 1011, 1119; 1928, 453). R. A. MORTON.

Share of "reflexion" in the total effect of the action of slow electrons on gas molecules. R. KOLLATH (Physikal. Z., 1928, **29**, 834—836).—The effective cross-sectional area arises from three factors : (*a*) reflexion without loss of velocity, (*b*) absorption, temporary or permanent, (*c*) velocity loss, with or without deflexion. In an attempt to ascertain the relative importance of these factors it is shown that the first rising portion of the cross-section curves (starting from low velocities) in the argon group and the first maxima in the nitrogen and carbon dioxide groups arise from factor (*a*). With higher velocities factor (*b*) appears. In some cases the curve connecting cross-sectional area with electron velocity in volt$^{\frac{1}{2}}$ shows two maxima; the first is always due to "vertical" reflexion without velocity loss, but no clear evidence is available as to the origin of the second, or as to the rôle of factor (*c*).

R. A. MORTON.

Determination of the wave-length of the $K\alpha$ line of carbon. B. B. WEATHERBY (Physical Rev., 1928, [ii], **32**, 707—711).—A simplified form of vacuum spectrometer with line grating was used, connected directly with the X-ray tube, and based on Compton's theory of a line grating used at grazing incidence with the X-rays striking within the angle of total reflexion. The region investigated lay between the soft X-rays and the extreme ultra-violet. Measurements made for varied angles of incidence and distances from grating to plate gave a mean value of 45·4 Å. for the $K\alpha$ carbon line. N. M. BLIGH.

Total reflexion of X-rays from nickel films of various thicknesses. H. W. EDWARDS (Physical Rev., 1928, [ii], **32**, 712—714).—Measurements were made of the critical angles for nickel sputtered films of various thicknesses. The maximum value agrees with that calculated from the Lorentz dispersion formula. It is concluded that the values decreasing to a minimum found for thinner films are not due to abnormal values of the density of nickel in these films, but that the phenomenon of total X-ray

reflexion requires an electron layer of definite thickness and is not a superficial effect. Evidence was found that the density of silver films is independent of the method of deposition. N. M. BLIGH.

Study of physical purity by X-ray powder spectrograms. II. N. H. KOLKMEIJER (Z. physikal. Chem., 1928, **138**, 311—312; cf. A., 1928, 1078).—Polemical against Levi (A., 1928, 1079). The fact that yellow and red mercuric oxide give the same X-ray spectrogram does not prove that there is only one form. There may be red and yellow oxide in each in different proportions. M. S. BURR.

Are characteristic X-rays polarised ? E. O. WOLLAN (Proc. Nat. Acad. Sci., 1928, **14**, 864—867). —The polarisation of characteristic X-rays has been determined by a method using integrated intensity measurements. It is found that the $K\alpha$ lines of molybdenum are not polarised to a greater extent than 1%. A. J. MEE.

Polarisation of characteristic X-rays. H. MARK and K. WOLF (Z. Physik, 1928, **52**, 1—7).— By means of a new photographic method it has been shown that there is no polarisation of the characteristic K-radiation from copper, within an experimental error of about 1%. A. J. MEE.

Coloration of kunzite and hiddenite by X-rays. P. L. BAYLEY (J. Opt. Soc. Amer., 1928, **17**, 350— 355).—Kunzite, a pale pink variety of spodumene (lithium aluminium silicate), turns bluish-green under the action of X-rays and resembles hiddenite, another variety of spodumene. Spectrophotometric examination of irradiated kunzite and hiddenite from 3000 Å. to 4·5 μ shows that these two green varieties have not the same absorption curve and are not identical.

W. E. DOWNEY.

Structure of the Compton shifted line. J. W. M. DUMOND (Proc. Nat. Acad. Sci., 1928, **14**, 875—878). —Special apparatus is described for investigating the structure of the Compton shifted line. The experimental curves are compared with those calculated from Jauncey's theory. The agreement for scattering by aluminium is good, but the experimental distribution for beryllium is wider than the theoretical. Two faint lines also appear at wave-lengths 768 and 777 X., the shift of which is too great for them to be regarded as Smekal transitions, and the lines do not correspond with the characteristic fluorescent radiation of any known element. The possibility of accounting for the extra breadth of the shifted line by considerations of double scattering is being investigated. A. J. MEE.

K **X-Ray absorption edge of iron.** G. A. LINDSAY and H. R. VOORHEES (Phil. Mag., 1928, [vii], **6**, 910—920).—The multiple structure of the X-ray absorption edge of iron has been examined both for the metal and for compounds. The principal edge moves to shorter wave-lengths with increase of valency. With mechanical mixtures of bi- and tervalent iron the absorption patterns of the two ions are superimposed. In the case of the compound lepidomelane in which both ions occur no such superposition occurs, suggesting that in such compounds the iron ions are all alike. The multiple structure

extends over a wide range, the magnitude of which is explained by the ejection of electrons from the outer orbits together with the K-electron.

A. E. MITCHELL.

Quantum efficiency for the action of X-rays on silver bromide. II. J. EGGERT and W. NODDACK. (Z. Physik, 1928, **51**, 796—804; cf. A., 1927, 841, 1154).—It is shown for two additional types of emulsion that each quantum of absorbed X-radiation sets free about 1000 atoms of silver, all within a single grain. The quantum efficiency in terms of grains rendered developable is about 1, and for the wave-length 0·5 Å. this result is independent of the type of emulsion. With smaller quanta, the number of liberated silver atoms in each grain becomes less, so that with ultra-violet and visible light more quanta will be needed to make the grain developable. With harder X-rays, the primary photoelectron may reach a neighbouring grain and two or more may be rendered developable by each absorbed quantum. The discrepancy between the data of March (A., 1928, 492) and the authors is discussed.   R. A. MORTON.

Mode of formation of Neumann bands. I. **Mechanism of twinning in the body-centred cubic lattice.** II. **Evidence that the bands are twins.** III. **Movement from which the twinning results.** S. W. J. SMITH, A. A. DEE, and J. YOUNG (Proc. Roy. Soc., 1928, **A**, **121**, 477—486, 486—500, 501—514).—I. Artificial or mechanical twinning may be regarded as the result of a movement within a crystal by which the orientation of the atoms, in a band bounded by parallel planes, becomes a mirror image with respect to these planes of that in the unchanged matrix on either side. An examination has been made of the atomic movements which can occur under the influence of a transient shearing stress in a single crystal possessing a body-centred cubic lattice. It is shown that the mirror image relation can result from each of several different atomic movements with respect to the same twin plane.

II. The simplest way of testing whether the twin relationship exists between the orientation in a band and that in the neighbouring matrix is to make a section of the material perpendicular to the {112} plane to which the band is parallel and to compare the pits produced simultaneously on band and matrix by suitable etching. In such case, the etch-pits in the band and those in the matrix, if similarly developed, should be mirror images of one another in planes represented by the traces of the bands. For the meteorites examined, the most suitable etching agent was found to be a dilute solution of copper ammonium chloride. A number of photomicrographs, illustrating the results obtained, are reproduced.

III. Examination of the etching pits alone is not sufficient to fix the precise character of the movement from which the twinning results. For this purpose, the extent and the direction of the movement of the matrix on one side, with respect to that on the other, when a band of measurable width is formed must be determined. Since all the bands are not formed simultaneously, the tracks of some must pass through the matrix across the tracks of others formed earlier. The displacement of the parts of an earlier track

with respect to one another, produced during the formation of a later band, can then be used to determine the movement from which the later band results. A study of the phenomena accompanying the crossing of one band by another indicates that twinning movement of the type shown in Part I should occur most easily.   L. L. BIRCUMSHAW.

Diffraction of cathode rays by calcite. S. NISHIKAWA and S. KIKUCHI (Proc. Imp. Acad. Tokyo, 1928, **4**, 475—477).—An extended account of work already published (A., 1928, 1312).

W. E. DOWNEY.

Diffraction of cathode rays by mica. IV. S. KIKUCHI (Proc. Imp. Acad. Tokyo, 1928, **4**, 471—474; cf. A., 1928, 1174).—Using monochromatic radiation, it is found that the net-like pattern produced by thin mica is due to the diffraction by a two-dimensional lattice, of which the scattering centres are arranged in an equilateral triangle network.

W. E. DOWNEY.

Measurement of absolute intensity of X-rays. M. STEENBECK (Ann. Physik, 1928, [iv], **87**, 811—849).—A method is described for the determination of the absolute number of quanta which pass in unit time through the area of cross-section of a beam of X-rays. The number of quanta absorbed over a given track are counted as ions, the rays being made to pass perpendicular to the lines of force of a homogeneous electric field, and the resulting ions counted by means of a Geiger counter. It is necessary to ascertain the fraction of ions registered by the counter. The ionising power of a monochromatic ray was measured and its intensity obtained in this way. For the formation of ionic doublets the necessary energies for Cu-$K\alpha$ and Cr-$K\alpha$ are practically the same, and are in agreement with other determinations. The possible errors in the method are discussed.

A. J. MEE.

X-Ray studies in the system lead–thallium. F. HALLA and R. STAUFER (Z. Krist., 1928, **67**, 440—454; Chem. Zentr., 1928, ii, 319).—The lattice parameter of pure lead (using sodium chloride for comparison) is $4·924\pm0·010$ Å. The constant for mixed crystals containing 35 at.-% Pb (i.e., at maximum m. p.) is $4·871\pm0·007$ Å. The cubic face-centred unit cell contains four molecules. The m. p. maximum is therefore not due to compound formation.

A. A. ELDRIDGE.

X-Ray studies of the univalent metal perchlorates. W. BÜSSEM and K. HERRMANN (Z. Krist., 1928, **67**, 405—408; Chem. Zentr., 1928, ii, 318).—The lattice constants of rhombic bipyramidal perchlorates are : ammonium : a 9·22, b 5·80, c 7·42 Å.; potassium : a 8·85, b 5·66, c 7·24 Å.; rubidium : a 9·27, b 5·81, c 7·53 Å.; cæsium a 9·82, b 6·00, c 7·79 Å.; tellurium : a 9·42, b 5·88, c 7·50 Å. The unit cell contains four molecules; space-group V_h^{16}.

A. A. ELDRIDGE.

X-Ray studies on the nitrides of iron. G. HÄGG (Nature, 1928, **122**, 962; cf. A., 1928, 605, 1081).—All preparations with maximum nitrogen content give the same photograms which are ascribed to a new phase, ξ, in which the iron atoms form an orthorhombic lattice having a 2·758, b 4·819, c 4·419 Å.

Close relations exist between the ε and ξ phases. The latter is probably the nitride Fe_2N.

A. A. ELDRIDGE.

Diffraction of X-rays in liquids containing heavy atoms. J. A. PRINS (Nature, 1929, **123**, 84). Heavy atoms are introduced into a liquid, and their mutual arrangement is determined by an X-ray spectrographic method. Application to solutions of iodine ions in water, and of carbon tetrachloride and methylene iodide in benzene supported the author's theoretical views, the amount of scattering at small angles being considerable. At higher concentrations of iodine ions, however, the effect was reversed; in explanation, electrostatic repulsion of the iodine ions is suggested. The method has also been applied to the study of long-chain organic acids.

A. A. ELDRIDGE.

Energy levels of the elements chromium to lanthanum in the X-ray region. F. P. MULDER (Arch. Néerland., 1928, **11**, 167—205; cf. Coster and Mulder, A., 1926, 987).—A spectrograph of the Siegbahn type was used, having an analysing crystal of gypsum which oscillated automatically through an angle of 1—2°, this being necessary to eliminate the defects of the crystal. The source of the X-rays was a modified Siegbahn tube with a tungsten anticathode. The substance to be examined was placed in the path of the rays in the form of a screen. The absorption of a few of the substances was measured by special methods which are given. In the L_I, L_{II}, and L_{III} series the wave-lengths of the discontinuities for a number of elements have been measured to within about 2X. From these values, and those found by other workers, the energy levels L_I, L_{II}, L_{III}, M_I, M_{II}, M_{III}, M_{IV}, M_V, N_I, N_{II}, N_{III}, N_{IV}, N_V, O_I, and $O_{II, III}$ have been calculated for the elements from chromium to lanthanum. The probable sources of error are discussed and their magnitudes indicated. Curves are given showing the relation of $\sqrt{\nu/R}$ to the atomic number for the various Röntgen terms and explanations are given for the breaks in these curves. It is found that the X-ray method gives lower values for the energy levels than does the optical method, for in the latter case the atoms are free, whilst in the former they are combined in a crystal.

J. L. BUCHAN.

Lattice dimensions of spinel ($MgAl_2O_4$). E. POSNJAK (Amer. J. Sci., 1928, [v], **16**, 528—530).—Examination of a sample of artificially prepared spinel by the powder method showed the length of the edge of the unit cube containing eight $MgAl_2O_4$ molecules to be 8.03 ± 0.01 Å., whence $d_{calc.} = 3.628$.

R. CUTHILL.

Crystal structure of phosphides of bivalent and tervalent metals. L. PASSERINI (Gazzetta, 1928, **58**, 655—664).—X-Ray examination of the phosphides of zinc, cadmium, and magnesium shows that these compounds crystallise in the cubic system with a non-ionic structure of the zinc arsenide type (cf. A., 1928, 1313), the elementary cell containing two molecules of M_3P_2. For the three phosphides in the above order the values of a are 5·68, 6·06, and 5·92 Å., and of $d_{calc.}$ 4·678, 5·956, and 2·162, respectively. The distances between the metal and phosphorus atoms are Zn—P 2·46, Cd—P 2·62, and Mg—P 2·56 Å.,

from which the values 1·13, 1·13, and 0·94 Å., respectively, are calculated for the radius of the neutral phosphorus atom. Aluminium phosphide has a cubic structure of the zinc-blende type with a unit cell containing four molecules of AlP; $a = 5.42$ Å. and $d_{calc.} = 2.424$. The distance Al—P is 2·34 Å., which gives a value of 0·91 Å. for the radius of the phosphorus atom.

O. J. WALKER.

Alums of organic bases. I. Alums of methylamine. A. QUILICO (Gazzetta, 1928, **58**, 682—690). —By means of the Laue and powder methods it is shown that the structure of methylammonium alum, $NH_3MeAl(SO_4)_2,12H_2O$, is similar to that of the unsubstituted ammonium alum. The replacement of the hydrogen atom by a methyl group merely causes a slight increase in the length of the unit cell, which in both cases contains four molecules of $M'M'''(SO_4)_2,12H_2O$, from 12·16 to 12·44 Å. The corresponding values of $d_{calc.}$ are 1·674 and 1·614. From the increase in the lattice constant the molecular volume of the methyl radical is calculated to be 18·67 cm.^{3}

O. J. WALKER.

Crystal structure of praseodymium dioxide. P. SCHERRER and J. PALACIOS (Anal. Fís. Quím., 1928, **26**, 309—314).—An X-ray examination has been made, by the Debye–Scherrer method, of grey and black specimens of praseodymium dioxide. The photographs in each case were identical. The structure is of the fluorite type, the side of the unit cube being 5·39 Å. The unit cell contains 4 molecules, and $d_{calc.} = 7.32$ (cf. Goldschmidt, Z. Krist., 1928, **67**, Strukturber., 198).

R. K. CALLOW.

Crystal structure of Cu_9Al_4. A. J. BRADLEY (Phil. Mag., 1928, [vii], **6**, 878—888).—δ-Copperaluminium containing 16—19% Al has a cubic structure with 52 atoms per unit cell comprising 36 copper atoms and 16 aluminium atoms, corresponding with the formula Cu_9Al_4. The space-group is T_d^3 with eight sets of structurally equivalent atoms. The structure is essentially of the cæsium chloride type, each lattice point being replaced by a cluster of 26 atoms with tetrahedral symmetry. The atomic co-ordinates are almost the same as those in Cu_5Zn_8 (Bradley and Thewlis, A., 1926, 1087).

A. E. MITCHELL.

Crystal structure of zircon. L. VEGARD (Z. Krist., 1928, **67**, 482—484; Chem. Zentr., 1928, ii, 318).—Polemical (cf. Wyckoff and Hendricks, A., 1928, 821).

A. A. ELDRIDGE.

Isomorphism between hexachloro-salts of pyridine and cerium, thorium, tin, lead, and quadrivalent titanium. V. CAGLIOTI (Atti II Cong. Naz. Chim. pura Appl. 1926, 1182—1193; Chem. Zentr., 1928, ii, 519—520).

Crystallographic investigation of some rare-earth nitrates. E. E. FLINT (Trans. Inst. Econ. Min. Met. Moscow, 1928, No. 34, 59—72).—A study of the salts $3Mg(NO_3)_2,2X(NO_3)_3,24H_2O$, where X = Ce, Nd, Pr, or La. CHEMICAL ABSTRACTS.

Crystal structure of n-monopropylammonium halides. S. B. HENDRICKS (Z. Krist., 1928, **67**, 465—471; Chem. Zentr., 1928, ii, 321).—The lengths of the edges of the tetragonal unit cell (containing

one molecule) are : *n*-propylammonium chloride *a* 4·48, *c* 7·40; bromide *a* 4·57, *c* 7·36; iodide *a* 4·85, *c* 7·33 Å. A. A. ELDRIDGE.

Crystal structure of triethylammonium halides. S. B. HENDRICKS (Z. Krist., 1928, **67**, 472—481; Chem. Zentr., 1928, ii, 320).—The dimensions of the unit cell of the dihexagonal-pyramidal crystals are : triethylammonium chloride *a* 8·38, *c* 7·08; bromide *a* 8·56, *c* 7·49; iodide *a* 8·78, *c* 7·74 Å. The cell contains two molecules. The space-group is C_6^4. A. A. ELDRIDGE.

Crystallographic data for " cardiazol," pentamethyleneaminotetrazole, and " dilaudid." H. STEINMETZ (Z. Krist., 1928, **67**, 434—439; Chem. Zentr., 1928, ii, 321).—" Cardiazol " (pentamethylenetetrazole), monoclinic prismatic, has $a : b : c=$ 1·8171 : 1 : 1·5690, β 120° 15′; *n* 1·617, from toluene, benzene, or ether. Pentamethyleneaminotetrazole, monoclinic prismatic, has $a : b : c=1\cdot6455 : 1 : 2\cdot4725$, β 95° 23′; *n* 1·592; hydrate (from water) monoclinic prismatic, $a : b : c=0\cdot5368 : 1 : 0\cdot5943$, β 95° 52′. " Dilaudid " (Knoll A.-G.), $C_{17}H_{19}O_3$, rhombic, has $a : b : c=0\cdot75(16) : 1 : 0\cdot49(12)$. A. A. ELDRIDGE.

Crystal structure of bixbyite and artificial manganese sesquioxide. W. ZACHARIASEN (Z. Krist., 1928, **67**, 455—464; Chem. Zentr., 1928, ii, 318—319).—Bixbyite, hitherto supposed to be $Fe^{III}Mn^{IV}O_3$, and to be isomorphous with perowskite, has a regular hemihedral symmetry; the body-centred unit cube has *a* 9·35±0·02 Å. and contains sixteen molecules of FeMnO₃. It cannot be isomorphous with perowskite, and no space-group corresponding with the above formula is possible; the difficulty vanishes if the formula $(Fe,Mn)_2O_3$, space-group T^5, is assumed; moreover, relationship to sesquioxides is apparent from the Laue diagram. Artificial manganese sesquioxide has the same structure; *a* 9·41±0·01 Å. Metal–oxygen distances are 2·08 and 2·10 Å., respectively. The dependence of the structure type (corundum-, C-, A-, and As₂O₃-types) in which sesquioxides crystallise to the ion radii ratio $R_M/R_O=r$ is indicated by : corundum- $0\cdot43<r<0\cdot53$, C- $0\cdot53< r<0\cdot80$, A- $0\cdot80<r< ?$. A. A. ELDRIDGE.

Structural relation between beryl and cordierite. B. GOSSNER (Zentr. Min. Geol., 1928, **A**, 204—207; Chem. Zentr., 1928, ii, 531).—Cordierite has *a* 9·78, *b* 17·1, *c* 9·33Å., with 4 mols. of $Mg_2Si_5O_{12},2Al_2O_3$ in the unit cell. The structure is compared with that of beryl. A. A. ELDRIDGE.

Constitution of nitrated cellulose. F. D. MILES and J. CRAIK (Nature, 1929, **123**, 82).—X-Ray studies on nitrated ramie afford little support for Herzog and Náray-Szabó's view (A., 1928, 48; Náray-Szabó and Susich, *ibid.*, 818) that " nitrocelluloses " are mixtures of cellulose trinitrate and cellulose. The diagram of nitrated ramie containing less than 7·5% N shows the same spacings as that of its denitrated product, but different relative intensities, and is much weaker. The spacings remain constant with increasing degree of nitration. Diffractions characteristic of the trinitrate do not appear. With 7·5—10·5% N the nitrated material partly loses its fibre structure, but the denitrated product is of the same type as

previously. The structure of the denitration product from more highly nitrated ramie is indistinguishable from that of pure cellulose, and different from that of the other denitration products. A. A. ELDRIDGE.

Crystallography of aliphatic dicarboxylic acids. W. A. CASPARI (J.C.S., 1928, 3235—3141).—The crystal structures of adipic, pimelic, suberic, azelaic, sebacic, brassylic, and hexadecanedicarboxylic acids have been determined, the lengths of the axes *a*, *b*, and *c* of the unit cell and the angle β being recorded. In each case *a* and *b* are approximately the same, whilst *c* is proportional to the number of carbon atoms, there being two series, one for those acids with an odd number of carbon atoms and the other for those with an even number. It is concluded that all these long-chain aliphatic compounds are built up of two parallel chains of carbon atoms. Suggested models for these molecules are given. J. L. BUCHAN.

Hall effect and magnetic induction in a bar of electrolytic iron. E. M. PUGH (Physical Rev., 1928, [ii], **32**, 824—828).—The Hall effect was measured in a bar of electrolytic iron in contrast to the usual method of measuring it in thin sheets, and the magnetic induction was also measured simultaneously. Plotting the Hall *E.M.F.* and the permeability against the magnetic induction, the linear relation is found in each case to break down at maximum permeability, whence it is concluded that the condition of the iron which causes the break from a linear relation in the Hall effect is the same as that which causes maximum permeability. The Hall coefficient is of the same order of magnitude in the bar as in a thin sheet if the value of B instead of H is used in the calculation. N. M. BLIGH.

Magnetic properties of complex compounds and their electronic constitution. P. RÂY and H. BHAR (J. Indian Chem. Soc., 1928, **5**, 497—511).—The magnetic susceptibilities of 47 complex compounds, mostly containing iron, nickel, or cobalt, have been measured. The magneton values deduced from these measurements are discussed from the points of view of Cabrera, Welo and Baudisch, and of Bose. No one of the theories of these workers appears to be uniformly applicable. F. G. TRYHORN.

Monel metal. I. Electrical and thermal properties and magnetostriction. A. SCHULZE (Z. Metallk., 1928, **20**, 403—406).—The electrical resistance, thermoelectric power against copper, coefficient of thermal expansion, and magnetostriction of several samples of monel metal after different mechanical treatments have been determined. Above the Curie point (100°) the temperature coefficient of electrical resistance falls to about one fifth its value at 0—100°. Like nickel, monel metal undergoes contraction in a magnetic field, but the magnetostriction effect is much less marked, maximum contraction occurring in a field of 20—30 gauss. Work-hardened monel metal, however, does not undergo magnetostriction. A. R. POWELL.

Monel metal. II. Magnetisation curves of monel metal. A. KUSSMANN (Z. Metallk., 1928, **20**,

406—407).—The intensity of magnetisation of monel metal in a constant magnetic field is about twice as great for the alloy slowly cooled from 600° as it is for the alloy quenched from 600°. For pure nickel–copper alloys of the same composition, however, the same results are obtained in both cases. It appears, therefore, that some of the minor constituents of monel metal have a greater solid solubility at 600° than at the ordinary temperature. A. R. POWELL.

Rôle of conductivity electrons in ferromagnetism. J. DORFMAN and R. JAANUS (Naturwiss., 1928, **16**, 1026).—The question whether the elementary magnet consists of the electron bound to the positive metallic ion, or the "free" conductivity electron, has been investigated. The specific heat of the latter in metallic nickel undergoes a sudden change at the Curie point, identical in sign and magnitude (per electron) with the change in specific heat of metallic nickel (per atom) measured calorimetrically. The conducting electron in metallic nickel therefore acts as the elementary magnet. R. A. MORTON.

Electromotive behaviour of single metal crystals. P. A. ANDERSON (Nature, 1929, **123**, 49).—The primary cleavage face (basal pinacoid) of a zinc crystal yields potentials constant to 0·0001 volt, and reproducible to less than 0·001 volt. The potential is identical with that of the electrolytically deposited crystal conglomerate within the range of variation of duplicate conglomerate electrodes. Measurements on artificially prepared surfaces indicate a qualitatively regular decrease of potential with increase of inclination to the primary cleavage plane. A. A. ELDRIDGE.

Magnetic properties in relation to chemical constitution. T. M. LOWRY and F. L. GILBERT (Nature, 1929, **123**, 85).—A magnetic study of pervalent salts (PCl_5, $SbCl_5$, $SbMe_3Cl_2$, $SbMe_3Br_2$, $SbMe_3I_2$, α- and β-$TeMe_2Cl_2$, $TeMe_2Br_2$, and $TeEt_2I_2$, α-$TeMe_2I_2$, and α-$TeMe_2I_4$) and analogous compounds (PCl_3, $POCl_3$, $AlCl_3$, TeI_3, BiI_3, CsI_3) and co-ordination compounds, including the lithium, beryllium, aluminium, cobalt, nickel, and ferric derivatives of benzoylcamphor shows that all except those containing a metal of the transition series are diamagnetic. Hence all the electrons in these compounds to which single-electron linkings have been assigned are magnetically paired. Mercurous chloride, mercuric chloride, and cuprous iodide are diamagnetic, whilst cupric chloride is paramagnetic. The mercurous salts contain bivalent mercury, whilst the copper in cuprous salts is univalent; cupric sulphide may, in reality, be cuprous disulphide. A. A. ELDRIDGE.

Crystal structure and ferromagnetism. O. VON AUWERS (Physikal. Z., 1928, **29**, 921—927).

Electrical conductivity [of metals]. W. J. DE HAAS (J. Phys. Radium, 1928, [vi], **9**, 265—277).—A short critical discussion is given of conductivity theories, with evidence against the theory of free electrons. Experiments are described for the two last-named of the super-conductors thallium, indium, lead, mercury, and tin recognised by Onnes, showing that the electrical resistances exhibit a hysteresis effect in a magnetic field. The effect was investigated for various temperatures. Sharp changes in the resistances of these metals were observed, and are explained as being connected with the formation of metallic crystals. For intense magnetic fields the resistance curve is found to be that of normal metals. The super-conductivity state may be stable or unstable. N. M. BLIGH.

Thermal and electrical conductivity of a copper crystal at various temperatures. W. G. KANNALUIK and T. H. LABY (Proc. Roy. Soc., 1928, A, **121**, 640—653).—Whilst the thermal method for the determination of the thermal conductivity of metals is the simplest, the electrical method is considered to be better adapted for very low temperatures, *i.e.*, near 20° Abs. The thermal conductivity of a copper crystal has been determined by the thermal method over the temperature range 19° to −183°. The heat losses have been considerably diminished by the use of a high vacuum, and eliminated at the ordinary temperature by a special method. The thermal conductivity λ is found to be 0·989 g.-cal. cm. sec. deg. at 19·4°, 1·054 at −73·7°, and 1·131 at −174·8°. The value of λ at 19·4° is about 4% higher than that of polycrystal copper (in agreement with Schott, Ber. Deut. physikal. Ges., 1916, **18**, 27), whilst the values obtained at lower temperatures are considerably less than Schott's values. The electrical conductivity, κ, of the single crystal is found to be the same as that of ordinary polycrystal copper. The values obtained for the Wiedemann–Franz constant, $\lambda/(\kappa T)$, at 90·2° and 273·2° Abs. are 1·69 and 2·42 × 10⁻⁸ watt ohm deg.⁻², respectively. L. L. BIRCUMSHAW.

Resistance of alloys. L. NORDHEIM (Naturwiss., 1928, **16**, 1042—1043).—Matthiessen's rule regarding the resistance of alloys is considered from the point of view of the modern theory of metallic conduction. Resistance is due to the distortion of the exact periodicity of the metal lattice. In alloys, even in the absence of irregularity due to heat, there are irregularities due to the different powers of single lattice points for scattering the electrons. For very low temperatures the resistance plotted against the concentration gives a hyperbolic curve. For small concentrations the relationship is linear. The results obtained by calculation were tested practically with silver–gold alloys and the agreement is good. A. J. MEE.

Allotropic modifications of phosphorus. A. SMITS (Compt. rend., 1928, **187**, 980—982).—The results of Nicolaïev (A., 1928, 827) are brought into line with the author's theory of allotropy and confirm his conclusion that phosphorus consists of three types of molecules, α_1, α_2, and β, white phosphorus being a mixture of the two α types, the transition point of which is at the ordinary temperature, whilst the α → β transformation occurs appreciably only at high temperatures. J. GRANT.

Heat of fusion of *s*-phenylallylthiocarbamide. V. P. SCHISCHOKIN (Ann. Inst. Anal. Phys. Chem., 1928, **4**, 183—194).—The specific heat of phenylallylthiocarbamide increases with rise of temperature from 0·307 at 50° to 0·423 at 99·8°, and the heat of fusion is 6600±100 g.-cal./mol. R. TRUSZKOWSKI.

K

Relationship between surface tension and heat of vaporisation. H. SIRK (Z. Physik, 1928, **52**, 21—26).—The relationship existing between surface tension and heat of vaporisation is calculated on the basis of Debye's dipole theory. The constant obtained by dividing the molecular heat of vaporisation by the product of the total surface energy per sq. cm. and the molecular surface is $2 \cdot 71 \times 10^8$, a value in approximate agreement with the experimental number obtained by Walden. The deviation of the experimental from the calculated figure arises in the fact that approximations are made in the theory, and that the surface layer is not necessarily unimolecular.

A. J. MEE.

Determination of isotherms at high pressures. A. MICHELS and R. O. GIBSON (Ann. Physik, 1928, [iv], **87**, 850—876).—A new apparatus for determining isotherms at high pressures is fully described. In particular, the isotherms of neon between 0° and 100° at 20—500 atm. are determined. The accuracy is estimated to be not greater than 1 in 2000.

A. J. MEE.

Application of the rule of Dulong and Petit to molecules. D. H. ANDREWS and E. HAWORTH (J. Amer. Chem. Soc., 1928, **50**, 2998—3002).—The heat capacities between 100° and 336° Abs. are recorded for mono-, di-, tetra-, and hexa-chlorobenzene and for mono- and di-bromobenzene. The heat capacity per halogen atom in the compounds is relatively independent of the number of halogen atoms attached to the ring and approaches the value of 6 g.-cal./1° at the ordinary temperature, suggesting the applicability of Dulong and Petit's rule. Theoretical considerations based on the observed frequencies of the compounds in the infra-red lend support to this suggestion. The carbon–halogen linking seems to have the same mechanical strength in the above compounds. S. K. TWEEDY.

The Majorana thermal effect. A. L. T. MOESVELD (Chem. Weekblad, 1928, **25**, 702—703).—The fact that certain metals which have been fused or strongly heated, and then quenched, may remain for long periods at temperatures slightly higher than those of the surroundings is attributed to the liberation of energy accompanying slow transition from a metastable to a stable state. S. I. LEVY.

Determination of the pressure and density of moist, saturated ammonium bromide vapour. A. SMITS and R. PURCELL (J.C.S., 1928, 2936—2944). —Using the densi-tensimeter (cf. A., 1928, 1209) the vapour pressures and vapour densities of moist ammonium bromide were determined. Log p was found to be a linear function of $1/T$, hence the latent heat of evaporation between 300° and 400° is independent of temperature. Total dissociation of the salt was observed in this range of temperature. This heat calculated from the experimental data is 44,000 g.-cal. The vapour-pressure equation is $\log_e p = -10980/T + 20 \cdot 8$. The densi-tensimeter measurements were checked by finding the pressure of the saturated and unsaturated vapour of a weighed quantity of salt in a known volume. The straight lines formed by plotting $\log p$ against $1/T$ did not intersect but merged into one another, indicating perceptible adsorption of ammonium bromide on the walls of the vessel. The work of Smith and his co-workers (A., 1914, ii, 628; 1915, ii, 86) is critically examined and possible sources of inaccuracy are pointed out. H. INGLESON.

Determination of the pressure and density of moist, saturated ammonium chloride vapour. A. SMITS and W. DE LANGE (J.C.S., 1928, 2944— 2952; cf. preceding abstract).—The heat of vaporisation of ammonium chloride within the range 254— 353° is not a temperature function and the density determinations showed that dissociation of the saturated vapour is practically complete over the same range. The results of Smith and his collaborators indicating some 60% dissociation are incorrect. The results of Braune and Knoke (A., 1928, 829) agree with those of the authors. The vapour-pressure equation is $2 \cdot 303 \log_{10} p = -9903/T + 20 \cdot 5$ and the heat of vaporisation is 39,600 g.-cal., giving a sublimation temperature of 339·3°.

Unlike the bromide, ammonium chloride is not appreciably adsorbed on the quartz and on the glass walls of the apparatus. H. INGLESON.

Velocity of sound in air, nitrogen, and oxygen, with special reference to the temperature coefficients of the molecular heats. W. G. SHILLING and J. R. PARTINGTON (Phil. Mag., 1928, [vii], **6**, 920—939).—The velocity of sound in air, nitrogen, and oxygen has been determined by the method previously described (ibid., 1927, [vii], **3**, 273) up to 1000°. In the case of air the temperature range has been extended to 1300°. The molecular heats of the gases over the temperature range have been calculated and are tabulated. A criticism by Cornish and Eastman (A., 1928, 468) of the method of determination of the tube correction is answered satisfactorily. A. E. MITCHELL.

Vapour pressures in small capillaries. I. Water vapour. II. [Toluene.] J. L. SHERESHEFSKY (J. Amer. Chem. Soc., 1928, **50**, 2966— 2980, 2980—2985).—I. The vapour pressure of water in glass or quartz capillaries was measured by exposing capillaries containing water to the vapour of dilute solutions of known vapour pressure and measuring the rate of condensation or evaporation of water in the capillary. The pressure at which the rate of evaporation or condensation is zero, and is equal to the vapour pressure of the water in the capillary, is then obtained graphically. The lowering of vapour pressure of water is much larger than that calculated by Kelvin's equation; the large value is probably to be attributed to an increase in the surface tension of the liquid in the capillary. The abnormally great lowering observed in glass capillaries is due to the solubility of the glass.

II. In similar experiments with toluene, results are obtained which are not in agreement with the classical theory; this theory is believed to be incorrect. S. K. TWEEDY.

Vapour density of formic acid. H. C. RAMSPERGER and C. W. PORTER (J. Amer. Chem. Soc., 1928, **50**, 3036—3038).—The recent measurements of Coolidge (A., 1928, 1084) are in agreement with the

authors' results (A., 1926, 659), but not with the figures of earlier investigators, whose measurements may have been vitiated by traces of impurities.

S. K. TWEEDY.

Properties of substances and mixtures at 0° Abs. connected with change of state. R. D. KLEEMAN (J. Physical Chem., 1928, 32, 1841—1855; cf. A., 1927, 1142).—Mathematical. At 0° Abs., the internal heat of evaporation is zero, and the three possible physical interpretations of this result are discussed. The form of the equation of state of the vapour of a substance at or near 0° Abs. is investigated and it is deduced that the change in molecular motion of a gas with rise in temperature is zero at this point. The bearing of this result on specific heat is then considered. The properties of the heat and work of mixing substances in the gaseous state, of the change in free energy, and the heat of formation of gaseous substances at 0° Abs. are developed together with those of the internal specific heat of a vapour in contact with the condensed state. Other theorems are developed. L. S. THEOBALD.

Determination of reaction affinity in systems of solid salts. J. N. BRÖNSTED and W. T. RICHARDS (J. Amer. Chem. Soc., 1928, 50, 3028—3035).—A thermodynamic method is described for calculating the free energy change of reactions between solid salts, from vapour-pressure measurements on solutions of individual components of the system saturated with respect to one or more of the other components, or to allied substances. From such measurements, carried out in a special tensimeter, the vapour pressure of the reaction $CuCl_2,2H_2O(s)+2NH_4Cl(s)=CuCl_2,2NH_4Cl,2H_2O(s)$ is found to be 3560 g.-cal.

S. K. TWEEDY.

Viscosity constants and surface layers. J. TRAUBE and S. H. WHANG (Z. physikal. Chem., 1928, 138, 102—122).—The effect of numerous substances of varying chemical character on the viscosity of water has been determined by measuring the rate of flow of water through a capillary tube (inclined at differing angles to the horizontal) of which the walls were coated with a film of the substance under investigation. Oleic acid and, in general, polar substances, as well as capillary-active water-soluble compounds, such as amyl alcohol, octyl alcohol, and amyl acetate, increase greatly the rate of flow of water. The viscosity constant is uninfluenced by films of non-polar substances such as paraffin, benzene, and carbon tetrachloride. Films of solid polar substances such as stearic acid, lac, rubber, and benzene derivatives act similarly to those of liquid polar compounds in lowering the viscosity constant of water. The theoretical, biological, and technical aspects of the phenomenon are discussed.

F. G. TRYHORN.

Fluidity of mercury. E. C. BINGHAM and T. R. THOMPSON (J. Amer. Chem. Soc., 1928, 50, 2878—2883).—The viscosity of mercury measured in a copper capillary is abnormally high (Tammann and Hinnüber, A., 1927, 304), particularly when the copper tube is amalgamated, and decreases with increasing time. This is due, not to a " slipping " effect, but to dissolution of copper in the mercury

and subsequent recrystallisation on the walls of the capillary, the effective diameter, and therefore the " constant," of the capillary being progressively changed as a consequence. Values are recorded for the viscosity of mercury over the temperature range 0—100°, measured in glass tubes.

S. K. TWEEDY.

Calculation of intermolecular forces of organic compounds. M. DUNKEL (Z. physikal. Chem., 1928, 138, 42—54).—Reasons are advanced for considering the heat of sublimation of a compound at 0° Abs. to be an additive function of its constitution, and to be a measure of the molecular cohesive forces. As an approximation, an examination has been made of the values of the molar heats of evaporation (λ) of numerous substances between 0° and 100°, and it has been shown that these exhibit additive relationships within fairly narrow limits of accuracy. The average increment in the normal paraffin and normal monohydric alcohol series is 980 g.-cal. per CH_2 group. The introduction of an *iso*-group in these compounds reduces λ by 460 g.-cal. The numerical alteration in λ has been calculated for a number of atomic groupings and substituent groups; values of λ calculated from these factors are in satisfactory agreement with experimental data.

F. G. TRYHORN.

Diffusion of aspherical particles. R. GANS (Ann. Physik, 1928, [iv], 87, 935—947).—Mathematical. Equations for the diffusion of oblate and prolate particles are worked out. A. J. MEE.

Metallic diffusion. A. E. VAN ARKEL (Metall-Wirt., 1928, 7, 656—657; Chem. Zentr., 1928, ii, 334).—Determinations of the change in electrical conductivity of a copper wire coated with nickel, and of a nickel wire coated with copper, kept at 800°, gave a diffusion constant of 5×10^{-11}.

A. A. ELDRIDGE.

Determination of concentration gradients by means of curved light rays. A new method of observation. O. LAMM (Z. physikal. Chem., 1928, 138, 313—331).—The curvature of the path of a beam of light as it passes through a medium of continuously changing refractive index can be made the basis of a photographic method of determining concentration gradients. The deformation of the image of a scale as seen through the medium of varying concentration can be determined by measurements on the photograph. The theory of the method is discussed and the method has been tested experimentally by a determination of the diffusion coefficient of sucrose in water at 20°. The value found, 0·399, is in good agreement with the results of other investigators. M. S. BURR.

Suitable vapour–gas mixtures for experiments with Wilson's cloud method. L. MEITNER (Z. physikal. Chem., 1928, 139, 717—721).—An equation is deduced showing that the factor which determines the expansion necessary for cloud formation is γ, the ratio of the specific heats of the vapour-gas mixture. This ratio is determined by $γ_1$ and $γ_2$, the respective ratios for the gas and the vapour. If $γ_1$ and $γ_2$ be equal, the expansion ratio is independent of pressure; this condition is nearly realised in a water

vapour–carbon dioxide mixture. With water vapour, gases with high values of γ_1 such as the inert gases require the lowest expansion ratios. Where water vapour is not suitable, the use of alcohol vapour is suggested. R. N. KERR.

Viscosity of binary liquid systems. N. N. EFREMOV (Ann. Inst. Anal. Phys. Chem., 1928, **4**, 118—159).—For mixtures of allyl alcohol and chloral the viscosity curves exhibit a maximum when equimolecular quantities of the constituents are present; this is attributed to the formation of a compound. A corresponding maximum is also shown by the temperature coefficient of the viscosity. The density increases continuously with the chloral content. The vapour pressure passes through a maximum at 85—95 mol.-% of chloral. The viscosity isotherms for the system nitrobenzene–isobutyl alcohol are smooth curves with a minimum which is progressively displaced with rise in temperature towards the axis of the more viscous constituent, isobutyl alcohol. The density curves are very nearly straight lines. The curves representing the influence of temperature on the viscosity are also continuous curves, the shape of which, however, depends on the temperature and on the content of isobutyl alcohol, which has a much higher coefficient than nitrobenzene.
R. TRUSZKOWSKI.

Molecular association. I. Connexion between the vapour pressures of binary liquid mixtures and the polarity of the molecules forming them. J. ERRERA (Z. physikal. Chem., 1928, **138**, 332—344).—An extended account of work already published (A., 1928, 1316).

Molecular association. Relations between the viscosity of binary liquid mixtures and the polarity of the molecules of the constituents. J. ERRERA (Compt. rend., 1928, **187**, 1278—1280; cf. A., 1928, 1316).—When the molecules of the two components of a binary liquid mixture are non-polar or are of opposite polarity, the viscosity–concentration curves for a particular temperature are always concave if they are not straight lines. When the curve is convex the two components are both dipolar. Evidence for the validity of these rules is quoted and certain anomalies are discussed. J. GRANT.

Constant-boiling mixture of hydrogen fluoride and water. C. W. MUEHLBERGER (J. Physical Chem., 1928, **32**, 1888—1889).—The constant-boiling mixture, d^{20} 1·138, b. p. 110·8°/732 mm., contains $38·18 \pm 0·10\%$ of hydrogen fluoride at 735 mm. pressure. Deussen's value for the concentration of hydrogen fluoride in the constant-boiling mixture (A., 1906, ii, 531) is too high. L. S. THEOBALD.

Equilibria of certain binary systems containing 2 : 4 : 6-trinitro-m-xylene. N. N. EFREMOV and A. M. TICHOMIROVA (Ann. Inst. Anal. Phys. Chem., 1928, **4**, 65—91).—Fusion diagrams are given for the systems: 2 : 4 : 6-trinitro-m-xylene–naphthalene, –acenaphthene, –anthracene, –phenanthrene, –fluorene, –2 : 4 : 6-trinitrocresol, –m-dinitrobenzene, –2 : 4 : 6-trinitrotoluene, –2 : 4 : 6-trinitroresorcinol, –picric acid, –picryl chloride, –tetryl, –1 : 3 : 5-trinitrobenzene. 2 : 4 : 6-Trinitro-m-xylene differs from other trinitro-compounds in not forming definite compounds with hydrocarbons. None of the substances studied depresses the m. p. of trinitro-m-xylene to any great extent unless added in comparatively large amount. Solid solutions are formed only in the cases of trinitrobenzene and trinitrotoluene. The properties of the above mixtures are advantageous for the filling of moulds with the fused mixtures, in spite of the high viscosity and lack of mobility of the latter. R. TRUSZKOWSKI.

One of Kurnakov's problems. N. V. LIPIN (Ann. Inst. Anal. Phys. Chem., 1928, **4**, 39—47).—Mathematical. A general expression is derived for the fusion curves of binary mixtures, in the presence or absence of dissociation. R. TRUSZKOWSKI.

Representation of binary fusion curves by a general expression. N. V. LIPIN (Ann. Inst. Anal. Phys. Chem., 1928, **4**, 48—58; cf. preceding abstract).—The expression derived in the preceding paper is given in a simplified form. R. TRUSZKOWSKI.

Fusion curves in a special co-ordinate system. N. V. LIPIN (Ann. Inst. Anal. Phys. Chem., 1928, **4**, 59—64; cf. preceding abstracts).—By using a modified system of co-ordinates the expressions derived in the preceding papers are obtained in a simpler form. R. TRUSZKOWSKI.

Electrical conductivity of binary liquid systems containing amines [or pyridine] and allylthiocarbimide. N. VOSKRESENSKAJA (Ann. Inst. Anal. Phys. Chem., 1928, **4**, 160—182).—The electrical conductivity of the systems allylthiocarbimide–dimethylaniline, –diethylaniline, –pyridine, –methylaniline, and –ethylaniline changes for some time after a given mixture is prepared, but finally attains a constant value. The first three systems, in which compound formation does not occur, show a maximum conductivity at a particular concentration. In the case of the secondary amines, which combine with allylthiocarbimide, two maxima are to be found on the conductivity curves, and a minimum which corresponds with equimolecular proportions of the components. R. TRUSZKOWSKI.

Thermodynamic potential curves of fused mixtures in which compound formation occurs. A. B. MLODZIEJOVSKI (Ann. Inst. Anal. Phys. Chem., 1928, **4**, 247—281; cf. A., 1926, 25).—Theoretical. A number of types of curves of the ξ function are discussed, the geometrical consideration of which leads to the conclusion that if a binary compound does not dissociate into its components in the liquid phase, it must be considered as an independent component of the system. R. TRUSZKOWSKI.

Solubility of carbon dioxide in water. K. BUCH (Förh. III nord. Kemistmötet, 1928, 184—192).—The absorption coefficient of carbon dioxide has been determined by two methods. In the first series of experiments carbon dioxide and air were shaken for 15 min. with water containing a few drops of hydrochloric acid, and the resulting aqueous solution and residual gas analysed. The quantities of carbon dioxide used were chosen so that its partial pressure ranged from 8×10^{-4} to $0·67 \times 10^{-4}$ atm., and the corrected mean value of the coefficient from a

number of experiments at 20·8° is 0·83, or 0·85 if the three determinations where the concentration was lowest be omitted. In the second series, carbon dioxide at atmospheric pressure was passed through distilled water for $\frac{1}{2}$ hr. at 19·8°, followed by shaking of the water with the gas for 15 min., and analysis of residual gas and solution as in the previous method. The mean value thus obtained for the absorption coefficient is 0·856. The results agree fairly well with those previously obtained by Bohr, and the higher figures obtained by Hantzsch and Vagt are regarded as incorrect. H. F. HARWOOD.

Solubility of sodium benzenesulphonate in water and in solutions of sodium sulphate. F. H. RHODES and A. W. LEWIS (Ind. Eng. Chem., 1928, **20**, 1366—1367).—Measurements of the solubility in water and in solutions of sodium sulphate containing 5, 10, and 15% Na_2SO_4 were made between 0° and 105°. At 0° the solubility of the sulphonate in water is 26·8 g./100 g. of solution, rising to 58·5 g. at 105°. The solubilities at 50° in pure water, and in 5, 10, and 15% Na_2SO_4 solutions are, respectively, 41·9, 38·6, 34·4, and 25·8 g. At temperatures below 66·8° the stable solid phase in contact with aqueous solutions is the dihydrate $C_6H_5 \cdot SO_3Na, 2H_2O$, whilst above this temperature the anhydrous salt is the stable form. H. INGLESON.

Solubility of mercuric bromide in ethyl and methyl alcohols. K. L. MALHOTRA (J. Indian Chem. Soc., 1928, **5**, 545—547).—The solubility of mercuric bromide has been measured in 99·73% and 87·73% ethyl alcohol, and in 99·78% methyl alcohol at temperatures between 0° and 80°. Needle-shaped crystals of an additive compound, $HgBr_2, MeOH$, are slowly deposited from a saturated solution of mercuric bromide in methyl alcohol.
F. G. TRYHORN.

Solubility. XI. Solubilities of liquid stannic iodide in several liquid paraffins. (MISS) M. E. DICE and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1928, **50**, 3023—3027).—The critical solution temperatures of stannic iodide, and the solubility of this substance in the neighbourhood of these temperatures, were measured in n-octane, n-heptane, n-hexane, and isooctane. The order of the critical temperatures is in accord with the internal pressures of the solvents, which increase for the normal hydrocarbons in the order of increasing mol. wt. n-Octane has a higher internal pressure than isooctane; this difference between a normal and an isoparaffin is probably general. For symmetrical binary systems of non-polar liquids (i.e., systems in which the mol. fraction of each constituent is 0·5 at the critical solution temperature), the mutual solubility curves may be represented by $\log [(1 - N_1)/N_1] = k(1 - 2N_1)/T$ as a first approximation, where N_1 is the mol. fraction of component 1 in one phase, and k is a constant depending, in part, on the difference in internal pressure of the two components. S. K. TWEEDY.

Solubility relations for lactose–sucrose solutions. I. Lactose–sucrose solubilities at low temperatures. P. N. PETER (J. Physical Chem., 1928, **32**, 1856—1864).—The solubility of lactose in aqueous sucrose solutions and of sucrose in solutions of lactose has been determined at 0° and at −3°. In the former case, the changes in solubility are inversely proportional, approximately, to the concentration of the sucrose. In saturated solutions of sucrose, the solubility is reduced to about one half that in water. Owing to the limited solubility of lactose at 0° and −3°, the solubility of sucrose at these temperatures is practically unaltered by the presence of the former sugar. Concentrated solutions of sucrose readily yield strongly supersaturated solutions of lactose, but on account of the high viscosity of the solution the latter may crystallise but slowly. Viscosity and not solubility appears to be the prime factor controlling crystallisation. The crystallisation of lactose in dairy products is discussed in the light of the above conclusions. L. S. THEOBALD.

Phenylallylthiocarbamide as a solvent. V. P. SCHISCHOKIN (Ann. Inst. Anal. Phys. Chem., 1928, **4**, 195—224).—The heat of fusion of phenylallyl-thiocarbamide is derived on the basis of the Hildebrand–Mortimer theory of concentrated solutions (A., 1921, ii, 23; 1922, ii, 621) from measurements of the temperatures at which crystallisation takes place from various mixtures containing different proportions of this substance. Where no chemical interaction takes place, as with aniline, o-nitroaniline, and diphenylamine, the curves connecting the reciprocal of the saturation temperature with the logarithm of the molecular concentration of the substance which first crystallises out are rectilinear; in the case of chloroform, paraldehyde, trichloroacetic acid, acetic anhydride, acetic acid, benzene, toluene, naphthalene, p-dibromobenzene, allylthiocarbimide, nitrobenzene, and ethyl and methyl alcohols the curves deviate more or less from the rectilinear, indicating chemical reaction between the components, such as combination, solid solution, or solvatation. The value calculated for the latent heat of fusion is in good agreement with that obtained experimentally (see this vol., 127). R. TRUSZKOWSKI.

Solubility in mixed solvents. II. Solubility of a substance which is miscible in all proportions with one of the solvents. E. ANGELESCU (Z. physikal. Chem., 1928, **138**, 300—310).—The solubility of phenol in mixtures of water with the different dihydroxybenzenes in various proportions has been determined. The values obtained are in good agreement with those calculated from the formula previously deduced (A., 1928, 579), $S_c - S_0 = KC^p$, where S_c is the solubility in 100 g. of one solvent mixed with C g. of the other, S_0 the solubility in 100 g. of pure solvent, and K and p are constants. This is the limiting case of a sagged curve when the difference in solubility in the two solvents is very large. M. S. BURR.

Selective solvent action. VII. Solubilities in mixed solvents. (MISS) N. GREGG-WILSON and R. WRIGHT (J.C.S., 1928, 3111—3115).—The solubility of acetonitrile in mixed solvents has been measured at 20°. The solvents used were water or benzene with various alcohols and also mixtures of different alcohols. In each case measurements were carried out with mixtures containing various proportions of the constituents. The solubility of phenanthrene

in aqueous ethyl alcohol has also been determined. It is suggested that the increased solubility usually noted with mixed solvents is due to the effect of the different solvents on the different radicals of the solute molecule. J. L. BUCHAN.

Solubility and dissolution velocity of solid substances. E. N. GAPON (Z. Elektrochem., 1928, **34**, 803—805; cf. Noyes and Whitney, A., 1897, ii, 479; Nernst, A., 1904, ii, 315).—Mainly theoretical. It is deduced thermodynamically (i) that the critical increment in the velocity of dissolution is equal to the heat of dissolution of the dissolving substance in nearly saturated solution plus $0.5RT$, and consequently is dependent only on the nature of the solute, and (ii) that the velocity coefficient is, at all temperatures, proportional to the solubility and $T^{\frac{1}{2}}$. On the other hand, it can be shown from the Noyes–Nernst diffusion theory (loc. cit.) that the critical increment depends entirely on the nature of the solvent and is equal to $W + RT$, where W is the value obtained for the solvent by Drucker, and that the velocity coefficient changes with the fluidity of the medium. Solubility measurements for benzoic acid at 20°, 30°, and 40° support the first set of conclusions. L. S. THEOBALD.

Significance of lower and higher critical solution temperatures. Ternary system water–nicotine–acetone. P. LEONE (Atti II Cong. Naz. Chim. pura Appl., 1926, 1209—1220; Chem. Zentr., 1928, ii, 525—526).—Acetone increases the mutual solubility of water and nicotine; the two-phase system disappears at acetone concentrations >35— 44%. The molecular variations (Timmermans) in the critical solution temperature are for a given ratio water/nicotine not constant, but increase somewhat with the acetone concentration. The molecular variations for the lower critical solution temperature are between 100 and 150, and for the upper usually below 100. A. A. ELDRIDGE.

Partition coefficient in the fractional crystallisation of radium barium bromide solutions. Z. T. WALTER with H. SCHLUNDT (J. Amer. Chem. Soc., 1928, **50**, 3266—3270).—The partition of radium between crystals and mother-liquor is characterised by a constant ratio. The fractionation process is represented with equal approximation by the equations of Doerner and Hoskins and of Schlundt, but not by the equation of Chlopin and Nikitin (A., 1927, 1133). The results show that radium is more efficiently concentrated by using the bromide than by using the chloride or sulphate. S. K. TWEEDY.

Distribution coefficients of ions. N. BJERRUM (Förh. III nord. Kemistmötet, 1928, 92—105).—The sum of the ionic distribution coefficients for various salts dissolved in alcohol and water respectively can be calculated from the solubilities of the salts in these liquids. The distribution exponent, P, may be used instead of the distribution coefficient, V, in expressing the results, the relationship being $P = \log V$. In the case of weak acids the sum of the ionic distribution exponents can be calculated by employing Larsson's formula $P_{anion} + P_{H} = \log K_{H_2O} - \log K_{alc.} + P_{undiss. acid}$: the last term can be calculated from solubility determinations of the acid in the two media. The values of the distribution exponents of the individual ions have been calculated from electropotential measurements: the figures obtained range from 4·1 for potassium ion to −3·9 for the stearate ion. The results always show a tendency for the ions to be concentrated in the aqueous rather than in the alcoholic solution, and this is ascribed to the high dielectric constant of water. The theoretical importance of these ionic distribution coefficients in the study of the properties of solutions of electrolytes, and the need for further experimental data, are emphasised.
H. F. HARWOOD.

Adsorption [of gases at low pressures]. W. KÄLBERER and H. MARK (Z. physikal. Chem., 1928, **139**, 151—162).—The adsorption of carbon dioxide and argon by silicic acid and of carbon dioxide by aluminium foil at various temperatures between −22° and 225° and mainly at very low pressures has been investigated. When no special outgassing is carried out, the adsorbing surface behaves uniformly and yields linear adsorption isotherms at low pressures; these isotherms pass through the origin of the co-ordinate system. In the case of carbon dioxide at 0°, the isotherm at pressures less than 0·2 mm. shows a rise from linearity which is accentuated by heating the adsorbent between 200° and 300° in a high vacuum and avoiding contact with air before adsorption takes place. This treatment reveals in the surface active centres which have taken up gases by contact with air in the usual conditions. Aluminium foil is similarly activated and the processes of activation by outgassing and of de-activation by contact with air are reversible. The heats of adsorption of argon and of carbon dioxide by silicic acid in the linear range of the isotherm are 2500 and 6200 g.-cal./mol. respectively, whilst in the steeper range the mean value for carbon dioxide is 7500 g.-cal./mol. The thickness of the adsorption layer of carbon dioxide on aluminium is of the order 1.5×10^{-8} cm. Equations representing adsorption are discussed. L. S. THEOBALD.

Influence of temperature on gas adsorption. H. ZEISE (Z. physikal. Chem., 1928, **138**, 289—299).—Theoretical. On the basis of previous experimental data for the adsorption of different gases by charcoal, the author discusses the variation with temperature of the coefficients c_1 and c_2 in Langmuir's adsorption isotherm for gases, $x = c_1 c_2 p / (1 + c_2 p)$, where x is the weight of gas adsorbed per g. of charcoal and p the pressure. It is shown that $c_1 = a_1 - b_1 T$ and $c_2 = 10^{a_2} / T^{b_2}$, where a_1, b_1, a_2, and b_2 are constants for any particular gas. There must therefore be a critical adsorption temperature $T' = a_1/b_1$ above which no pressure, however great, will bring about adsorption. Expressions are also obtained for the dependence on temperature of $N_{max.}$, the maximum number of adsorbed molecules, and of σ, the relative time of attachment of adsorbed molecules.
M. S. BURR.

Adsorption of gaseous mixtures of alcohol and ether from air by different silica gels. L. VON PUTNOKY and G. VON SZELÉNY (Z. Elektrochem., 1928, **34**, 805—812).—The simultaneous adsorption of alcohol and ether from mixtures of their vapours

with air at 20° by various brands of commercial silica gel and by one prepared by hydrolysis of silicon tetrachloride has been studied by a new dynamic method in which analysis of the gas mixtures has been effected by means of a three-chambered gas interferometer. The six gels were heated immediately before use to constant weight at 200° under a pressure of 15—20 mm. The total weight of alcohol and ether adsorbed increases with an increase in the proportion of these substances in the air used, and the ratio weight of alcohol adsorbed/weight of ether adsorbed varies with, but is always greater than, the ratio weight of alcohol/weight of ether in the mixture before adsorption. When the latter is 1 : 2, the former varies from 0·56 to 0·66, according to the nature of the gel; with an initial ratio 7 : 8, it varies from 0·94 to 1·1; and with ratios 1 : 1 and 4 : 3, more alcohol than ether is adsorbed. At the ratio 7 : 8, the ratio of the amounts of alcohol to ether adsorbed for a given gel is practically unchanged by doubling or trebling the absolute amounts of these substances in the gas mixture. Adsorption data for the six gels are given.　　　　L. S. THEOBALD.

Sorption of carbon tetrachloride at low pressures by activated charcoals. I. R. CHAPLIN (Proc. Roy. Soc., 1928, A, 121, 344—358).—The sorption of carbon tetrachloride vapour by charcoal has been investigated in the absence of other gases between 0° and 70° and at pressures of 1×10^{-4} to 2.3×10^{-1} mm. The pressure was measured by means of a Pirani gauge calibrated by a method which is given. The apparatus and method are described in detail; the experimental results will be given in a later paper.　　　　J. L. BUCHAN.

Adsorption of gases at heteropolar crystal faces. J. H. DE BOER (Metall-Wirt., 1928, 7, 657; Chem. Zentr., 1928, ii, 334).—The author's mathematical conceptions are supported by experiments on the adsorption of iodine vapour by calcium fluoride.　　　　A. A. ELDRIDGE.

Adsorbing power and vapour pressure of adsorbed water by acidic, neutral, and alkaline earths. H. ISOBE (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 1133—1159).—The adsorbing power for water vapour of earths from various localities in Japan has been measured. For the earth from a particular locality, the adsorbing power is maximal when the earth is neutral, and decreases if it becomes either acid or alkaline. Vapour-pressure measurements have also been made at a series of temperatures on earths containing varying amounts of moisture. The form of the vapour-pressure isotherms for water contents of 2—4% and 4—8% is different according as the earth is acid, alkaline, or neutral.　　　　R. CUTHILL.

Adsorption of quinine, oxalate, and dextrose by fuller's earth and charcoal (norit). N. R. GUERRANT and W. D. SALMON (J. Biol. Chem., 1928, 80, 67—89).—Different samples of fuller's earth vary both qualitatively and quantitatively in their adsorptive capacities. For a given sample the most important determining factor is p_H in the case of electrolytes (quinine hydrogen sulphate and oxalic acid) and effective surface in the case of non-electrolytes (dextrose). Treatment of the earth with acid diminishes its power of adsorbing oxalate and, to a smaller extent, of quinine, whilst its adsorptive capacity for dextrose is not affected; subsequent electrodialysis restores the adsorptive power for quinine only. Ignition of the earth has little effect on its adsorptive capacity for oxalate and for dextrose, and electrodialysis of otherwise untreated earth slightly reduces its power of adsorbing quinine. Adsorption of quinine and of dextrose by "norit" is affected by the p_H in a similar way; oxalic acid is adsorbed by norit only in acid solution, in which, however, the degree of adsorption is higher than that obtained with fuller's earth at any p_H.　　　　C. R. HARINGTON.

Absorption of ions by solutions of aluminium hydroxide and vanadium pentoxide. D. N. CHAKRAVARTI and N. R. DHAR (J. Indian Chem. Soc., 1928, 5, 539—543).—The adsorption of bromate, chloride, iodate, chromate, ferrocyanide, and oxalate ions by an aluminium hydroxide sol, prepared in the cold, has been found to decrease in magnitude in the above order. The order of decreasing adsorption of positive ions by a dialysed vanadium pentoxide solution was found to be : K, Al, Th, Ba. The experimental results show that with both these sols a univalent ion is adsorbed in greater quantity than a bivalent or tervalent ion.　　　　F. G. TRYHORN.

Kinetic theory of absorption. T. PECZALSKI (Compt. rend., 1928, 187, 1035—1037).—The phenomena associated with the absorption of a gas by a porous substance and with the action of salts on metals (A., 1927, 634) may be expressed in terms of the diminution in the mean path of the molecules of the adsorbed substance when it enters the pores, the linear dimensions of the latter being smaller than the mean path of the molecules of the surrounding gas. Expressions are obtained for the pressure inside the pores, and for the rise in temperature due to the adiabatic compression it produces, and it is shown that those molecules which have the greatest mean free path are, as a rule, most readily absorbed.　　　　J. GRANT.

Lyosorption in organic liquids. W. HALLER (Kolloid-Z., 1928, 46, 366—367).—When a fine suspension is allowed to settle, the volume of the sediment attains a definite value in time, but this value varies by more than 50% according to the liquid employed. Experiments with nine different powders in a number of liquids showed that the liquid is a more important factor than the solid phase. In all cases the volume of the sediment was greatest in carbon tetrachloride and least in alcohol or acetone. The phenomenon bears no relation to the density or viscosity of the liquid and is not due to an electric P.D. between the solid and liquid phases, but appears to be due to retention of the liquid by the solid particles, each of which acquires a sheath of molecules of the dispersion medium. The phenomenon has been named "lyosorption." The process can be reversed by tightly packing the powder in a tube and measuring the rate of flow of various liquids through the tube. In those liquids showing lyosorption it is evident that the pores of the powdered mass

gradually increase in size. Such a process is analogous to swelling and it is suggested that many cases of swelling of gels can be explained in terms of lyosorption.　　　　　　　　　　　　　　　　E. S. HEDGES.

Area of internal surface of charcoal as determined by the adsorption of normal aliphatic alcohols from aqueous solution. W. E. GARNER and F. E. T. KINGMAN (Trans. Faraday Soc., 1929, 25, 24—29).—The adsorption isotherms of n-butyl alcohol in aqueous solution have been measured for "norit" (ash content 0·2% after purification), using a Zeiss interferometer to determine the concentrations of the alcohol solutions (cf. Adams, A., 1915, ii, 478). The effect of cleaning the charcoal by evacuation and admitting air at high temperatures is to increase the adsorption. In all cases there are no obvious breaks in the adsorption isotherms, which are not of the same type as those previously obtained by the surface-tension method (A., 1927, 617). Some abnormality occurs in one or other of the methods at low concentrations. A photomicrographic investigation of the surface of the charcoal gave a value of 0·18 m.^{2} per g., which is obviously a very small proportion of the total area of the charcoal.　　O. J. WALKER.

Thickness of adsorbed vapour films. II. G. H. LATHAM (J. Amer. Chem. Soc., 1928, 50, 2987—2997).—The adsorption experiments of Frazer, Patrick, and Smith (A., 1927, 722) are continued with acetonitrile, nitromethane, and toluene. These substances are strongly adsorbed on glass surfaces which have been treated with acid, the layers being 30—60 mols. thick; they are not adsorbed at all, or only in unimolecular layers, on fire-polished glass surfaces, and such surfaces may be regarded as plane from the point of view of adsorption. Adsorption experiments in presence of silica gel indicate that treatment of glass surfaces with acid may produce a thin layer of silica. Amalgamated platinum surfaces absorb water strongly, a layer about 30 mols. thick being formed, whereas on amalgamated silver surfaces the layer never exceeds the thickness of one molecule.

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Oxide films responsible for the tints on heated copper. U. R. EVANS (Nature, 1929, 123, 16).—Removal of metal by anodic treatment in potassium sulphate solution has permitted isolation of oxide films from copper; the colours are due to cuprous oxide. Cupric oxide, which is formed under strongly oxidising conditions, obscures the colours. Within the interference-colour range, the cuprous oxide films are transparent. Opaque areas, due to metallic copper, are observed in films isolated from copper showing the first-order tinting colours.

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Theoretical aspects of the Traube–Whang phenomenon. L. J. WEBER and H. NEUGEBAUER (Z. physikal. Chem., 1928, 138, 161—168; cf. Traube and Whang, this vol., 129).—When a liquid is flowing through a capillary tube on the wall of which is a layer of a second substance, the boundary conditions will be largely dependent on the polarity of the wall substance. If this is sufficiently strongly polar, the tangential field within the layer of liquid adsorbed on it will be more or less homogeneous, so that movement of the liquid molecules in this layer will be possible in a direction parallel to the wall, their mobility being dependent on the degree of homogeneity of the field. Under these conditions, the amount of liquid Q flowing out per second is given by the extended form of Helmholtz's equation $Q=\pi(p-p_0)\{R^4+8B\eta R^2(v/\phi+R/2)\}8\eta l$, where p and p_0 are the pressures at the two ends of a capillary of length l and radius R, π is the surface tension and η the viscosity, ϕ is the molecular surface of the adsorbed layer and v the molecular volume of the liquid, and B is a constant given by the equation $u_0=KB$, where u_0 is the boundary velocity, and K the average force exerted on the molecules in the adsorbed layer. By means of this expression, the mobility of the molecules in the adsorbed layer in the experiments of Traube and Whang (loc. cit.) may be calculated. From similar considerations, Stokes' formula for the velocity v of a sphere of radius R falling under the influence of a force F becomes $F=6\pi\eta vR(1+2B\eta/R+8B\eta v/R^2\phi)/(1+3B\eta/R+8B\eta v/R^2\phi)$.　　R. CUTHILL.

Diffusion rings. G. LINCK (Chem. Erde, 1928, 4, 88—94).—Observation on the diffusion of silver nitrate and potassium chromate solutions in gelatin have been made under the microscope.

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Electro-osmosis of mixtures of electrolytes. A. BOUTARIC and M. DOLADILHE (Compt. rend., 1928, 187, 1142—1144).—The rate of transport (v) of solutions of copper sulphate and nitrate, which are electro-osmotically opposite, follows the same laws for the mixed as for the pure solutions, i.e., v varies directly with the current and inversely as the concentration. No simple relation exists between v and the ratio (s) of the normalities of the solutions constituting the mixture, but the composition corresponding with zero transport is related to s by a hyperbolic expression of the form $x \times s^{8\cdot7}=72\cdot5$, and if $s=1$, v varies linearly as a function of x.　　J. GRANT.

Diffusion and membrane potentials. IV. Comparison of anion and cation effects. E. B. R. PRIDEAUX (Trans. Faraday Soc., 1929, 25, 20—23; cf. A., 1927, 1033).—Previous measurements of the potentials which are set up at a parchment paper membrane between solutions of the alkali salts of organic acids of different concentrations have been extended to different types of electrolytes over one concentration range, viz., $0\cdot1N$ and $0\cdot01N$. Diffusion and membrane potentials for solutions of acetic acid and of piperidine are given. In the case of acetic acid the membrane causes only a very slight increase in the diffusion potential, whilst with piperidine instead of the expected diminution a slight increase was observed. The nature of the membrane potential is discussed.

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Measurement of osmotic pressure. R. V. TOWNEND (J. Amer. Chem. Soc., 1928, 50, 2958—2966).—An apparatus for measuring osmotic pressure is described, based on the following principle. The solution is placed in contact with its vapour, and pure solvent at the surface of a thin porous plate is also placed in contact with the vapour. The rate of evaporation of pure solvent into the vapour is

measured for varying downward tensions applied to the porous plate. These rates are plotted as a function of the applied tension and the curve is extrapolated to zero rate, which corresponds with a tension equal to the required osmotic pressure. The measurements are made under air-free conditions.

S. K. TWEEDY.

Condition of iodic, hydrofluoric, and chromic acids and their salts in aqueous solutions. N. R. DHAR (J. Indian Chem. Soc., 1928, 5, 558—592).— Comparison of the data for the electrical conductance, lowering of f. p., and elevation of b. p. of solutions of iodic acid indicates that this substance is partly polymerised in solution. The precipitation concentrations of solutions of the acid and of its salts for ferric hydroxide solutions show that the iodate ion exists in the bivalent form I_2O_6''. Similar experiments with hydrofluoric acid and with fluorides show that these also are associated in aqueous solutions. The second dissociation constant of chromic acid has been determined from measurements of the increase in solubility of carbon dioxide in solutions of potassium chromate. The constant is of the order of 5×10^{-8}. The data for electrical conductance and coagulating power of potassium dichromate solutions are in agreement with the view that this substance in solution exists partly as $KHCrO_4$ molecules.

F. G. TRYHORN.

Extinction coefficients of mixtures of mercuric chloride and organic acids in the ultra-violet as experimental evidence of the formation of unstable intermediate compounds. III. J. C. GHOSH and T. L. K. RANGACHARYA (J. Indian Chem. Soc., 1928, 5, 569—578; cf. Ghosh and Mitra, A., 1928, 687). —To verify the assumptions (a) that an equilibrium exists in solution between mercuric chloride and an organic acid and an intermediate complex formed by the loose combination of one molecule of each reactant, and (b) that a definite value of molecular extinction coefficient for each wave-length characterises the intermediate complex, measurements have been made of the molecular extinction coefficients of solutions of mercuric chloride ($0.001M$) containing, respectively, varying concentrations of formic, acetic, propionic, oxalic, malonic, succinic, glycollic, lactic, tartaric, and mandelic acids. It was found that the value of the equilibrium constant which characterises the intermediate compound (a) decreases for each successive addition of a CH_2 group in a homologous series, (b) increases roughly fifteen-fold on passing from a monobasic to a dibasic acid, and (c) increases in the case of a monobasic acid on the introduction of a terminal hydroxyl group. F. G. TRYHORN.

Colour of iodine solutions. F. H. GETMAN (J. Amer. Chem. Soc., 1928, 50, 2883—2890).—Iodine solutions were investigated spectrophotometrically between 680 and 430 mμ. Violet solutions exhibit an almost constant absorption maximum between 520 and 540 mμ, whilst brown solutions show a smaller, less constant, intensity maximum between 460 and 480 mμ. Lachman's conclusion, that saturated solvents (hydrocarbons and their halogen derivatives) produce violet solutions, and unsaturated solvents (ethyl alcohol, acetone, pyridine, etc.) brown

solutions, is confirmed (A., 1903, ii, 283). Iodine solutions tend to change on keeping; their colour and stability on exposure to ultra-violet radiation seem to depend somewhat on the degree of saturation of the solvent. S. K. TWEEDY.

Preparation of colloidal gold solution. R. A. KILDUFFE and W. W. HERSOHN (J. Lab. Clin. Med., 1927, 12, 810—813).—The method permits the preparation of solutions requiring minimal adjustment of reaction, and invariably giving normal or paretic curves with normal or paretic fluids, respectively. CHEMICAL ABSTRACTS.

Preparation of highly sensitive negative emulsions in the laboratory. K. KIESER (Z. angew. Chem., 1928, 41, 1292—1295).—A bromide solution is prepared of 100 g. of ammonium bromide and 2·5 g. of potassium iodide in 1 litre of water; 245 g. of silver nitrate are dissolved in 500 c.c. of water and the solution is treated with ammonia (d 0·91) until the brown precipitate of silver oxide just redissolves (about 250 c.c. of ammonia are required). In a large flask are placed 20 g. of gelatin, 80 c.c. of water, and 100 c.c. of the above bromide solution and, after 1 hr., the mixture is digested on the water-bath at 45° until a homogeneous liquid is obtained. The whole is transferred to a dark room lit by a ruby lamp and 30 c.c. of the silver solution are quickly added with vigorous agitation. After 45 min. on the water-bath at 45° a further 30 c.c. of the silver solution are added as before and heating is continued for 15 min. with frequent agitation. The flask is then cooled by rotation in ice water so that a thin layer of emulsion is formed over the inside surface; this is then cooled for several hours in an ice-chamber, and washed for 10 hrs. in a slow current of ice-cold water passed through the flask. The washed emulsion is melted at 45°, treated with 2 c.c. of 10% potassium bromide solution and 2 c.c. of 10% chrome alum solution, filtered, and kept at 45° for 1—3 hrs. to ripen; it is then ready for coating the plates or films in the usual way. A. R. POWELL.

Electric moment of colloidal particles of vanadic anhydride. J. ERRERA (J. Phys. Radium, 1928, [vi], 9, 307—309).—The electric moment of colloidal particles of vanadic anhydride has been calculated by a method due to Debye from a knowledge of the dielectric constants of the colloidal solution at low concentrations. The value found is 415×10^{-18}, which is considerably greater than that for molecules of substances such as ether and water. It appears that with age not only are long chains of colloidal particles formed in the solution, but that there is also a rearrangement of atoms and molecules within the colloidal particles themselves.

A. J. MEE.

Effect of non-electrolytes on the stability of colloids. II. Ferric hydroxide sol. S. G. CHAUDHURY and A. GANGULI (J. Physical Chem., 1928, 32, 1872—1874; cf. A., 1928, 1187).—The effect of methyl and ethyl alcohol, carbamide, sucrose, glycerol, and pyridine on the coagulation of a ferric hydroxide sol by potassium chloride, sulphate, and ferricyanide [?] has been studied. Methyl and ethyl alcohol and pyridine sensitise the sol irrespective of

the valency of the precipitating ions. Carbamide sensitises the sol towards the chloride and ferricyanide, whilst sucrose and glycerol show the same effect towards the sulphate and ferricyanide.

L. S. Theobald.

Figures produced by the desiccation of colloidal solutions. P. Bary (Rev. gén. Colloïd., 1928, 6, 209—221).—The deposit produced by evaporating a colloidal solution of ferric hydroxide at 50—60° in a porcelain basin consists of numerous filaments arranged either concentrically or radially, the latter form tending to appear when the chloride content of the solution is high. Examination under the microscope has shown the concentric filaments to be composed of a number of fibrils, having a diameter of about 3 μ with their centres about 9 μ apart, arranged parallel to each other with their long axes in the direction of the filament. The radial filaments consist of fibrils oriented transversely to the filament and thus apparently identical with the former case. In either instance, the fibrils are yellow and have a composition represented by $20Fe_2O_3,Fe_2Cl_6+aq.$ and are separated by a gelatinous reddish-brown material containing a higher percentage of chlorine. The proportion of fibrillar matter to the interfibrillar cement is greater during the initial stages of evaporation. It is believed that the yellow matter composing the fibrils is pre-existent in the solution and is not produced at the moment of deposition, for solutions of colloidal ferric hydroxide were observed to deposit a similar substance when kept for 12 or 15 months. Similar structures produced by other colloids can be examined by evaporating the sol at 50—60° in a small beaker in which is inclined a small microscope slide. Under these conditions, a periodic structure of regularly-spaced lines of deposit is formed and to these preparations the term " pectograph " has been given. The pectographs of colloidal solutions of antimony sulphide, arsenious sulphide, gold, tannin, sulphur, molybdenum sulphide, Congo-red, diamond-green P extra, and fuchsin are described and it is suggested that the method may be utilised in the determination of the structure of different colloidal solutions.

E. S. Hedges.

Electrical double layer of colloids. Silver iodide sol. H. R. Kruyt and P. C. van der Willigen (Z. physikal. Chem., 1928, 139, 53—63).—The peptisation of silver iodide, prepared from silver nitrate and potassium iodide, by various potassium salts has been investigated in connexion with the formation of the electrical double layer. Stable sols are obtained by the peptising action of the chloride, bromide, iodide, cyanide, and thiocyanate of potassium, all of which possess anions which, apparently, are able to fit into the space lattice of silver iodide. Such electrolytes can produce an electrical double layer. On the other hand, the nitrate, sulphate, carbonate, monohydrogen phosphate, and dichromate of potassium bring about flocculation, whilst the ferricyanide occupies an intermediate position. Cataphoretic measurements of the positively-charged silver iodide sol show that with dilution the positive charge decreases to zero and then changes in sign, whilst the stability of the sol corresponds with this behaviour.

Dialysis brings about coagulation of the positive but not of the negative sol. The conductivities of these sols were also measured. The connexion between isomorphism and peptising power supports the conception put forward that the electrical double layer is brought about by lattice forces. The formation of the negative charge of silver iodide in contact with pure water is still an open question. The hydroxyl ion, although not fitting into the space lattice of the iodide, appears to possess a special facility for forming the double layer. The charge in pure water remains below the critical value and a small concentration of potassium iodide (0·005—0·01 mol./litre) suffices to cause peptisation, whereas with silver nitrate a much higher concentration (0·1—0·5 mol./litre) is required to reach the positive critical value for peptisation.

L. S. Theobald.

Critical potential in the coagulation of colloids by electrolytes. J. N. Mukherjee and S. P. Raichoudhuri (Nature, 1928, 122, 960—961).—The nature and mode of preparation of the colloid have considerable influence on the cataphoretic speed at the coagulating concentration of the electrolyte. Curves correlating the concentration of electrolyte with the cataphoretic speed contradict the assumption that coagulation takes place at a critical potential. A fall in the cataphoretic speed during the course of the coagulation indicates some irreversible change during aggregation.

A. A. Eldridge.

Lyophilic colloids. I. Agar. H. R. Kruyt and H. G. B. de Jong (Kolloidchem. Beih., 1928, 28, 1—54).—Methods of purification of agar are detailed. For dilute agar sols, the relative increase in viscosity has a definite value at each temperature and decreases with rising temperature. The connexion between the relative increase in the viscosity and the concentration of the sol is somewhat complicated, the curve being at first slightly convex to the concentration axis, and later slightly concave. The viscosity of agar sols is lowered by all electrolytes at small concentrations. Equivalent concentrations of the chlorides of potassium, sodium, lithium, ammonium, and of potassium sulphate, thiocyanate, and ferrocyanide produce a practically constant lowering of viscosity. A similar relation is found in the series barium chloride, strontium chloride, magnesium sulphate, and cadmium sulphate, the decrease in viscosity being greater than in the former case. The magnitude of the effect depends on the valency of the cation. Cataphoretic experiments show that the agar sol is negatively charged; the charge is capillary-electric in nature. The decrease in viscosity caused by hydrochloric acid on potassium hydroxide is greater than that caused by barium chloride. In accordance with the strong adsorption of organic ions, fuchsin produces a much stronger decrease in viscosity than potassium chloride. With high concentrations of electrolytes, where the electro-viscous effect is absent, the relative decrease in viscosity is a measure of the degree of hydration; this increases in the series potassium sulphate < chloride < nitrate < thiocyanate. Experiments have been conducted on the salting out of agar solutions by various electrolytes at high concentrations and also on the effect of adding alcohol or acetone in

presence and in absence of electrolytes. When the charge on the agar particles is removed by electrolytes in water as the dispersion medium, the sol still remains stable, but when the dispersion medium is alcohol–water or acetone–water the sol is flocculated under these conditions. Alcohol or acetone has the greatest influence at medium concentrations, for which the viscosity of their mixtures with water is greatest. It would therefore seem that the stability of agar sols is due not only to the charge on the particles, but also to hydration of the particles. This factor is considered to constitute the chief difference between the suspensoid and emulsoid types of colloids. In the suspensoid type, removal of the charge on the particles causes immediate coagulation because the particles are feebly hydrated, if at all, whilst in the emulsoid type the sol preserves its stability unless a dehydrating agent such as alcohol is present simultaneously. The relations found with agar are thus generalised to a theory of stability of hydrosols and are applied in particular to sols of proteins. E. S. HEDGES.

Jellies and gels. Wo. OSTWALD (Kolloid-Z., 1928, 46, 248—267).—Previous schemes for the classification of gels are reviewed and a new scheme is proposed, which is based on the mode of production of the gel. Different types thus arise according to whether the gel is formed by falling of temperature, by chemical reaction, by coagulation, swelling, fermentation, or by geological influences. Allied systems include undercooled melts and solutions, slimes, and foams. A distinction is also made between lyogels, which are rich in liquid, and xerogels, which are in a relatively dry state. The process of gelatinisation is discussed together with the existing experimental data in regard to the changes taking place within the gel. As a result, gels are defined as systems rich in liquid, of varying composition (liquid–liquid, liquid–solid, solid–liquid, etc.) and of varying degree of dispersion, although mainly colloidal, the particles of which either by mechanical growth or through other causes are in such proximity to each other that the liquid exists mainly in the form of lyospheres. Theories of swelling are critically examined, and since so many factors have to be considered in special cases the author concludes that no general theory of swelling can be given. E. S. HEDGES.

Free and bound liquid in gels. W. B. HARDY (Kolloid-Z., 1928, 46, 268—277).—Published work on the ratio of free to bound liquid in gels is discussed and the problem is treated from the point of view of adhesion forces. The range of attraction of the particles is considered to be of the utmost importance in colloid-chemical problems. As an analogy to a gel system, a system consisting of a layer of lubricating material between two metal plates is described. E. S. HEDGES.

Concentration differences of dissolved substances in opposition to osmotic pressure in gels. R. AUERBACH (Kolloid-Z., 1928, 46, 321—323).—It is shown that differences of concentration of dissolved substances can be set up at the boundary of a gel and water or at the boundary of two gels of different concentration. The phenomenon is of importance in biological systems, where differences of concentration are encountered which are far removed from those required by osmotic equilibrium. E. S. HEDGES.

Jellies and gelatinous precipitates. P. P. VON WEIMARN (Kolloid-Z., 1928, 46, 356—358).—A summary of the author's views and previously published experiments on the classification of gels, the conditions of formation, the form of the disperse particles, the effect of mechanical agitation, and the relation of gelatinous precipitates to flocculent precipitates and to gels. E. S. HEDGES.

Cooling curves of gelatinising systems. H. H. FISCHER (Kolloid-Z., 1928, 46, 359—366).—Cooling curves for various soap solutions have been constructed and in each case at the point of setting a break occurs in the curve, indicating evolution of heat. In a note added to the paper, A. LOTTERMOSER states that he has obtained similar results with soap solutions and has observed the same phenomenon in the cooling of gelatin sols. E. S. HEDGES.

Dependence of swelling on the amount of solid phase. P. P. KESTENBAUM (Kolloid-Z., 1928, 46, 367—368).—Observations on the swelling of different quantities of gelatin in a constant volume of water show that small amounts of gelatin undergo the most swelling. At higher temperatures this effect is enhanced. Similar experiments in solutions of electrolytes show that these have a great influence on the results and in some cases a large amount of gelatin may swell the most, whilst in others a maximal or minimal amount of gelatin may be observed. E. S. HEDGES.

Thermal, mechanical, and X-ray analysis of swelling. R. O. HERZOG and K. WEISSENBERG (Kolloid-Z., 1928, 46, 277—289).—A theoretical paper, which considers the analysis of gels from both the energetic and material points of view. The energetic analysis is treated from the point of view of thermodynamics, mechanics, and molecular kinetics, and the material analysis includes the degree of dispersion, distribution of phases, volume, texture, and fine structure of the particles. The processes of gelatinisation and swelling are discussed in the light of the views expressed. E. S. HEDGES.

Thixotropy. H. FREUNDLICH (Kolloid-Z., 1928, 46, 289—299).—A summary of the author's and other work on thixotropy. It is pointed out that alteration of temperature is not the only factor controlling the sol–gel transformation and that many gels, if not all, can be converted into the sol state by sufficient mechanical agitation, the sol setting to a gel once more when left at rest. This is important in considering the structure of gels. Gels are considered to have a liquid dispersion medium. E. S. HEDGES.

Syneresis. A. KUHN (Kolloid-Z., 1928, 46, 299—314).—A critical examination is made of a considerable amount of published work on syneresis, and the following general conclusions are reached. Certain gels (silicic acid, caoutchouc, etc.) show increased syneresis with rising concentration, whilst others (dyes, starch, agar, cellulose acetate, etc.) behave in the reverse way. There appears to be no general rule for the influence of temperature. The

degree of syneresis varies with the dispersion medium and is sensitive to small amounts of additive agents : in general, the syneresis is greatest when the gel is in the least stable state. The influence of pressure and of surface and the composition of the exuded liquid are also discussed. Syneresis is discussed as a combined process of structural alterations and de-solvation.   E. S. HEDGES.

Syneresis and swelling of gelatin. M. KUNITZ (J. Gen. Physiol., 1928, **12**, 289—312).—When solid blocks of isoelectric gelatin gel containing less than 10% of the protein are immersed in distilled water or buffer solution at p_H 4·7 they contract and lose water, whilst if the concentration of protein is more than 10% they tend to imbibe water and swell. The loss of water which is finally suffered by a block containing less than 10% of gelatin immersed in water is the same as that which a similar block loses by syneresis when this process is induced by mechanical means, and it is concluded that the shrinkage in water is similar in nature to syneresis and that this term may be conveniently used for the former phenomena. Gelatin gels containing acid, alkali, or salt suffer a greater loss of water than isoelectric gelatin of the same concentration after the acid, alkali, or salt has been removed by dialysis. Quantitative measure-ments of the loss of water by dilute gels of various gelatin content satisfy an expression similar to that deduced by Northrop (cf. A., 1927, 825) for the swelling of more concentrated gels. The theory of the swelling and contraction of gelatin gels is dis-cussed.   W. O. KERMACK.

Birefractometry of plastic masses. W. STAUF (Kolloid-Z., 1928, **46**, 345—350).—A lecture on the characterisation of plastic materials by optical methods.   E. S. HEDGES.

The bioelectric model. R. BEUTNER and T. KANDA (Z. physikal. Chem., 1928, **139**, 107—116).—A survey of previous work shows that the maximum variation of $P.D.$ obtained when various parts of plants are placed in contact with salt solutions of varying concentration can be reproduced only by a few substances such as salicylaldehyde or solutions of fatty acids in cresol or similar substances. These substances, however, give an $E.M.F.$ in the opposite direction to the parts of the plants which have been investigated. On the other hand, substances which give an $E.M.F.$ in the required direction do not give the necessary variation with concentration. It has now been found that collodion furnishes a suitable model. A collodion membrane gives an $E.M.F.$ of the same order and in the same direction as an apple when both are in contact with a potassium chloride solution of the same concentration.
                    R. N. KERR.

$E.M.F.$ in acid and alkaline plant-tissue. K. STERN (Z. physikal. Chem., 1928, **139**, 224—234).—The $E.M.F.$ developed in plant-tissue under different conditions have been investigated. Mechanical irrit-ation by brushing, or the action of chemical substances such as concentrated sulphuric acid, citric acid ($0.1N$), and concentrated ammonia solution gives rise to an $E.M.F.$ of about 0·01 volt, and in all cases the side irritated is negative with respect to that not irritated. Potassium chloride solutions give rise to similar $E.M.F.$ and in arrangements of the type dilute electrolyte|plant-tissue|concentrated electro-lyte, the side of the tissue in contact with the dilute electrolyte is positive with respect to the other side. The effect is practically reversible and is greater with $0.01N/0.001N$ solutions than with $0.1N/0.01N$ solutions. The results are discussed in relation to the conclusions of Haber and Klemensievicz (A., 1909, ii, 785) on the electrical effects observed in muscle-tissue.   L. S. THEOBALD.

Van der Waals' equation and the principles of thermodynamics : the Maxwell–Clausius relation and Clapeyron's formula deduced from this equation. V. KARPEN (Compt. rend., 1928, **187**, 1039—1042).—If van der Waals' equation holds for the liquid and vapour phase of a fluid, it may be used for the direct calculation, independently of Carnot's principle, of the Clapeyron and Maxwell–Clausius relationships.   J. GRANT.

Rapid calculation of the degree of dissociation. Application to carbon dioxide. P. JOLIBOIS and P. MONTAGNE (Compt. rend., 1928, **187**, 1145—1147).—A graphic method is described.
                    J. GRANT.

Symmetrical and asymmetrical hydrogen and the third law of thermodynamics. Thermal equilibrium and the triple point pressure. W. F. GIAUQUE and H. L. JOHNSTON (J. Amer. Chem. Soc., 1928, **50**, 3221—3228).—The vapour pressure of hydrogen at the triple point falls from 5·38 to 5·34 cm. when the hydrogen has been kept at the temperature of liquid air for 197 days. This may be due to a change of the hydrogen molecules from the asym-metric to the symmetric form (Heisenberg, A., 1927, 290 ; Dennison, *ibid.*, 291, 817). Fowler's statistical calculation of the entropy of hydrogen containing the two forms of molecules (A., 1928, 469) is inaccurate ; 4·39 g.-cal./1° must be added to the molar entropy calculated by the usual methods.   S. K. TWEEDY.

Electrolytic dissociation. M. A. RABINOVITSCH (Ukraine Chem. J., 1928, **3**, 237—434).—A theory of solution and electrolytic dissociation is proposed. It is shown that there is no abrupt transition from electrolytes to non-electrolytes, the difference between which is due to the degree of intramolecular ionisation. The electrolytic properties of solutions are due to the peculiar molecular structure of the solvates formed, these complex molecules having their chemical affinities satisfied to a greater extent than are those of the molecules of the solvent alone. Strong electrolytes are considered to be those the molecules of which exhibit high polarity, and dissociation is greatest in a highly polar solvent. Dissociation is thus considered as a phenomenon having its origin in the interaction of molecules. The consequences of this point of view are that it becomes unnecessary to assume complete dissociation of strong electrolytes, or to consider the solvent merely as a dielectric medium. Ostwald's equation is not applicable to strong electrolytes, the solvated molecules and ions of which have a marked tendency towards association, as a result of their high polarity. Anomalous dissociation curves, where the degree of dissociation first falls to a minimum with

rising concentration, and then rises to a maximum, are the result of the simultaneous action of two opposing influences, solvation, favoured at low concentrations, and polymerisation, favoured at high concentrations. At the minimum, both influences affect conductivity to an equal extent, whilst at the maximum dissociation of the polymerised solvate complex is practically complete. R. TRUSZKOWSKI.

Ethyl acetate equilibrium. R. C. CANTELO and R. D. BILLINGER (J. Amer. Chem. Soc., 1928, **50**, 3212—3215).—The esterification of acetic acid by ethyl alcohol was investigated at 78° in presence of the chloride, thiocyanate, and iodide of sodium, which salts form a Hofmeister series. The equilibrium constant, $K =$ [ester] [water]/[acid] [alcohol] increases with rising salt concentrations, the relation being linear in the case of sodium chloride. The order of the effects of the anions is not that of a Hofmeister series (cf. Schlesinger, A., 1926, 1109). S. K. TWEEDY.

Ebullioscopic determination of complexes formed by mercuric chloride and alkali chlorides. Association of mercuric chloride. F. BOURION and E. ROUYER (Ann. Chim., 1928, [x], **10**, 263—355; cf. A., 1928, 1185).—The association of mercuric chloride in aqueous solution has been studied ebullioscopically for C 0·175—1·75 mol./litre. Whilst the authors agree with Linhart (A., 1915, ii, 99) that at 25° and 40° the equilibrium is $2HgCl_2 \rightleftharpoons Hg_2Cl_4$ for $c<0·37$ they consider that at 100° between 0·5 and 1·75 mols./litre it is exclusively $3HgCl_2 \rightleftharpoons Hg_3Cl_6$, although double molecules possibly exist when c is less than 0·2. The density of mercuric chloride in aqueous solution at 15° is 5. In the application of the ebullioscopic method to the determination of complexes formed with alkali chlorides it is necessary to consider the concentration of both the single and the associated molecules of mercuric chloride. The maximum deviation of the rise in b. p. for corresponding solutions containing mercuric chloride and potassium, ammonium, or sodium chloride from the additive value for the separate salt solutions corresponds with 0·4 of mercuric chloride and 0·6 of the alkali chloride, which suggests the existence of a mixture of the complexes M_2HgCl_4 and $MHgCl_3$ (M=K, NH_4, or Na), a view which is confirmed by other evidence. The values of $k=C_{HgCl_2} \times C^2_{MCl}/C_{M_2HgCl_4}$ are 0·0545 for potassium and 0·131 for sodium chlorides (concentrations calculated at 15°). A study of the reduction of mercuric chloride with sodium formate, a stoicheiometrically termolecular reaction, confirms Linhart's result (A., 1915, ii, 91) that the bimolecular velocity coefficient is constant when a large excess of sodium formate is used. A similar result is obtained in presence of an excess of sodium acetate, the value of the termolecular coefficient decreasing as the reaction proceeds. An explanation is suggested in terms of the complexes formed by mercuric chloride and sodium acetate (and hence, presumably, with sodium formate) at 100°, the most probable composition being $4HgCl_2,5Me·CO_2Na$. The reduction is thus formulated by the bimolecular reaction $[4HgCl_2,5H(Me)·CO_2Na]+H·CO_2Na= 2HgCl+HCl+NaCl+CO_2+5H(Me)·CO_2Na+2HgCl_2$, a constant bimolecular coefficient being obtained

with a sufficient excess of sodium formate or acetate, but with insufficient excess the sodium chloride produced forms a stable, more difficultly reducible complex with the mercuric chloride, thus causing the bimolecular coefficient to diminish as the reaction proceeds. Mercuric cyanide raises the b. p. normally at all concentrations up to 1·75 mols./litre (except for evidence of slight association at the highest concentrations) and the absence of hydrolysis is shown to be due to its very small ionisation constant (10^{-15}). By methods similar to those employed above, the formation of complexes between mercuric cyanide and alkali or alkaline-earth halides has been studied. With potassium, sodium, and ammonium chlorides and potassium iodide these are of the type M'[HgCNX] (M'=metal, X=halogen), and with magnesium, calcium, and strontium chlorides of the similar type $M''[Hg(CN)_2X_2]$, and, with the exception of the last two, all these *complexes* have been isolated. No evidence of any complex formation with the double molecule $Hg_2(CN)_4$ was obtained. Unlike the other alkaline-earth metals, barium chloride forms the complex $Ba[Hg_2(CN)_4Cl_2]$. The value of $k=c_{Hg(CN)_2} \times c_{MX}/c_{M[Hg(CN)_2X]}$ is 1·3 for potassium chloride and 0·87 for the bromide (concentrations calculated at 15°). The density of mercuric cyanide in aqueous solution at 15° is 4. J. W. BAKER.

Buffer studies. X. Buffering of fæces. II. M. KARTAGENER (Helv. Chim. Acta, 1928, **11**, 1084—1094; cf. *ibid.*, 548).—The hydrogen-ion concentrations of sodium hydroxide solutions of progressively decreasing concentrations have been measured alone and after shaking with secondary and tertiary calcium orthophosphates. On addition of these salts the p_H is always displaced towards the acid side. The amount of displacement depends on the p_H of the original solution, being smaller for the more alkaline solutions. The amount also differs for the two salts; above an initial alkali concentration of 0·0025N the displacement is greater with the secondary salt, but below that concentration the tertiary salt has the greater effect. The amounts of calcium and phosphate ions in the supernatant liquid have been determined analytically for one series. The ratio Ca : PO_4 increases with diminishing alkalinity and is lower for liquids shaken with tertiary salt than for those with secondary salt. These results are explained on the hypothesis that calcium hydroxide is formed from the phosphate in solution by hydrolysis and is adsorbed on the surface of the solid phosphate.

The effect of adding solid calcium phosphate to a buffer solution was also investigated. An acetic acid–acetate buffer was titrated electrometrically with acid and alkali. Quantities of this solution were then shaken with tertiary calcium phosphate and again titrated (*a*) with solid phase present and (*b*) after filtering. The degree of buffering, measured by the slope of the titration curve, of the heterogeneous buffer system does not differ greatly from that of the original solution, but the buffer capacity, measured by the amount of acid required before a turning point is reached on the curve, is increased to an extent depending on the concentration of the solid phase. The increase in the buffering capacity is much less marked

if the solid phase be removed by filtration. The composition of the acetate buffer was so chosen that addition of the phosphate caused a lowering of p_H, but it is emphasised that, despite this, the acid capacity of the heterogeneous system is raised.

R. N. KERR.

Chemical antagonism of ions. I. Effect of sodium–magnesium and potassium–magnesium mixtures on the activity of the oxalic ion, C_2O_4. II. Antagonism between anions and also between cations and anions in their effect on oxalate activity. H. S. SIMMS (J. Gen. Physiol., 1928, **12**, 241—258, 259—267).—I. The activity of the oxalic ion has been derived from conductivity measurements of magnesium chloride and sodium chloride (or potassium chloride). The activity is depressed by sodium chloride but more so by magnesium chloride. When, however, sodium chloride is present as well as magnesium chloride the depression of the activity is less than when magnesium chloride alone is present. The following equation, which is partly empirical, has been found to fit the experimental observation : $k = [(\text{inactivated } C_2O_4'')/(\text{active } C_2O_4'')] \times [(\text{Na}^+ + \text{K}^+ + 2\text{Mg}^{++} + A)/\{\gamma \text{Mg}(C_2O_4'')^{1.5}\}]$, where A is an empirical constant depending on the concentration of oxalate ion and γMg is the activity of the magnesium ion.

II. The anomalous effect of the sulphate ion on the activity of the oxalate ion which is exerted in a direction opposite to that of magnesium ion is antagonised by sodium chloride and an equation similar in form to that given above is also satisfied in this case. In solutions of magnesium sulphate more dilute than $0.03M$, the effect of magnesium predominates over that of sulphate, whilst in more concentrated solutions the effect of the sulphate ion predominates. In solutions containing both sodium sulphate and magnesium chloride marked antagonism between the magnesium and sulphate ions is observed. As the activity of proteins is presumably influenced in a similar way by inorganic ions, biological antagonism of ions may be related to these phenomena. W. O. KERMACK.

Ionic concentrations and activity coefficients of weak electrolytes in certain salt solutions. H. S. HARNED and R. A. ROBINSON (J. Amer. Chem. Soc., 1928, **50**, 3157—3178).—A general method is described for measuring the activity coefficients and the hydrogen- or hydroxyl-ion concentrations of weak acids and hydroxides in salt solutions of varying concentrations by $E.M.F.$ measurements on cells with no liquid junction potentials and also on cells with negligibly small such potentials. The method was applied to acetic acid by using cells of the type $H_2|HCl,MCl|AgCl|Ag$ and $H_2|HOAc,MCl|AgCl|Ag$, where $M = K$, Na, Li, or 0.5Ba. With the progressive addition of salt, the dissociation of the acid passes through a maximum, whilst the ionic activity coefficients pass through a minimum (cf. Harned, A., 1927, 206). A method of correcting the calculated results for the influence of the undissociated acetic acid molecules in the solution is given. The above general method is also applied to weak bases, BOH, viz., ammonia and its methyl derivatives, by measuring the $E.M.F.$ of cells of the type : $H_2|MOH,MCl(c)|$ $MCl(c)|AgCl|Ag$ and $H_2|BOH,MCl(c)|MCl(c)|AgCl|Ag$, M being K, Na, or Li, which, when combined, represent a cell with a negligible junction potential. The activity coefficients of ammonia in sodium chloride solutions are progressively diminished as methyl groups are introduced into the molecule or as the salt concentration is increased. The order of the salt effects is the same as in the case of acetic acid. The results show that the ionic activity coefficients of acetic, mono- and di-chloroacetic acids (cf. A., 1928, 251) are smaller in the solution of a given concentration of that salt which possesses the higher activity coefficient in pure water. The same is true for ammonia and monomethylamine, and probably also for di- and tri-methylamines. In the presence of more than $0.1M$-sodium chloride, $0.01M$-tetramethylammonium hydroxide seems to be more highly dissociated than sodium hydroxide. S. K. TWEEDY.

Transformation of chromates into dichromates. E. CARRIÈRE and P. CASTEL (Compt. rend., 1928, **187**, 1292—1294).—The ionic equilibrium $2CrO_4'' + 2H^{\cdot} \rightleftharpoons Cr_2O_7'' + H_2O$ has been studied at $20°$ by the conversion of barium chromate into barium dichromate by the addition of a measured amount of hydrochloric acid, the end-point being reached when the solution becomes clear. The hydrogen-ion concentration of the equilibrium mixture was calculated from the law of mass action applied to the ions concerned assuming complete dissociation, and good agreement was found between the observed and calculated values for low concentrations. The concentration of acid required decreases with temperature, and the equilibrium constant at $18°$ is 3×10^{-15}.

J. GRANT.

Transformations of rubidium halides by pressure. P. W. BRIDGMAN (Z. Krist., 1928, **67**, 363—376; Chem. Zentr., 1928, ii, 317).—The conversion of rubidium chloride, bromide, and iodide at high pressure into a second modification has been studied by a differential volumetric method. Thermodynamic data are tabulated. A. A. ELDRIDGE.

Vapour pressures of aqueous solutions of potassium iodide and sodium bromide at 25°. J. N. PEARCE, M. D. TAYLOR, and R. M. BARTLETT (J. Amer. Chem. Soc., 1928, **50**, 2951—2958).—The above vapour pressures were measured up to saturation by the method previously described (Pearce and Snow, A., 1927, 302). The osmotic pressures of the solutions calculated by Fraser's formula deviate from those obtained by Lewis' expression above $0.8M$. Other thermodynamic properties of the solutions are calculated also. S. K. TWEEDY.

Volatility with steam of water-soluble organic substances. A. I. VIRTANEN and L. PULKKI (J. Amer. Chem. Soc., 1928, **50**, 3138—3151).—If a solution containing y_1 parts of volatile substance in x_1 parts of water is distilled and a solution of y_2 parts of substance in x_2 parts of water is left, then, according to Wiegner ($\log y_1 - \log y_2) = k(\log x_1 - \log x_2)$, where k is the distillation constant of the substance and indicates its volatility in steam, supposing condensation of the steam to be eliminated. Values of k are recorded for some organic substances in water; in a homologous series k increases 0.6 for each CH_2 group

in acids and 10 for each such group in amines, due to the degree of hydration regularly decreasing as the carbon chain is lengthened. A method is given whereby an aqueous solution of two volatile substances may be analysed by a single distillation provided the values of k are less than 5. The method may be extended to mixtures of three volatile substances, two distillations then being necessary. The presence of neutral salts in the solution of the volatile substance generally augments the value of k, the anion having a much greater influence in this respect than the cation. The effect is due to a diminution in the hydration of the substance. S. K. TWEEDY.

Iron–zinc system. Y. OGAWA and T. MURAKAMI (Tech. Rep. Tôhoku, 1928, **8**, 53—69).—The compounds $FeZn_7$ and $FeZn_2$ are formed. C. W. GIBBY.

System tungsten–carbon. K. BECKER (Z. Metallk., 1928, **20**, 437—441).—Röntgenographic and micrographic examination of the system tungsten-carbon shows the presence of only two carbides at the ordinary temperature, namely W_2C and WC. At 2600°, however, the latter dissociates, leaving a residue of the composition W_3C_2 which on cooling decomposes into a eutectoidal equimolecular mixture of W_2C and WC. The lower carbide melts undecomposed in an atmosphere with a sufficiently high partial pressure of carbon, but it is decarburised by melting in hydrogen or in a vacuum; at 2400° it undergoes a transformation into β-W_2C. On heating tungsten wire in methane–hydrogen mixtures carburisation ensues, the minimum concentration of methane to produce carburisation increasing with rise of temperature; at this minimum concentration WC is the first product formed up to 1900°, α-W_2C from 1900° to 2400°, and β-W_2C above 2400°. A. R. POWELL.

Cryoscopic studies of the transition points of compounds of organic solvents with salts. I. H. OSAKA (Bull. Chem. Soc. Japan, 1928, **3**, 289—297; cf. A., 1928, 1095).—The lowering of the transition point (25·5°) at which the compound $NaI,3COMe_2$ loses acetone by the dissolution of foreign substances has been studied and the molecular depression, referred to 100 g. of acetone, has been determined as 24·0, using as solutes naphthalene, camphor, benzoic acid, acetanilide, p-nitroaniline, phthalic anhydride, benzil, and coumarin. The maximum variation in the constant so obtained was less than 5%. For the compound $HgCl_2,COMe_2$, transition point 20·7°, the same mean value was obtained for the molecular depression of the transition point, but the results were less concordant than with the former substance. F. G. TRYHORN.

Ammonium sulphite and hydrogen sulphite. I. Solubility and transition point of ammonium sulphite. F. ISHIKAWA and H. MUROOKA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 1160—1176).—The solubility of ammonium sulphite in water has been determined from the cryohydric point up to 100°, and some f.-p. measurements have been made. The transition point of the monohydrate to the anhydrous salt is 80·8°±0·2°. R. CUTHILL.

Solution of the ternary equilibrium diagram and a contribution to the Al–Cu–Zn system. M. HAMASUMI and S. MATOBA (Tech. Rep. Tôhoku, 1928, **8**, 71—98).—A general method for the interpretation of ternary equilibrium diagrams based on its resolution into solubility surfaces is described. By this method the results of Hanson and Gayler (A., 1925, ii, 974) and of Nishimura (Mem. Coll. Eng. Kyoto, 1927) for the system Al–Cu–Zn are compared with one another and with experiments by the authors. Hanson and Gayler's diagram is considered to be the more acceptable. C. W. GIBBY.

System lead nitrate–ammonium nitrate–water. G. MALQUORI (Atti II Cong. Naz. Chim. pura appl., 1926, 1135—1140; Chem. Zentr., 1928, ii, 517).—Only lead nitrate and ammonium nitrate exist as solid phases. The lead nitrate content of solutions (at 0°, 10°, and 20°) is but little affected by large amounts of ammonium nitrate; that of the latter is greatly influenced by the former. A. A. ELDRIDGE.

Physico-chemical investigation of amino-acids. G. TAKAHASHI and T. YAGINUMA (Proc. Imp. Acad. Tokyo, 1928, **4**, 561—564).—Equilibrium data are recorded for the system l-leucine–HCl–H_2O at 15° and 30°; specific rotation and rotatory dispersion have been determined at different concentrations. A metastable form of l-leucine is obtained by crystallisation from hot alcoholic hydrogen chloride. S. J. GREGG.

Equilibrium of silver oxide and silver chloride with aqueous potassium chloride and potassium hydroxide. R. F. NEWTON (J. Amer. Chem. Soc., 1928, **50**, 3258—3261).—The ratio of the chloride- and hydroxide-ion concentrations at equilibrium at 25° is independent of the method of preparation of the silver oxide and is substantially the same as that found by Noyes and Kohr (A., 1903, ii, 201). It has the same value in 0·05M-solution of hydroxide ions as in 0·1M-solution. S. K. TWEEDY.

Synthesis of carbamide from ammonia, carbon dioxide, and water from a physico-chemical point of view. E. TERRES and H. BEHRENS (Z. physikal. Chem., 1928, **139**, 695—716).—The study of the ternary system ammonia–carbon dioxide–water (A., 1921, ii, 448) has been extended to temperatures above 60°. As considerable pressure was developed at these higher temperatures the use of steel bombs for reaction vessels was found necessary. The equilibrium conditions were determined at 80°, 100°, and 120° with both ammonium hydrogen carbonate and carbamate as solid phase and ammonia solutions of gradually increasing concentrations as liquid phase. The amounts of ammonia and carbon dioxide in the liquid phase were determined and the relation between them is shown graphically. The isothermals at 80° and 100° so obtained afford evidence of a double salt, hydrogen carbonate–carbamate. The formation of this solid phase is also proved by microscopical examination. No similar formation of double salt is obtained at 120°. The temperature at which it is no longer formed is 106°, which is also the m. p. of ammonium hydrogen carbonate. Above this temperature the solid phase consists only of hydrogen carbonate or carbamate. Experiments were also made at 135° and, in spite of experimental difficulties, it is

shown that at this temperature both hydrogen carbonate and carbamate are converted into carbamide and can no longer exist as the solid phase. A space diagram of the ternary system is given. From the experimental data the solubility of ammonium hydrogen carbamate in water over the range of temperature investigated can be deduced. The solubility curve is a straight line.   R. N. KERR.

Equilibrium between aluminium carbide and nitrogen at high temperatures. C. H. PRESCOTT, jun., and W. B. HINCKE (J. Amer. Chem. Soc., 1928, **50**, 3228—3237).—The reaction $4AlN+3C=Al_4C_3+2N_2$ was studied between 1774° and 1909° Abs. The equilibrium pressures are represented by the equation $\log p$ (mm.)$=12\cdot772-27697/T$, whence the free energy change at 1 atm. is 253,630—90·58T g.-cal. and the heat of reaction $-253,630$ g.-cal. For the reaction $Al_2O_3+3C+N_2=2AlN+3CO$ the free energy change is 127,065—67·57T g.-cal. at 1 atm. and the heat of reaction $-127,065$ g.-cal., in agreement with the observations of Fraenkel (A., 1913, ii, 509).

S. K. TWEEDY.

System Al(NO₃)₃–KNO₃–HNO₃–H₂O between 0° and 60°. G. MALQUORI (Gazzetta, 1928, **58**, 781—791; cf. A., 1928, 1328).—The solubility data for the ternary systems which are possible with the above components are completed by determining the isotherms for the system $Al(NO_3)_3-HNO_3-H_2O$ at 0°, 40°, and 60°. These results are combined to give a model which shows the equilibrium relationships for the quaternary system and defines the conditions in the Blanc process for the fractional crystallisation of potassium and aluminium nitrates from solutions of leucite in nitric acid.   O. J. WALKER.

Eutectic surfaces. W. WAHL (Förh. III nord. Kemistmötet, 1928, 180—183).—In four-component systems a eutectic surface results when three of the components form mixed crystals in which the fourth is insoluble, the surface being defined by the three binary eutectic points and the eutectic lines of the three ternary systems. A eutectic surface likewise results if the four components form mixed crystals in pairs, the pairs being mutually insoluble in one another. Systems of the latter type are of theoretical importance in dealing with the crystallisation of the igneous rocks, and have been hitherto little investigated. The author has studied the system naphthalene–β-naphthol–azobenzene–stilbene, in which the two binary systems naphthalene–β-naphthol and stilbene–azobenzene form mixed crystals which are insoluble in one another. The six binary and four ternary systems have been studied in detail, and the form of the eutectic surface has been determined. This latter cuts one side of the concentration tetrahedron close to the azobenzene corner, and consequently lies very obliquely in the tetrahedron. Eutectic surfaces of this type are to be expected in the systems involved in the crystallisation of the igneous rocks. One of the simplest cases is afforded by the meteoric stones consisting of anorthite and a pyroxene of the enstatite-augite series, containing three isomorphous components. The remaining igneous rocks contain as a rule several series of isomorphous components. In general, if the rocks crystallise so rapidly that equili-

brium is not attained, then crystallisation takes place mainly along the paths leading to the eutectic surface (volcanic rocks), but when equilibrium can be established the final crystallisation takes place along eutectic surfaces (plutonic rocks).

H. F. HARWOOD.

Heat capacity and entropy of barium bromate from 16° to 300° Abs. Entropy of bromate ion. B. S. GREENSFELDER and W. M. LATIMER (J. Amer. Chem. Soc., 1928, **50**, 3286—3290).—The heat capacities of barium bromate monohydrate were measured between 16·36° and 295·88° Abs. by the method previously described (A., 1928, 1096). The absolute molal entropy of this salt at 298·1° Abs. was calculated as 80·72 g.-cal./1°. The molal heat and free energy of solution are 15064 and 7171 g.-cal. at 25°, whence the entropy of solution is 26·48 g.-cal./1°, and the entropy of the bromate ion 43·6 g.-cal.|1°.

S. K. TWEEDY.

Calorimetric investigations. II.b. Benzoic acid as a standard for the calibration of bomb calorimeters. P. E. VERKADE (Chem. Weekblad, 1928, **25**, 666—667; cf. ibid., 1923, **20**, 513; A., 1922, ii, 740).—A critical account of the recent determinations of the heat of combustion of benzoic acid by Roth, Doepke, and Banse (A., 1928, 712) and by Jaeger and von Steinwehr (ibid., 1096).

S. I. LEVY.

Calorimetric researches. XV. Thermochemical study of cycloparaffins and their derivatives. I. Experimental data for five- and six-membered cyclic diols. P. E. VERKADE, J. COOPS, jun., C. J. MAAN, and (FRAU) A. VERKADE-SANBERGEN (Annalen, 1928, **467**, 217—239).—The heats of combustion of several pairs of cis- and trans-1 : 2-diols have been determined by methods previously described (A., 1925, ii, 490; 1926, 893), the values being based on that of benzoic acid, 6324 g.-cal. ¹⁵/g. (air) (A., 1925, ii, 871). The following numbers give the molecular heats of combustion (kg.-cal. 15°) at constant volume, Q_v, the figures in parentheses being the values at constant pressure, Q_p: cis-cyclopentane-1 : 2-diol, b. p. 79°/1·5 mm., 695·2 (696·0); trans-cyclopentane-1 : 2-diol, setting pt. 53·7°, 693·3 (694·1); cis-1-methylcyclopentane-1 : 2-diol, b. p. 95°/7 mm., 846·5 (847·6); trans-1-methylcyclopentane-1 : 2-diol, m. p. 64·8—65·6°, 844·2 (845·3); cis-1-phenylcyclopentane-1 : 2-diol, m. p. 64·6—65·4°, 1412·6 (1414·1); cis-hydrindene-1 : 2-diol, m. p. 107·6—107·8°, 1097·5 (1098·4); labile cis-hydrindene-1 : 2-diol., m. p. 100·5—101·5°, obtained by hydrolysis of the cis-1 : 2-diacetate, 1098·6 (1099·5); trans-hydrindene-1 : 2-diol, m. p. 158·6—159·6°, 1095·8 (1096·7); cis-1 : 2 : 3 : 4-tetrahydronaphthalene-1 : 2-diol, m. p. 102·5—103·5°, 1249·6 (1250·8); trans-1 : 2 : 3 : 4-tetrahydronaphthalene-1 : 2-diol, 1248·3 (1249·5); cis-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 3-diol, m. p. 124·2—125°, 1249·7 (1250·8); trans-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 3-diol, m. p. 135·5—136°, 1248·4 (1249·5); cis- + trans-1 : 2 : 3 : 4 - tetrahydronaphthalene - 2 : 3 - diol, m. p. 141—142·4°, 1247·7 (1248·9); cis-cyclohexane-1 : 2-diol, m. p. 98·4—99·2°, 840·4 (841·6); trans-cyclohexane-1 : 2-diol, m. p. 103·6—104·4°, 841·4 (842·6); cis-1-methylcyclohexane-1 : 2-diol, m. p.

67·5—68·5°, 991·1 (992·6); *trans*-1-methyl*cyclo*hexane-1 : 2-diol, m. p. 84—85°, 993·6 (995·1); *cis*-1-phenyl-*cyclo*hexane-1 : 2-diol, m. p. 95·5—96°, 1561·4 (1563·1); *trans*-1-phenyl*cyclo*hexane-1 : 2-diol, m. p. 99—99·5°, 1562·3 (1564·0).

The *cis*-diols in the *cyclo*pentane and *cyclo*hexane series have lower m. p. than the corresponding *trans*-diols. Permanganate oxidation of *cyclo*pentenes and *cyclo*hexenes yields the *cis*-compounds, whilst the *trans*-forms are obtained by acid hydrolysis of the corresponding oxides. The *cis*-derivatives form acetone compounds and with boric acid in presence of potassium hydroxide give crystalline complexes. The *trans*-forms do not form such derivatives. A critical discussion on the structure of *cyclo*paraffins is to be published. H. BURTON.

Constitution and thermochemistry. A. GOS-SELIN and M. GOSSELIN (Compt. rend., 1928, **187**, 1050—1052).—The formulæ derived from Werner's theory and the theory of partial valency are shown to be in accord with the additivity of the heats of linking of the atomic groups. These thermal data may be obtained from the heats of separation of simple binary or ternary compounds, and the heat of formation of the complex compound then derived from its formula. The heats of formation of 38 organic and inorganic compounds have been calculated from the values of the heats of atomic dissociation of the 17 elements concerned, and the values obtained are shown to be in agreement with experimental results. J. GRANT.

Moving boundary method applied to the measurement of the absolute velocity and the transport number of ions and of the rate of migration of colloidal particles. J. N. MUKHER-JEE (J. Indian Chem. Soc., 1928, **5**, 593—607).—When a homogeneous solution AR has two indicator solutions BR and AR', of lower density, on its surfaces the ions A and R will be moving at the two boundaries ←—AR|BR and AR'|AR—→, through a uniform ionic environment, and if the potential gradient, or the current density and the concentration, in the solution AR of constant concentration be known their transport numbers can be determined, because although the drag at the boundary may have a disturbing effect its magnitude will be very small inside the electrolyte AR. The conditions at the boundary will not be governed by Kohlrausch's equations. In this respect the current density and the transport numbers of the anion in the two layers are important factors. It is shown that even in those cases in which it is possible to determine the transport numbers by the boundary method the movement of the boundary does not necessarily give the correct mobilities of both ions unless the transport number of the common ions has the same value in both electrolytes. In extending these considerations to the determination of cataphoretic velocities it would appear that the theoretical basis of such measurements must rest on securing a uniform ionic environment during the movement of the colloidal particles. F. G. TRYHORN.

Theory of the mobilities of the hydrogen and hydroxyl ions in aqueous solution. E. HÜCKEL (Z. Elektrochem., 1928, **34**, 546—562).—It is assumed that the reaction $H_3O^+ + H_2O = H_2O + H_3O^+$ pro-

ceeds, without heat exchange, with a frequency which increases as the temperature is raised. A model is adopted for the H_3O^+ ion which leads to a deduction of the proportionality between mobility and field strength (Ohm's law), and an expression is deduced for the velocity of the H_3O^+ ions in unit field. The two terms of the expression relate to the motion of the ions as a whole and to the transference of protons according to the above equation, respectively. Expressions are also deduced for the mean life of the H_3O^+ ion, which is of the order of 3×10^{-11} sec. at the ordinary temperature. The theory applies equally well to hydroxyl ions, the assumed reaction being $OH' + H_2O = H_2O + OH'$. Suggestions are offered for testing the theory experimentally. In certain non-aqueous solutions the usual transport process may be accompanied by another, anomalous transport process. S. K. TWEEDY.

Incompatibility between theories of complete dissociation and migration data for bivalent ions. J. W. McBAIN and P. J. VAN RYSSELBERGE (J. Amer. Chem. Soc., 1928, **50**, 3009—3017).—Migration experiments with salts of cadmium, magnesium, lithium, potassium, and calcium in 0·05M-solution in presence of a large excess of anion indicate that the excess of anion combines with undissociated salt molecules to form complex ions. Salts containing multivalent ions, therefore, cannot be completely dissociated in solution except at extreme dilution (MacInnes and Cowperthwaite, A., 1927, 1031). S. K. TWEEDY.

Electrical conductivities of uni-univalent salts in benzonitrile. A. R. MARTIN (J.C.S., 1928, 3270—3293).—The conductivity of solutions of certain uni-univalent inorganic salts in benzonitrile has been determined using a pure sine wave alternating current of 1000 cycles per sec. Tables are given showing the conductivities of potassium, sodium, and lithium iodides, lithium bromide, and silver nitrate at various concentrations and temperatures. The viscosity of benzonitrile over the same temperature range has also been measured and it is found that Λ_0 is directly proportional to the fluidity of the solvent. The results are discussed from the point of view of the Debye–Hückel–Onsager theory, postulating incomplete dissociation which conforms to the mass action law, and it is shown that the variation of conductivity with concentration can be satisfactorily explained on this basis. In very dilute solutions dissociation is complete and it is only the coulomb forces between the ions which determine their mobilities. J. L. BUCHAN.

Electrical conductivity as a criterion of type of combination. G. VON HEVESY (Z. Elektrochem., 1928, **34**, 463—472).—The question is discussed, in the light of previous work by the author (cf. A., 1926, 667; 1927, 815; 1928, 112), from the point of view of solid diffusion and conductivity in the molten state. S. K. TWEEDY.

Dispersion of the conductivity of strong electrolytes. P. DEBYE and H. FALKENHAGEN (Z. Elektrochem., 1928, **34**, 562—565).—A short account of the above phenomenon together with the authors' theory is given (cf. A., 1928, 596, 957). S. K. TWEEDY.

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System aluminium bromide–potassium bromide in benzene. W. A. PLOTNIKOV and S. JAKUBSON (Z. physikal. Chem., 1928, **138**, 251—259).— Solutions of aluminium bromide in benzene possess only very slight electrical conductivity, but the conductivity of mixed solutions of aluminium bromide and potassium bromide is considerable. If the amount of potassium bromide in these latter solutions is kept constant, and the amount either of benzene or of aluminium bromide increased, the conductivity falls, whilst if the amount of potassium bromide is increased and the amounts of benzene and aluminium bromide remain the same, the conductivity rises. Benzene solutions of aluminium bromide contain principally Al_2Br_6 molecules; addition of potassium bromide to such solutions causes a rise in the f. p., from which it is concluded that further polymerisation accompanied by complex formation occurs. When the mixed solution is electrolysed, metallic aluminium separates at the cathode, the decomposition tension being 1·9 volts. R. CUTHILL.

Electrochemistry of solutions of phosphorus pentachloride in bromine. W. A. PLOTNIKOV and S. JAKUBSON (Z. physikal. Chem., 1928, **138**, 235—242).—The specific conductance of solutions of phosphorus pentachloride in bromine first increases with increase in the chloride concentration, then passes through a maximum, and falls until the point of saturation of the solution is reached. A maximum is present also on the concentration–molecular conductivity curve, but is preceded by a minimum. This anomalous behaviour may be explained by supposing that with increasing dilution ionisable complexes of the type $nPCl_5,mBr_2$, which are present in concentrated solutions, break down into the non-ionised components, and finally with further dilution the chloride ionises. When the solution is electrolysed chlorine is liberated at the anode approximately in accordance with Faraday's laws, and the current passing is directly proportional to the voltage applied. R. CUTHILL.

Electrode potential of nickel. III. Mechanism of the re-activation of the passive state of nickel. K. MURATA (Bull. Soc. Chem. Japan, 1928, **3**, 267—276; cf. A., 1928, 846).—In a discussion of previous experimental results the reactivating action of hydrogen on a nickel electrode which has been affected by oxygen is attributed to the catalysing action of the nickel on the union of hydrogen and oxygen. In this process the superficially oxidised nickel is reduced. Thermodynamically it is deduced that the equilibrium conditions in the nickel half-cells are expressed by $p_{H_2} \times a_{Ni^{..}} \times a_{OH'}^2 = 10^{-19\cdot56}$, whence it is calculated that when the activity product ($a_{Ni^{..}} \times a_{OH'}^2$) is equal to the solubility product of the nickelous hydroxide the corresponding partial pressure of hydrogen is 0·22 atm. This is the critical pressure above which equilibrium can alone be established and below which nickel will tend to go into solution with the precipitation of nickelous hydroxide until p_{H_2} rises to the critical value. The changes with time of the $E.M.F.$ of cells prepared in an atmosphere of hydrogen or nitrogen are explained by the above behaviour.

The abnormally low potentials obtained by some previous workers are attributed to the reduction by hydrogen of superficially oxidised nickel with the production of a layer of extremely finely-divided nickel. Calculations have been made of the free energy changes occurring at nickel electrodes with the following results : $Ni(s)+O_2+H_2=Ni(OH)_2(s)$, $\Delta F_{298}=-112228$ g.-cal. ; $Ni^{..}+2OH'=H_2+Ni(s)+2H_2O$, $\Delta F_{298}=-26695$ g.-cal. ; $NiO(s)+H_2=Ni(s)+H_2Ol$, $\Delta F_{298}=-6752$ g.-cal. ; $Ni(OH)_2(s)+H_2=Ni(s)+2H_2O(l), \Delta F_{298}=-892$ g.-cal. ; $Ni^{..}+2OH'=Ni(OH)_2(s)$, $\Delta F_{298}=-25800$ g.-cal. ; $Ni^{..}+2OH'=NiO(s)+H_2O(l)$, $\Delta F_{298}=-19940$ g.-cal. ; $NiO(s)+H_2O(l)=Ni(OH)_2(s)$, $\Delta F_{298}=-5860$ g.-cal.
F. G. TRYHORN.

P.D. at the surface of separation between metal and air. (FRL.) M. ANDAUER (Z. physikal. Chem., 1928, **138**, 357—368).—By the method previously employed (A., 1927, 316) a large number of metals have been examined. Contrary to the earlier observations, the metal–air $P.D.$ is not the same for all metals and cannot therefore be neglected. It also varies with the amount of ionisation of the air. Attempts have been made to determine the absolute $P.D.$ by heating the metal above 180° to remove any film of water at the surface. For the same piece of metal the value obtained is reproducible, but it varies with different samples of the same metal and with the treatment. Attempts to determine the absolute potential of the decinormal calomel electrode gave the value −0·26 volt, which differs by 0·83 volt from the value previously found (*loc. cit.*). M. S. BURR.

Effect of gases on the electrical double layer of aqueous solutions. A. BÜHL (Ann. Physik, 1928, [iv], **87**, 877—908).—A new method for investigating the double layer is described which makes use of the measurement of the $P.D.$ of the layer. It is thus possible to find the effect of gases on the layer by a static method, the surface being undisturbed. It is first shown that when gaseous nitrogen, hydrogen, or oxygen is dissolved in pure water or in dilute solutions of alkali chlorides there is no change in the conductivity. The gases form no ions, and they do not affect the degree of dissociation of the water or salt solutions. Hence the diffusion potential at the boundary between a solution containing, and one not containing, dissolved gas is zero. This fact renders the method possible. The apparatus used is described. It was found that the gas in the space above the liquid had no effect on the $P.D.$ of the double layer at the surface of aqueous solutions. The $P.D.$ of the double layer is, however, increased by dissolved gases, the increase being dependent on the concentration of the electrolyte. The $P.D.$ varies with the time of absorption, finally reaching a steady value. An attempt is made to use these facts to explain the nature of the double layer. Gas absorbed from the space above the solution forms at first only an electrically neutral " capillary layer." Gas dissolved in the liquid is positively adsorbed on the surface. A. J. MEE.

Metallic–non-metallic electrode pairs. B. KAMIENSKI (Z. physikal. Chem., 1928, **138**, 345—348).—Carborundum forms an ideal inert electrode the potential of which is almost independent of the

concentration of electrolytes in the solution in which it is placed. Such an electrode, combined with a metallic electrode, should form a suitable electrode pair for electrometric titration. The method of construction of a suitable form of carborundum electrode is described. M. S. BURR.

Electrocapillary curve of mercury. A. FRUMKIN and A. OBRUTSCHEVA (Z. physikal. Chem., 1928, **138**, 246—250).—The method used by Bennewitz and Delijannis to determine the electrocapillary curve of mercury (A., 1927, 316) is defective, for there is probably no simple relation between the potential of dropping mercury and that of stationary mercury under the conditions of their experiments. If the two are placed in conducting communication and their common potential is measured with an electrometer, the maximum on the electrocapillary curve observed by Bennewitz and Delijannis is absent.
R. CUTHILL.

Explanation of the "electro-capillary" Becquerel phenomenon. H. FREUNDLICH and K. SÖLLNER (Z. physikal. Chem., 1928, **138**, 349—356).—If a solution of a metallic salt is separated by a porous wall from a solution which gives an insoluble precipitate with the metal ion, it is found that separation of metal takes place if (a) the precipitate behaves partly or wholly as a metallic conductor, or (b) the $E.M.F.$ of the concentration chain between the higher concentration of the metal ions in the metal salt solution, and the very low concentration in the other solution, is greater than the decomposition potential leading to the separation of the metal. If, in place of the sodium sulphide solution combined with a metal salt solution which was studied by Becquerel, a sodium selenide solution is employed, separation of metal takes place very readily because the copper selenide is a metallic conductor. The porous wall is not necessary, except as a support to the precipitate. The necessity for the presence of an anodic depolariser in the case of pairs such as silver nitrate–potassium hydroxide, and copper sulphate–potassium hydroxide, studied by Becquerel, is to be explained by a reduction of the decomposition potential until requirement (b) is fulfilled. No copper separates from the pair copper sulphate–potassium ferrocyanide because there is no metallic conduction. M. S. BURR.

Preparation of photo-electric cells of thallium. Q. MAJORANA and G. TODESCO (Atti R. Accad. Lincei, 1928, [vi], **8**, 9—14).—Photo-electric cells have been constructed with thallium sulphides prepared by heating mixtures of thallium and sulphur under varying conditions and in different atmospheres. Various media for the support of the sulphide were investigated, the best being, respectively, Wood's metal, and an amalgam of equal parts of cadmium, zinc, tin, and mercury, which hardens after some hours. Details are given of the preparation and performance of photo-electric cells made from these materials. F. G. TRYHORN.

Properties of Fournier's photo-electric cells. R. DUBOIS (J. Phys. Radium, 1928, [vi], **9**, 310—336).—These cells make use of a fine crystalline deposit of metallic sulphides, the resistance of which falls immediately it is illuminated. The cells differ in properties from selenium cells. They can be used with light fluctuating at high frequencies (above audible frequency). The properties of these cells are complex, and a number of experiments are described to investigate their mechanism. A theory giving a simple explanation of dissymmetric photoconductivity is propounded and discussed. Some applications of the cells are given. A. J. MEE.

Electrochemical polarisation of platinum. E. I. SPITALSKI and V. V. PITSCHETA (J. Russ. Phys. Chem. Soc., 1928, **60**, 1351—1381).—Rotation has no influence on the velocity of depolarisation of platinum anodes. The depolarisation potential P_1 obtaining while the current is passing is distinguished from that found after the current has ceased (P_2); the latter potential is inversely proportional to the density of current previously used. The value of P_1 varies with the area of the anode. The processes taking place in the anode are characterised by P_2 rather than by P_1. The addition of chemical depolarisers, such as salts of iron, makes little difference to the value of P_1 at currents stronger than 0·033 amp./sq. cm.; at 0·005 amp./sq. cm. P_1 is, however, considerably smaller than in the absence of iron. The previous history of the anodes affects the magnitudes of P_1 and P_2 obtained. The above phenomena are explained on the basis of dissolution in platinum of atomic and molecular oxygen. R. TRUSZKOWSKI.

Corrosion and residual current. I. Significance of the residual current in the dissolution of metals. II. Significance of the residual current in the deposition of metals. F. TÖDT (Z. Elektrochem., 1928, **34**, 586—591, 591—595).—I. The current densities for pairs of metals in 0·1N-hydrochloric acid or in standard acetate solution (p_H 4·62) have been measured (cf. Centnerszwer and Straumanis, A., 1926, 131). In general the current strength is proportional to the area of the nobler metal and approximately independent of that of the other metal. It is independent of the overvoltage and, unless the internal resistance of the cell is sufficiently large, is increased by agitation of the electrolyte. The diminished current density observed when the electrolyte is heated and then covered with a layer of paraffin regains its original value when the oil layer is broken. The current density observed when air is bubbled through the solution is increased if the air is replaced by oxygen, and decreased if it is replaced by hydrogen. Addition of hydrogen peroxide also produces a large increase in current strength. The electrochemical process involves excess dissolution at the surface of the less noble metal; the process is maintained at the other electrode by the oxygen which diffuses to the surface of the latter. The results indicate that the process of corrosion involves a residual current of an intensity which depends on the quantity of oxygen which diffuses to the metal surface. The results of several previous investigations (e.g., those of Liebreich, A., 1928, 483) are explained on the basis of this theory.

II. The limited time during which a platinum electrode immersed in N-cadmium sulphate (with or without acid) assumes the cadmium potential is investigated. The higher the current density the smaller is

the amount of cadmium necessary to produce the cadmium potential for a given duration (cf. Oberbeck, Ann. Physik, 1887, **31**, 337). The phenomenon is adequately explained by means of the above residual current theory. The *P.D.* between platinum and a platinum sheet to which a small piece of cadmium has been fused is measured for three different electrolytes by means of an improved valve method in which the variations of the valves are automatically compensated, and the range of measurement is widened without increasing the grid potential.　　　S. K. TWEEDY.

Passivity of metals.　W. J. MÜLLER (Z. Elektrochem., 1928, **34**, 858).—A correction (cf. A., 1928, 1319).　　　　　　　　L. S. THEOBALD.

Passivity [of chromium].　(FRL.) A. M. HASEBRINK (Z. Elektrochem., 1928, **34**, 819—829; cf. Schmidt, A., 1923, ii, 732).—Chromium which has been previously rendered passive by treatment with nitric acid becomes active when heated in dry nitrogen at 500° for 30 min., and retains this activity for a definite time when preserved in the gas, but eventually becomes passive again. Chromium which has been treated with hydrochloric acid and allowed to become passive by exposure to air is also activated by treatment with nitrogen at 500°, but remains passive for an indefinite time in this gas at the ordinary temperature. Similar behaviour is shown by chromium which has been heated and kept in hydrogen, the formation of an oxygen layer in the last case being impossible. Nitrogen, hydrogen, and carbon dioxide in the molecular state do not activate chromium which has been passivated, and long contact with these gases in the cold does not passivate chromium which has been activated by scratching with a diamond. The passive state is brought about only by oxygen, and the readiness with which different specimens of chromium are activated or passivated depends on the nature and content of the occluded gases. These are not the cause of passivity or activity, but only modify the rate at which the oxygen layer, the true passivating agency, is formed. Iodine can also activate chromium, but, contrary to Hittorf, it can never render this metal passive.

Rubbing of the chromium with emery in an indifferent atmosphere is accompanied by a fall and then a rise in potential of the metal. Finally, after frequent rubbing a lower end-value is reached and this is independent of the nature of the atmosphere in which the rubbing takes place. Introduction of oxygen into the electrolyte raises the potential, which falls on rubbing the surface, and then quickly reaches its higher value. Prolonged and frequent rubbing is required to reduce the potential to its original value. Electrolytic hydrogen and oxygen change the potential markedly. The low potential arises from the hydrogen-free layer of the metal exposed by rubbing, and the large increase in potential produced by the passage of oxygen over the chromium supports the oxygen-layer theory of passivity.

Sheets of iron behave differently, according to their composition and treatment, in the electrolysis of potassium nitrate solutions; some are active and some are passive at low current densities. Generation of hydrogen or oxygen at one side of the sheet is accompanied by an apparent increase in electrolysis, but it is shown that this is a mechanical effect of the evolved gas which removes splinters of iron from the surface.

The results disprove the surface tension theory of Hittorf and Schmidt (*loc. cit.*) and the hydrogen theory of passivity, but support the oxygen-layer theory.
　　　　　　　　　　　　　L. S. THEOBALD.

Theory of passivity. III. Current density–time curves in cases of coating passivity.　W. J. MÜLLER and K. KONOPICKY (Monatsh., 1928, **50**, 385—391).—Further investigation of the current density–time curves (A., 1928, 1319) shows that the coating of such an electrode proceeds only to about 99% according to the law of surface deposition (*ibid.*, 247). From this point further growth of the layer is in thickness and not in area. The values of A in the formula $t = C + A[-1/(i_0 - i) + 2 \cdot 3/i_0 . \log (i_0 - i)/i]$ do not remain constant but show a steady increase, indicating that with considerable deposition another form of coating process is obtained. For the relation between current density and time in cases of growth of thickness the authors derive the formula $t - t_0 = B(1/i^2 - 1/i_0^2)$, where $B = \chi E F_0 s/k(1 - u)$ (all the terms of which with the exception of F_0 are measurable electrochemical data). The validity of this was demonstrated for copper (*ibid.*, 247), and for lead in sulphuric acid at an *E.M.F.* below that necessary for the formation of lead peroxide, and in part also for aluminium. The values of the active free surface (F_0) for copper and lead are found to be $0 \cdot 8 \times 10^{-3}$ cm.^{2} and $0 \cdot 93 \times 10^{-3}$ cm.^{2}, respectively, agreeing within the limits of experimental error with those deduced theoretically.　　　　　　　　H. BURTON.

Calculation of velocity coefficients. II.　A. L. T. MOESVELD and W. A. T. DE MEESTER (Z. physikal. Chem., 1928, **138**, 226—234).—The objections raised by Wagner (A., 1925, ii, 406) and Schmid (A., 1926, 480) to the method of determining velocity coefficients described previously (A., 1923, ii, 141) are without foundation. The modified method proposed by Schmid is of inferior accuracy.　　R. CUTHILL.

Ignition of gas by spark and its dependence on the nature of the spark.　T. TERADA and K. YUMOTO (Proc. Imp. Acad. Tokyo, 1928, **4**, 467—470).—A gaseous mixture containing 16% of carbon monoxide and 84% of air is more easily ignited by means of an inductive spark than by a capacity spark of the same energy.　　　W. E. DOWNEY.

Thermal decomposition of ozone at low pressures.　E. H. RIESENFELD and H. J. SCHUMACHER (Z. physikal. Chem., 1928, **138**, 268—285).—The thermal decomposition of ozone mixed with oxygen has been studied at 85° and 95° for partial pressures of ozone varying from about 60 to 6 mm. At these pressures, the unimolecular reaction predominates, the bimolecular reaction which occurs simultaneously at higher pressures (A., 1928, 24) being of little account, and the velocity coefficients of both reactions are not appreciably influenced by variations in the partial pressure of oxygen or by the presence of argon. Nitrogen, however, and still more carbon dioxide accelerate the bimolecular reaction. Alteration in the ratio of the surface to the volume of the reaction vessel affects the reaction velocity much less than it

would if the unimolecular reaction were purely a wall reaction, so that it seems that the main reaction is homogeneous, although under ordinary conditions there appears to be some slight wall effect in addition. From the facts that in the experiments of Perman and Greaves (A., 1908, ii, 480) and of Griffith and McKeown (A., 1925, ii, 1168) variation of the surface of the vessel affected the velocity considerably, and also that the observed velocities were exceptionally high, it appears probable that these authors' results were vitiated by the presence of catalysts in the gas or in the apparatus. The results of the present experiments for the unimolecular reaction may be considered to supersede those of Riesenfeld and Bohnholtzer (A., 1928, 24) on account of their greater accuracy.　　　R. Cuthill.

Explosion temperature of gas mixtures at various pressures. A. B. Sagulin [with G. Riabinin, Proskurnin, and A. Kowalski] (Z. physikal. Chem., 1928, **B, 1**, 275—291).—The relationship between temperature and minimum pressure p_m at which explosion occurs has been determined for a number of gaseous mixtures, and in all cases the relationships $\log (p_m/T) = A/T + B$ is valid, where A is a characteristic of the reaction and independent of the conditions thereof, and B a constant which usually has a minimum value when about 66% of one compound is present, increasing as the diameter of the vessel decreases. The following values of A have been determined: $H_2 + Cl_2$, 2500, $H_2 + Br_2$, 4000, $CS_2 + O_2$, 4000, $CH_4 + O_2$, 7000, $C_2H_6 + O_2$, 4200, $C_3H_8 + O_2$, 3800, $C_5H_{12} + O_2$, 2200; for the last three reactions A changes abruptly at 680° to a uniform value of 7000, i.e., that for methane and oxygen. The significance of the results is discussed.　　　H. F. Gillbe.

Gaseous explosive reaction at constant pressure. Effect of inert gases. F. W. Stevens (J. Amer. Chem. Soc., 1928, **50**, 3244—3258).—A more detailed account of an investigation of the kinetic effect of indifferent gases (nitrogen, helium, argon, carbon dioxide) on the reaction $2CO + O_2 = 2CO_2$ (cf. A., 1928, 1331). The velocity of propagation of the reaction zone is given roughly by $k'p_{CO}(p - p_{CO})a + \beta p_g$, where a is the fraction of oxygen in the initial components of partial pressure $p - p_{CO}$, p being the total pressure, β is a constant for a given indifferent gas, and p_g is the initial partial pressure of that gas.　　　S. K. Tweedy.

Striations in explosive flames. G. B. Maxwell and R. V. Wheeler (Nature, 1928, **122**, 995).—The frequency of striations in a photograph of the flame of a 3·35% pentane-air mixture at 4 atm. initial pressure ignited at one end of a horizontal cylinder was 1200 per sec., the value being independent of the composition and initial pressure of the explosive mixture, but varying inversely as the length of the vessel. Egerton and Gates' view that the striations are due to a stationary wave compounded of sound-waves reflected from the opposite end-plates of the cylinder is supported. The striated appearance of the flame during an explosion always preceded a "knock."　　　A. A. Eldridge.

Highly attenuated flames. III. M. Pólányi and G. Schay (Z. physikal. Chem., 1928, **B, 1**, 384).— A correction (cf. A, 1928, 1339). The nitrogen pressure

at which the sodium fluorescence is reduced to half is given as 20 mm. instead of 1·5 mm. This does not affect the conclusions. An error in calculation is also noted.　　　M. S. Burr.

Explosions in closed cylinders. I. Methane-air explosions in a long cylinder. II. Effect of length of the cylinders. W. A. Kirkby and R. V. Wheeler (J.C.S., 1928, 3203—3214; cf. Woodbury and others, J. Soc. Automotive Eng., 1921, **8**, 209; Morgan, A., 1927, 630).—Methane-air mixtures were exploded in a cylinder 200 cm. long and 10 cm. in diameter and records obtained of the movement of flame and the development of pressure. A close correlation was found between pressure development and flame movement, increase of pressure being always accompanied by increase in the velocity of propagation of the flame and vice versa. When the position of the point of ignition was varied, the maximum pressure was recorded with ignition at the middle point of the cylinder. No higher pressure was obtained with dual ignition, although a sustained period of maximum pressure occurred with the two ignition points a considerable distance apart.

When methane-air mixtures containing 8—11% of methane were ignited at one end of the cylinder the flames became strongly vibratory towards the end of their travel. Experiments on the ignition of 9·5% methane-air mixtures in a cylinder the length of which could be varied showed that the explosion ceased to become vibratory when the length was less than 140 cm.　　　F. J. Wilkins.

Explosions in closed cylinders. III. Movement of flame. O. C. de C. Ellis and R. V. Wheeler (J.C.S., 1928, 3215—3218; cf. preceding abstract).—In order to study further the manner of movement of flame in methane-air mixtures, "snapshot" photographs of the similar flames obtained by the ignition of carbon monoxide-oxygen mixtures were taken. The results permit of an explanation of the close correlation found in the earlier work between pressure development and flame movement.　　　F. J. Wilkins.

Effect of anti-knock materials on the speed of initial uniform movement of the flame in hydrocarbon-air mixtures. Y. Nagai (Proc. Imp. Acad. Tokyo, 1928, **4**, 525—528).—The speed of the initial uniform movement of the flame was determined photographically, using tubes 26 cm. in diameter and 108 cm. long, the hydrocarbon being obtained from redistilled petrol and its proportion in the mixture varying between 1·0 and 4·0 mol.-%. Diethyl selenide, lead tetramethyl, and tin tetramethyl were used as anti-knock materials, in proportions varying from 0·2 to 1·5 mol.-%.

In each case the speed of the initial uniform movement decreased to a minimum value and then remained constant as the concentration of anti-knock material increased. The addition of the anti-knock material is believed to raise the calculated minimum temperature at which the flame can be propagated until that of the anti-knock material is reached, when the latter itself burns and can therefore raise the flame propagation temperature of the hydrocarbon no further.　　　S. J. Gregg.

Decomposition of persulphates in aqueous solution. A. KAILAN and E. LEISEK (Monatsh., 1928, **50**, 403—428; cf. Kailan and Olbrich, A., 1927, 213).—The velocity of decomposition of sodium persulphate, alone and with the addition of sodium hydrogen sulphate, sodium sulphate, nitrate, or hydroxide, phosphoric acid, disodium hydrogen and trisodium phosphates, or potassium hydroxide, and of potassium persulphate, alone and with the addition of potassium nitrate, potassium and sodium hydroxides, has been studied at 99·4° by the method previously described (*loc. cit.*). For numerical data the original must be consulted, but the results show that in the autodecomposition of sodium persulphate the value of the unimolecular coefficient decreases with increasing original concentration; the values found are 2—8% higher than those for potassium persulphate (cf. *loc. cit.*). Addition of neutral sulphate causes a larger decrease in the coefficient than admixture of hydrogen sulphate (cf. Green and Masson, J.C.S., 1910, **97**, 2083). Comparison of the rates of decomposition of sodium and potassium persulphates with added sodium or potassium sulphate indicates that sodium ions retard the decomposition of the persulphate ions to a smaller extent than potassium ions. This is verified by the fact that increasing concentration of added sodium hydroxide to sodium persulphate causes an increase in the velocity of decomposition (cf. Levi and Migliorini, A., 1907, ii, 81) to a greater extent than potassium hydroxide. Nitrate and phosphates accelerate decomposition. In the series of sodium persulphate decompositions the agreement between the observed unimolecular coefficients and those calculated from an intrapolation formula expressed as a function of the concentrations of sodium, nitrate, hydroxide, and phosphate (HPO_4'') ions, and the difference between the hydrogen- and sulphate-ion concentrations, is fairly good.

The decomposition of approximately $0·1N$-potassium persulphate solution in $0·6$—$14N$-sulphuric acid at 25° was also examined, using the method described by Palme (A., 1920, ii, 685). The qualitative detection of Caro's acid is possible with $0·35N$-acid. In $2·7$ or $14N$-sulphuric acid the amount of hydrogen peroxide present is 1—2 or 6—12% of the then existing Caro's acid. The unimolecular velocity coefficient for the decomposition of persulphuric acid, with or without formation of Caro's acid, is shown to be a function of the sulphuric acid concentration.   H. BURTON.

Influence of concentrated electrolytes on the course of chemical processes. Potassium permanganate. M. BOBTELSKI and D. KAPLAN (Z. anorg. Chem., 1928, **177**, 323—336).—The velocity of decolorisation of a solution of potassium permanganate containing sulphuric acid and oxalic acid in presence of various chlorides, nitrates, and sulphates has been determined. Chlorides, especially of the alkali metals, have a much greater catalytic influence than have nitrates or sulphates. For the sulphates, the effect decreases in the order lithium, magnesium, ammonium, sodium, potassium, the last three functioning anticatalytically. Ammonium nitrate is a powerful catalyst, sodium nitrate has zero influence,

and potassium nitrate retards the reaction. The chlorides are moderately sensitive to temperature, the sensitiveness increasing in the order ammonium, potassium, magnesium, aluminium, whereas the influence of the nitrates varies but little with temperature, and that of the sulphates to a slightly greater degree than is the case with the nitrates. The temperature effect is maximal over the range 5—25°. The salts exhibiting the greatest temperature effect also show the greatest variation in their influence with concentration; ammonium nitrate is in this respect exceptional. The concentration effect decreases in the order aluminium chloride, cadmium sulphate, magnesium chloride, zinc chloride, zinc sulphate, potassium chloride, ammonium chloride, ammonium nitrate, sodium chloride, ammonium phosphate; lithium sulphate, magnesium sulphate, potassium sulphate, ammonium sulphate, sodium sulphate, potassium nitrate, sodium nitrate; and, in hydrochloric acid, calcium chloride, strontium chloride, barium chloride; the alkaline-earth chlorides come between magnesium chloride and potassium chloride in the first series.   H. F. GILLBE.

Molecular formula and constitution of hypophosphoric acid. A. ROSENHEIM and H. ZILG (Z. physikal. Chem., 1928, **139**, 12—20).—Measurements of the velocity of decomposition of sodium hydrogen hypophosphate by $0·5N$- and N-sulphuric acid at 60°, and by $0·5N$- and $0·25N$-sulphuric acid at 100° show the reaction to be unimolecular and dependent on the concentration of hydrogen ions. The decomposition of hypophosphoric acid should therefore be represented by the equation $H_4P_2O_6 + H_2O \rightleftharpoons H_3PO_3 + H_3PO_4$, and not by the equation $2H_2PO_3 + H_2O \rightleftharpoons H_3PO_3 + H_3PO_4$. The formula, $H_4P_2O_6$, thus obtained for the acid disagrees with that from the alkyl hypophosphates, R_2PO_3 (Rosenheim, A., 1910, ii, 708). The structural formula of hypophosphoric acid is discussed and a co-ordination formula $[O_3P \ldots PO_3]H_4$ assigned to it. In a comparison of the pyrophosphates and the hypophosphates the new *compounds*, $Na_4P_2O_6,1·5H_2O$, $Na_2(NH_4)_2P_2O_6,7H_2O$, $NH_4[CrP_2O_6],5H_2O$, $(NH_4)_2[CuP_2O_6],4H_2O$, and $Na_2[NiP_2O_6],12H_2O$, are described. The analogy between the composition and properties of these two classes of salt is complete only in a few cases. A transition temperature at 74·6° has been observed between the new hydrate and sodium hypophosphate decahydrate.   L. S. THEOBALD.

Rate of oxidation of quinol by oxygen. H. VON EULER and E. BRUNIUS (Z. physikal. Chem., 1928, **139**, 615—630).—A kinetic study of the rate of oxidation of quinol in a solution saturated with oxygen. The rate was measured by passing oxygen through a $0·1M$-solution to which a phosphate buffer solution had been added. The benzoquinone formed was determined by titration with titanous chloride. At constant pressure of oxygen the rate of reaction over the range of p_H investigated ($7·08$—$8·16$) is proportional to the square of the concentration of hydroxyl ions and also to the concentration of the doubly-charged quinol ions. For a given acidity the rate of oxidation is proportional to the concentration of oxygen; reaction takes place in a solution saturated

with oxygen five times as quickly as in one saturated with air.

The values of k[quinol]/[quinol^{--}] have been calculated from the experimental results for k and previously known figures for the dissociation constant. A good constant was obtained of which the average value was 5900. This gives a value of reactivity independent of oxygen pressure for $^-OC_6H_4O^-$ of $rq_{O_2} : [O_2] = 4.2 \times 10^7$.

The rate of oxidation of quinol in alkali solution is not checked by addition of potassium cyanide solution, showing that no iron ions or complexes function as catalysts. No evidence of the formation of hydrogen peroxide during the reaction was obtained.

It is shown that for quinhydrone electrodes in which there is large excess of either benzoquinone or quinol there are slight deviations from the usual formula for the electrode potential. R. N. KERR.

Velocity of hydrolysis of methyl mono- and dichloroacetates. A. SKRABAL and M. RÜCKERT (Monatsh., 1928, **50**, 369—384).—The velocity of hydrolysis of methyl chloroacetate by acid and alkali in aqueous solution and by water has been studied at 25°. The velocity coefficient for hydrolysis with hydrochloric acid (k_s) with the minute as the unit of time is 0.00507; for ammonia in presence of ammonium chloride (k_a) 8170, whilst for water (k_w) two values, 1.23×10^{-5} and 1.5×10^{-5}, are deduced, the former being considered the more probable. For methyl dichloroacetate the corresponding values are 14.03×10^{-3}, 1.7×10^5 (with disodium hydrogen phosphate), and 9.2×10^{-4}. In all the cases studied hydrolysis is much more rapid than with methyl, ethyl, or vinyl acetates. H. BURTON.

Piezochemical studies. XXIX. Effect of pressure on reaction velocity. Part played by the medium in homogeneous liquid systems. A. L. T. MOESVELD and W. A. T. DE MEESTER (Z. physikal. Chem., 1928, **138**, 169—225; cf. A., 1925, ii, 283).—In the case of homogeneous reactions occurring in solutions, the reaction velocity may be profoundly influenced by the attractions and repulsions existing between solvent molecules on the one hand and solute molecules on the other, for such forces, by bringing about deformation of the solute molecules, will, in general, affect their reactivity. It may be that one part of the solute molecule exerts an attraction on the solvent molecules greater than that exerted by the other part, so that with a mixed solvent partial local separation of the components is brought about, and as a result the deformation of the solute molecule is greater than is possible with a simple solvent. When a substance which is insoluble in a particular pure solvent is brought into solution by addition of a second solvent, the deformation will be maximal when the amount of the latter is only just sufficient to keep the solute in solution. If the external pressure is increased, effects due to intermolecular forces will be enhanced, owing to the molecules being brought into closer proximity to each other. It therefore seems probable that if in a mixed solvent medium in which a reaction is taking place the tendency for local differences in concentration to be set up can be opposed, e.g., by increasing the velocity of the molecules by raising the temperature, the effect of variations in pressure on the reaction velocity will be diminished. On the other hand, increase in the concentration of a solute will cause the system to approach more closely to heterogeneity, and the pressure coefficient of the reaction velocity ought therefore to rise. Such changes in concentration will also occur in the course of the reaction, so that even when the pressure remains constant the deformation, and consequently the velocity coefficient, will vary. Addition to the system of a foreign substance which causes partial separation of the solvent mixture will also cause the solute system to approach the point of separation, i.e., the deformation will increase. In order to test the truth of these conclusions, experiments have been made on the hydrolysis by sodium hydroxide of l-bornyl acetate dissolved in a 31.5% aqueous solution of ethyl alcohol, which contains just sufficient alcohol to keep the system homogeneous. The measurements were made at 17—32°, and under pressures of 1, 500, 1000, and 1500 atm., the progress of the reaction being followed by conductivity determinations. The pressure coefficient of the velocity coefficient is positive, and, as expected, decreases with rise in temperature. Addition of borneol or excess of the ester brings the system nearer to being heterogeneous, and the pressure coefficient consequently increases. Measurements of the rotatory power of the ester in aqueous-alcoholic solutions indicate that the optical activity is probably to some extent dependent on the composition of the solvent. R. CUTHILL.

Decomposition of formic acid by sulphuric acid. II. E. R. SCHIERZ and H. T. WARD (J. Amer. Chem. Soc., 1928, **50**, 3240—3243; cf. A., 1923, ii, 230).—The velocity of decomposition of formic acid by concentrated sulphuric acid (85—97%) over the temperature range 15—45° was investigated. The critical increment is practically constant over successive 10° intervals for all acid concentrations, in agreement with the conclusion that the critical increment is independent of temperature in isolated reactions. The temperature coefficient diminishes as the velocity coefficient increases. The sulphuric acid acts primarily as a dehydrating agent; the velocity coefficient is a continuous function of the percentage composition of the acid (Lichty, A., 1907, ii, 445). For equal acid concentrations, small quantities of water have a greater effect the higher is the temperature of decomposition. S. K. TWEEDY.

Polymerisation. I. Polymerisation of styrene. N. A. MILAS (Proc. Nat. Acad. Sci., 1928, **14**, 844—849).—The rates of absorption of oxygen by styrene, styrene and perbenzoic acid, styrene and anthracene, and benzaldehyde were measured at 110°. The oxidation of styrene alone showed an induction period of 10 min. The rate of oxygen absorption is increased by the addition of perbenzoic acid, but there is a corresponding increase in the rate of polymerisation. Anthracene, which is known to be an excellent absorber of light energy, when added to the styrene caused the oxidation to proceed at a relatively high rate, but completely inhibited the polymerisation. The anthracene alone, under the experimental conditions, was not oxidised. Anthracene will also

strongly inhibit the oxidation of the benzaldehyde formed by the oxidation of styrene. The reaction which takes place when styrene is oxidised in presence of anthracene shows selective inhibition. The polymerisation of styrene seems to be effected by energy which is liberated during the formation and subsequent reaction of the initial products of the oxidation with unoxidised styrene molecules.

A. J. MEE.

Absorption velocity of gases by liquids. S. HATTA (Tech. Rep. Tôhoku, 1928, 8, 1—25).— The rate of absorption of carbon dioxide by potassium hydroxide solution, when mixed with air, has been investigated. By using two independent stirrers the thicknesses of the gas and liquid films at the interface could be varied independently. The effects of changes of temperature, alkali concentration, and partial pressure of carbon dioxide were also studied. By considering the diffusion velocity through the double film, and the velocity of the chemical reaction, equations are obtained which are in good agreement with the experimental results. C. W. GIBBY.

Velocity coefficient of kinetic processes in heterogeneous systems as a function of temperature and intensity of agitation. W. HELLER (Rocz. Chem., 1928, 8, 445—474).—Measurements of the velocity of dissolution of plates of tin or cadmium in aqueous ferric chloride, or of magnesium in aqueous ammonium chloride, calculated according to the equation $K = (2.303 v/s . \Delta t) \log (a-x_1)/(a-x_2)$, where v is the volume of solution, s the surface of the plate, a the initial concentration of the reaction solution, and x_1 and x_2 are its concentrations at the beginning and end of an interval of time Δt, show that K is a linear function at constant temperature of the velocity of revolution n of the stirrer and, at constant n, of the temperature. It hence follows that the temperature coefficient of these reactions is independent of n. This dependence of K on temperature follows from Nernst's diffusion theory, assuming that the thickness of the adhesion layer is independent of temperature at constant value of n. K is given as a simultaneous function of n and t by the expression $K = (An + C_0) (t - J)$, where C and J are parameters characteristic of the given process without regard to the apparatus used, whilst A depends on both the process and the apparatus. It is possible by introducing the conception of a "normal" stirrer to eliminate the dependence on the given apparatus. Any value of K is taken as normal at any given temperature for any given apparatus, and the number of revolutions of another stirrer in another apparatus necessary to obtain the same value of K is determined. The A parameter can thus be made independent of the given apparatus, thereby rendering comparable results obtained on different apparatus. R. TRUSZKOWSKI.

Rate of dissolution of zinc in sulphuric acid under pressure. T. C. POULTER and G. E. FRAZER (Proc. Iowa Acad. Sci., 1927, 34, 215, 216).—Whilst surface condition, size, and shape of the pieces of zinc and local concentration of the acid are important, increase of pressure up to 6000 atm. has little effect. CHEMICAL ABSTRACTS.

Catalytic decomposition of hydrogen peroxide in an acid chlorine–chloride solution. II. Interpretation of the rate measurements in concentrated solution. R. LIVINGSTON (J. Amer. Chem. Soc., 1928, 50, 3204—3211).—The equation for the velocity of the above decomposition, $v = \chi[H_2O_2][H^{\cdot}][Cl]f_{HCl}^3$, where f is the activity coefficient and χ is a constant, is more accurately written $v = K[H_2O_2][H^{\cdot}][Cl]f_{HCl}^3 \times 10^{\mu k}$, where μ is the ionic strength and K, k are constants. This equation is supported by the experimental results previously obtained (A., 1926, 364). Further confirmation is obtained from determinations of the activity coefficients of hydrogen peroxide in solutions of sodium chloride and sulphate by means of partition experiments with isoamyl alcohol. The activity-rate theory does not appear to represent the facts. The results obtained in this and the analogous bromine reaction (A., 1926, 251) lend considerable support to the validity of Brönsted's reaction velocity theory.

S. K. TWEEDY.

Catalysis and processes of transformation of colloids. I. Catalysis of [decomposition of] hydrogen peroxide by ferric salts. II. Mechanism of hydrolysis of iron salts and the properties of colloidal hydrosols. III. Colloidal hydrogels of iron and their transformation. E. I. SPITALSKI, N. N. PETIN, and E. I. BUROVA (J. Russ. Phys. Chem. Soc., 1928, 60, 1271—1289, 1291—1316, 1317—1332; cf. A., 1925, ii, 53).—I. The catalytic action of ferric chloride on the decomposition of hydrogen peroxide is studied in slightly acid, neutral, and slightly alkaline solutions. In acid solutions a stable hydrosol of basic salt forms, in contrast to the precipitate which forms when ferrous sulphate is used. In spite of this difference, the reaction follows the same course in both cases, viz., in acid solution the velocity coefficient increases hyperbolically with increasing p_H, reaches a maximum at neutrality, and again falls as the reaction of the solution increases in alkalinity, attains a minimum value at a relative alkalinity expressed by $C_{NaOH}/3C_{Fe} = 0.8$, again rises to a second maximum at $C_{NaOH}/3C_{Fe} = 1.0$, at which p_H an iron hydrogel separates. This hydrogel is the actual catalyst in alkaline solution. It is concluded that in solution the ferric ion is the only catalyst able to decompose hydrogen peroxide present, but that the intermediate stages of the reaction are not sufficiently known to allow of the formation of any theories as to its mechanism.

II. The specific catalytic action of ferric ions on the decomposition of hydrogen peroxide affords the basis of a method for the examination of the mechanism of hydrolysis of iron salts and of the properties of colloidal hydrosols. The catalytic activity of ferric chloride hydrosols diminishes rapidly with time, whilst the conductivity of such solutions remains approximately constant, and this effect is the more marked the greater is the alkalinity of the medium. The gel precipitated from concentrated ferric chloride solutions by the addition of alkali acts as a powerful anticatalyst if added to hydrogen peroxide solutions containing active ferric chloride hydrosol, although these gels have a chlorine content and a specific electroconductivity little different from those of the

hydrosol. The above results show that the effect of hydrolysis is to lead to the adsorption of ferric ions on the colloid formed, the velocity of this process increasing with the active surface of the adsorbent.

III. The catalytic action of ferric salts on hydrogen peroxide in alkaline solutions is due to the formation of ferric hydroxide, which separates as a precipitate. These catalytically active hydrogels are irreversibly inactivated with time, this inactivation being initiated by alkali. The mechanism of the catalysis of hydrogen peroxide in alkaline solution consists in the dissolution of the iron hydrogels formed, to give rise to homogeneously soluble iron compounds, which are intermediate stages in the reaction. The ageing of the hydrogel appears to be due to the depressive influence of alkalis on its dissolution in alkaline solutions of hydrogen peroxide, and this again leads to the dehydration of the hydrogel particles to form larger aggregates at the expense of the smaller ones. As a result, the active surface is diminished, and possibly also the microcrystalline structure of the precipitate is changed.   R. TRUSZKOWSKI.

Velocity of oxidation of hydrogen bromide by chromic acid in presence of acids. M. BOBTELSKI and A. ROSENBERG (Z. anorg. Chem., 1928, **177**, 137—144).—The influence of a large number of metallic sulphates on the velocity of liberation of bromine from hydrogen bromide by chromic acid in presence of sulphuric acid has been studied. With the exception of the sulphates of the alkali metals and of cadmium, which retard the reaction, all the salts investigated have a marked accelerative effect which increases as the salt concentration increases; with increase of concentration of the salts which retard the reaction the retardation increases. The catalytic influence of chromic sulphate is much greater than that of ferric and aluminium sulphates at the same concentration. Manganous sulphate also exerts an abnormally large influence, the reaction velocity in presence of $2N$-manganous sulphate being about double that in $4N$-chromic sulphate solution. The catalytic influence of bivalent cations is in general much less than that of tervalent cations. $1.25N$-Cadmium sulphate reduces the oxidation velocity to less than one tenth of its normal value.

H. F. GILLBE.

Catalytic effects in concentrated salt mixtures. M. BOBTELSKI and D. KAPLAN (Z. anorg. Chem., 1928, **177**, 119—123; cf. A., 1928, 715).—The influence of salts at high concentrations ($2.5N$) on the velocity of decolorisation of potassium permanganate solution by oxalic acid in presence of various inductors has been studied. The greater influence is exerted by the anion, and in general the sulphate ion produces acceleration and the chloride ion retardation, whilst the nitrate ion occupies an intermediate position. Specific effects, however, are found for certain combinations of inductor and neutral salt; e.g., ammonium nitrate enormously increases the inductive action of potassium thiocyanate, but reduces that of the arsenite ion. It is observed that the effect of strong reducing agents at low concentrations is not destroyed by the presence of oxidising agents at high concentrations.   H. F. GILLBE.

Inhibition of chemical reactions. II. Mechanism of the inhibition of esterification by alkaline substances. K. C. BAILEY (J.C.S., 1928, 3256—3258; cf. A., 1928, 718).—The reaction between ethyl alcohol and acetic acid is inhibited not only by pyridine but also by other alkaline substances such as quinoline, piperidine, ammonia, and sodium hydroxide. It is suggested that these act by withdrawing acetic acid from an alcohol–acid complex formed preparatory to reaction on the surface of the containing vessel. In conformity with this theory the inhibiting action of the organic bases was found to be the greater the stronger was their basicity. Benzyl chloride acts as a weak positive catalyst; m-cresol, benzene, and chloroform have little effect.

F. J. WILKINS.

Acid and salt effects in catalysed reactions. XVIII. Dynamics of autocatalysed ester hydrolysis. H. M. DAWSON and W. LOWSON (J.C.S., 1928, 3218—3227; cf. A., 1928, 1101).—Since the autocatalysed hydrolysis of ethyl acetate, when carried out in glass vessels, is subject to considerable retardation owing to the dissolution of traces of alkali from the glass walls, the reaction has been studied in fused silica flasks. Up to the point at which the reverse action can no longer be neglected, the reaction may be divided into two stages. In the first, the velocity is determined by the joint catalytic action of the hydrogen and hydroxyl ions, and in the second by the catalytic action of the hydrogen ion only. The equations derived on this basis describe accurately the autocatalytic phenomena observed as well as the retarding influence of small quantities of alkali. The speed of the uncatalysed reaction and the catalytic activity of the water molecules are too small to have any measurable influence on the course of the reaction.

F. J. WILKINS.

Reversible addition of ethyl alcohol to p-bromobenzonitrile catalysed by sodium, potassium, and lithium ethoxides. C. N. MEYERS and S. F. ACREE (J. Amer. Chem. Soc., 1928, 50, 2916—2922).—The catalytic activities of the above ethoxides at $N/32$ to $N/2048$ on the above reaction were investigated. If both the ethoxide ions and non-ionised ethoxide molecules are catalytically active, the equation $vK = K_i \alpha + K_m(1-\alpha)$ should hold for any ethoxide, where K is the velocity coefficient of the reaction when the ethoxide is ionised to the extent α at the concentration N/v, v is the dilution, K_i is the sum of the velocity coefficients for unit concentration of ethoxide ions in the two opposing reactions, and K_m is the sum of the corresponding coefficients for un-ionised ethoxides. K_i is the same for the three ethoxides; K_m decreases in the order sodium, potassium, lithium. The theory outlined enables a satisfactory explanation to be given for the fact that vK is independent of α for sodium ethoxide, changes slowly for potassium ethoxide, increases greatly for lithium ethoxide, and becomes the same in all cases at high dilution. Any possible activity of the metal cations may be disregarded in dilute solution, but in concentrated solution a salt effect is apparent.   S. K. TWEEDY.

Catalysis in the hydration of acetic anhydride. M. KILPATRICK, jun. (J. Amer. Chem. Soc., 1928, 50,

2891—2902).—The rate of hydration of acetic anhydride in $0.07M$ solution was measured dilatometrically at $0°$. In pure water the effects of the H_3O^+, OH', and acetate ions are negligible over a wide range. The neutral salt effect is negative and specific. The formate ion, used as a sodium formate–formic acid buffer, is a remarkably good catalyst; experiments with butyrate and propionate buffers indicate that in these cases, and perhaps also in the case of formate, an intermediate compound is formed, which may be a mixed anhydride.   S. K. TWEEDY.

Mechanism of the formation of 2 : 4-dinitrophenol from benzene and nitric acid in presence of mercury salts as catalysts. A. I. ZAKHAROV (J. Chem. Ind. Moscow, 1927, **4**, 960—964).—When the mercuric nitrate catalyst has already been used in the oxidation of benzene, the reaction is of the second order; otherwise its course is complicated, since a certain amount of acid is withdrawn from the main reaction for the activation of the catalyst. When dilute acid is used its activity is directed towards oxidation and nitrophenols are formed; with acid of comparatively high concentration, nitrobenzene results. The rôle of the catalyst consists in the nitration of the original benzene. The fact that the nitrophenols are accompanied by some nitrobenzene is ascribed to the intermediate formation of mercury–nitrobenzene compounds. This explains the enhanced activity of used solutions. From solutions of 59—60% acidity containing 30% of catalyst, at 35—40°, the original yield of 40% of dinitrophenol is successively increased to 50—55, 65, 75, and 80%.
CHEMICAL ABSTRACTS.

Autoxidation of benzaldehyde. R. KUHN and K. MEYER (Naturwiss., 1928, **16**, 1028—1029).—By repeated vacuum distillation in an atmosphere of carbon dioxide, followed by fractional crystallisation under aseptic conditions at the temperature of liquid air, it has been possible to obtain benzaldehyde so pure that it no longer undergoes autoxidation. Small additions of salts of heavy metals such as iron, copper, nickel, and manganese greatly accelerate oxidation. Ferrous salts are fifteen times as effective as ferric salts. The catalysis by ferric salts shows an induction period followed by rapid oxidation, and concomitant with the increase in oxygen uptake an orange-brown colour appears in the aldehyde. The colour appears at once with ferrous salts, and the coloured product appears to be the intermediate catalytic compound. The iron in the hæmin complex is fifty times as active as ferrous iron, whilst phosphate hæmin is quite ineffective.   R. A. MORTON.

Catalytic decomposition of sodium hypochlorite solutions. II. Iron oxide as promoter in the copper oxide catalysis of sodium hypochlorite. J. R. LEWIS (J. Physical Chem., 1928, **32**, 1808—1819; cf. A., 1928, 376).—Data for the promoter action of iron oxide on the catalytic decomposition of sodium hypochlorite solution at 35° by copper oxide have been obtained by the method previously described (loc. cit.). The reaction is proportional to the concentration of the catalyst. With the unpromoted catalyst, the values of $k=$volume of oxygen evolved/time in min. and of k_1, the usual

unimolecular coefficient, decrease rapidly after 4—5% of the reaction has been completed. This decrease is modified by an increase in the amount of the promoter until constant values for k_1 are obtained. When small quantities of catalyst are added to an excess of the promoter, the values of k remain constant whilst those of k_1 increase. An equiatomic mixture of copper and iron is the most effective. The temperature coefficient for the unpromoted reaction lies between 2·1 and 1·2 over the range 25—45° and for the promoted reaction it is normal (2·3) between 25° and 35° but diminishes (1·7) between 35° and 45°. The function of the promoter is to preserve the active points on the catalyst and the results agree with the view that a catalyst–hypochlorite complex is formed. Reproducible results were obtained only when the hypochlorite solution was added to a solution of a mixture of ferric and copper chlorides and not when the mixed oxides were prepared by precipitation with sodium hydroxide. In this case, the treatment of the catalyst before use determined its activity.
L. S. THEOBALD.

Autoxidation and antioxygenic action. XXXIII. Catalytic properties of antimony, bismuth, and their derivatives, and of some derivatives of vanadium. C. MOUREU, C. DUFRAISSE, and M. BADOCHE (Compt. rend., 1928, **187**, 1092—1096).—In general, metallic antimony and its oxygenated compounds (1%) have only a slight catalytic activity, whilst the halogen compounds, bismuth and its compounds, with the exception of the trichloride and tribromide, and vanadium compounds (1%) are usually highly active. In most cases very small changes suffice to invert the sign of catalysis; e.g., bismuth triphenyl is antioxygenic to acraldehyde and pro-oxygenic to l-pinene, whilst two catalysts of similar structure may act in opposite senses towards the same autoxidisable substance.   J. GRANT.

Autoxidation and antioxygenic action. Catalytic properties of silicon, boron, and their derivatives. C. MOUREU, C. DUFRAISSE, and P. LAPLAGNE (Compt. rend., 1928, **187**, 1266—1269; cf. this vol., 36).—Both boron and silicon and their derivatives show positive and negative catalytic effects in concentrations of 1%, and a close resemblance exists between the curves representing the opposite effects for a particular substance. The catalytic properties of silica depend on its purity and on the method of preparation employed.   J. GRANT.

Heterogeneous catalysis of hydrogen peroxide by copper compounds. E. I. SPITALSKI, N. N. PETIN, and B. A. KONOVALOVA (J. Russ. Phys. Chem. Soc., 1928, **60**, 1237—1270).—Copper ions have no catalytic action on the decomposition of hydrogen peroxide; the catalyst is cupric hydroxide contained in the precipitate forming in the reaction mixture together with cupric peroxide, which is an intermediate product. In slightly acid solution the velocity coefficient of the reaction at first falls to a minimum and then rises to the end of the reaction, whilst in neutral or feebly alkaline solution this coefficient rises to a maximum value at completion of the reaction. The absolute velocity also depends on the reaction of the medium and is much smaller in

more concentrated solutions of substrate. When very concentrated solutions of peroxide are used (15N), the precipitate obtained consists chiefly of cupric peroxide, the velocity of decomposition of which is comparatively small; it has no catalytic action. In dilute peroxide solutions, however, the precipitate contains at first only active cupric hydroxide, which then becomes partly converted into peroxide; this process explains the initial fall in absolute velocity observed. Cupric peroxide, being unstable, breaks up into oxygen and cupric hydroxide, which again acts catalytically; this process corresponds with the increase in velocity which supervenes later. Active precipitates of cupric hydroxide become progressively inactivated by the introduction of fresh quantities of peroxide, whereby they are converted to an increasingly great extent into peroxide. The copper catalyst ages on keeping, but if a reaction mixture to which an aged catalyst has been added be constantly agitated, the velocity coefficient is then of the same order as that obtained by using freshly-precipitated catalyst.

R. TRUSZKOWSKI.

Catalytic processes in the solid phase. I. Decomposition of potassium permanganate. S. ROGINSKY and E. SCHULZ (Z. physikal. Chem., 1928, **138**, 21—41).—A study has been made of the velocity of decomposition at various temperatures of solid potassium permanganate and ammonium dichromate, and of the effect on these decompositions of traces of oxides. The decomposition of the pure substances is autocatalytic, the maximum velocity being attained after 0·75—2 hrs. from the beginning of the reaction. The velocity of decomposition increases with decrease in size of the particles of the material and in the presence of traces of the end-products of the reaction. The decomposition is greatly accelerated by the presence of the oxides of nickel, cobalt, manganese, iron, and copper. Oxides of tungsten, magnesium, titanium, mercury, calcium, uranium, and silicon appear to be without effect. Moderate catalytic activity is shown by the oxides of silver, tin, lead, antimony, chromium, zinc, aluminium, and cadmium. Of the oxides which are catalytically active in the decomposition of potassium permanganate the majority are of deep colour, electrically conducting, paramagnetic, and show similar activity in catalysing the decomposition of potassium chlorate, silver oxide, and mercuric oxide. No relationship is apparent between the crystal structure of these oxides and their catalytic powers. The kinetics of the above decomposition are considered from the point of view of the formation of centres of decomposition in the surface of individual crystals, and an equation is developed which applies satisfactorily to the case of potassium permanganate. F. G. TRYHORN.

Oxidation of mercury in presence of glowing platinum. A. J. LEIPUNSKY (Z. physikal. Chem., 1928, B, **1**, 369—374).—In presence of glowing platinum oxygen reacts with mercury vapour to form mercuric oxide. The reaction velocity increases with rise of temperature of the platinum. It is independent of the pressure of oxygen, but decreases with increasing pressure of mercury vapour. Glowing

nickel has no action. The results may be explained by the assumption that the reaction is catalytic and that oxygen is activated by adsorption on the platinum surface. No evidence of the excitation of mercury atoms has been obtained. M. S. BURR.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. II. Synthesis of methyl alcohol with catalysts composed of copper and zinc. P. K. FROLICH, M. R. FENSKE, P. S. TAYLOR, and C. A. SOUTHWICH, jun. (Ind. Eng. Chem., 1928, **20**, 1327—1330; cf. A., 1928, 1112).—The synthesis of methyl alcohol was carried out using a gaseous mixture composed of 70·8% of hydrogen, 26·5% of carbon monoxide, 2·1% of nitrogen, and 0·6% of oxygen, from which water vapour, carbon dioxide, and iron carbonyl had been removed. Small amounts of finely-powdered catalysts were placed, after reduction with methyl alcohol vapour at 220°, in a pressure-resisting converter. This vessel was externally heated in a lead bath and designed so that the gas mixture which passed through it was heated by counter-current. At 204 atm. the rate of the exit gases corresponded with 28 litres/hr./3 c.c. of catalyst. As no pyrometer was placed in contact with the catalyst the latter was placed in a roll of copper gauze to dissipate the heat of reaction. The assumption is made that the temperature of the bath is not more than 10° below that of the catalyst. A comparison of the efficiencies of the various oxide mixtures indicates that the activity slowly increases with rise in percentage of zinc oxide and, in the neighbourhood of 50 mol.-%, very rapidly, reaching a maximum at about 65 mol.-%. This conclusion is in good agreement with that arrived at previously (*loc. cit.*), thus emphasising the suitability of the decomposition method in catalyst testing. All the catalysts employed showed a slight but measurable decrease in activity after 8 hrs.' use. Although methyl formate was produced in the decomposition of methyl alcohol by the catalysts, no methyl formate was detected in the synthetic experiments. H. INGLESON.

Catalytic activity of metallised silica gels. V. Oxidation of ethylene. L. H. REYERSON and L. E. SWEARINGEN (J. Amer. Chem. Soc., 1928, **50**, 2872—2878; cf. A., 1928, 252, 376).—Silica gel metallised with copper, platinum, or palladium is very active in promoting the oxidation of ethylene. It begins to be effective at 100°. Silica gel metallised with silver is not so effective, but in all cases no intermediate compounds can be detected. The reaction rate is proportional to the oxygen concentration and inversely proportional to the ethylene concentration. A mechanism is suggested for the reaction which accounts for this. S. K. TWEEDY.

Efficiency of different contact substances for the sulphuric acid contact process. II. B. NEUMANN and E. GOEBEL.—See B., 1929, 51.

Theory of processes at unpolarisable electrodes. M. VALMER (Z. physikal. Chem., 1928, **139**, 597—604).—Electrolytic precipitation and dissolution of metals in the solid and liquid state are compared on the assumption that in the solid state an adsorption layer is formed round the crystals in which the

adsorbed atoms are in a state between the atomic and ionic. Polarisation, attributed to this adsorption layer, has been obtained in certain cases with zinc electrodes and zinc sulphate as electrolyte. No polarisation is obtained with liquid zinc amalgam electrodes or with two others in which the zinc is present as small crystals. Using two other electrodes with larger crystals considerable polarisation, both anodic and cathodic, is obtained with current densities of 0·25 milliamp. per cm.² R. N. KERR.

Electrolysis through a crystalline diaphragm. W. A. PLOTNIKOV, M. RABINOVITSCH, and P. B. ZYVOTINSKI (Z. physikal. Chem., 1928, **138**, 260—267).—If in the electrolysis of an aqueous solution of silver nitrate the electrodes are contained in separate vessels connected by a " bridge " which is composed of a mixture of solid silver iodide with 10% of silver chloride and is heated at 150—160°, the current passes through this diaphragm by means of the silver ions only, but the amount of decomposition at the electrodes is in accordance with Faraday's laws, whilst diffusion between the anode and cathode vessels is completely prevented. If, owing to photo-chemical action, or for other reasons, the bridge contains colloidal silver, the silver particles migrate towards the anode. R. CUTHILL.

Electrolysis of sodium sulphide solutions. W. R. FETZER (J. Physical Chem., 1928, **32**, 1787—1807).—The electrolysis of solutions of sodium sulphide (4·5N) at 20° yields, with low current densities, sodium polysulphide as the only product; with higher current densities, sodium sulphate and dithionate, but no thiosulphate, are formed. With sodium sulphide or polysulphide as electrolyte and low current densities, the electrochemical equivalent of sulphur is 16/F, and the electrolysis of a solution of sodium hydrogen sulphide yields polysulphide and hydrogen sulphide in the ratio $Na_2S_2 : 2H_2S$. The current required to liberate sulphur from solutions of mono- or poly-sulphide increases to a maximum with an increase in concentration of polysulphide and then falls towards zero. With the monosulphide, it increases with an increase in the rate of rotation of the anode, but with the polysulphide it remains unchanged over the range 220—700 r.p.m. An increase in current required accompanies a rise in temperature. An electrolytic method for the preparation of sodium hydroxide free from carbonate is described. L. S. THEOBALD.

Rate of photochemical combination of chlorine and hydrogen in glass capillary tubes. D. L. CHAPMAN and P. P. GRIGG (J.C.S., 1928, 3233—3235; cf. A., 1928, 970).—Under the same conditions of illumination the rate of photochemical union of hydrogen and chlorine in capillary tubes is con-siderably less than in wider tubes. This result is explained by the hypothesis that the union of the gases is due to an unstable catalyst which is formed by light and is destroyed when it comes into contact with glass. F. J. WILKINS.

Yield in photochemical reactions in [rapidly] intermittent light. M. PADOA and N. VITA (Atti II Cong. Naz. Chim. pura appl., 1926, 1256—1258; Chem. Zentr., 1928, ii, 524).—Experiments on the autoxidation of hydrogen iodide in light which had passed through a rotating sectored screen showed that the photochemical yield at first increased with the number of alternations (transparent and dark) of the sectors, and then decreased to a constant value. Alternations, without dark sectors, of two or more colours caused greater dependence of yield on the velocity. Maxima were observed.

A. A. ELDRIDGE.

Influence of photographic reactions on the Weigert effect in photochloride. H. ZOCHER and K. COPER (Z. physikal. Chem., 1928, **139**, 263—272; cf. A., 1928, 593).—The anisotropy of silver induced in the photochloride by the Weigert effect is shown to persist throughout many photographic reactions. Changes in concentration of the silver are accom-panied by characteristic variations in the anisotropy, which is also strongly modified by photographic processes such as washing, drying, fixing, etc. Aniso-tropic gold, platinum, and copper are formed by replacement of the silver when the plate coated with the anisotropic silver chloride is submitted to the action of toning baths of suitable salts of these metals. The results are discussed. L. S. THEOBALD.

Photochemical action of bromine on methyl maleate and fumarate. R. SCHMIDT (Z. physikal. Chem., 1928, B, **1**, 205—238).—It is assumed that the photosensitive reaction between bromine and methyl maleate depends on the formation of bromine atoms by the action of light. The quantum yield of methyl fumarate varies with the initial concentrations of ester and bromine, the intensity and wave-length of the incident light, and the temperature. The experi-mental results are in accordance with the equation $\Delta\phi/\phi_{00}=k_1[Br]^2/k_0I$, where ϕ_{00} is the quantum yield when a negligible number of bromine atoms are withdrawn by recombination or addition to the ester, $\Delta\phi$ is the difference between ϕ_{00} and a function of the ester concentration, I is the intensity of the incident light, and k_0 and k_1 are constants. The significance of the variations of the quantum yield with the wave-length of the light and the temperature is discussed. Study of the addition of bromine to methyl fumarate affords values for the quantum yield which are in agreement with those to be expected from Wach-holtz's investigation of the ethyl esters. The theoretical conception of the identity of the inter-mediate stages of the tautomeric change of the maleic ester and of the addition of bromine to the fumaric ester is supported by the relationship between the quantum yield $\alpha_{0·1N}$ and the bromine concen-tration. In aqueous solution the quantum yield is approximately the same as in carbon tetrachloride solution. H. F. GILLBE.

Changes in cellulose nitrate when exposed to light. V. COFMAN and H. B. DEVORE (Nature, 1929, **123**, 87).—The production of a red colour when celluloid containing malachite-green is exposed to sunlight (Rayleigh, A., 1928, 1341) is apparently due to the liberation of oxides of nitrogen. The wave-length most effective in the acid decomposition of cellulose nitrate is 3100 Å. A. A. ELDRIDGE.

Reaction of ketones with alcohols under the influence of light. IV. Photo-electric effect of benzophenone. G. H. VISSER (Rec. trav. chim., 1928, **47**, 1037—1041).—In order to determine the primary reaction in the photochemical oxidation of alcohols in presence of aromatic ketones, the photo-electric emission of electrons from benzophenone has been investigated by means of a Geiger ionisation chamber. The "threshold" wave-length necessary for the emission of electrons is between 302·5 and 253·7 mμ, which agrees well with the pronounced band at 260 mμ in the absorption spectrum of benzophenone and probably corresponds with an ionisation of the molecule. This is not the spectral region, however, which is active in the photochemical oxidation of alcohols. O. J. WALKER.

Photochemical yield in the chlorophyll assimilation [of carbon dioxide] with complex and intermittent lights. M. PADOA and N. VITA (Gazzetta, 1928, **58**, 647—654).—From a study of the photochemical action of light on green plants, as measured by the amount of oxygen evolved, it is shown that the sum of the separate actions of red, yellow, and green light is greater than the action of the corresponding amount of white light. Intermittent white light (cf. A., 1927, 528) also has a different effect from continuous light on the photochemical yield. At certain interruption frequencies maximum yields are obtained, which in some cases are three times as great as the yield obtained by using continuous illumination. These results are compared with those previously obtained (A., 1928, 1102) with other photochemical reactions.
O. J. WALKER.

Action of ultra-violet rays on the formation of sugars and complex aldehydes from solutions of alkali and alkaline-earth metals hydrogen carbonates and of carbon dioxide in presence of reducing and colloidal catalysts. G. MEZZADROLI and E. VARETON (Zymologica, 1928, **3**, 165—171; cf. A., 1928, 255).—Exposure of these hydrogen carbonate solutions to ultra-violet rays results in increase of the reducing power (determined iodimetrically) of the solutions to a maximum, followed by rapid decrease. Under similar conditions, solutions of carbon dioxide prepared by continuous passage of the gas through water show progressive increase in reducing properties. The presence of colloidal or reducing catalysts increases, in some cases three- or four-fold, the maximum reducing powers. The greatest yield of reducing substances, referred to the carbon dioxide reacting, is obtained with calcium hydrogen carbonate in presence of finely-powdered magnesium. T. H. POPE.

Effect of ultra-violet light on the dielectric properties of crystals. A. A. AARDAL (Proc. Iowa Acad. Sci., 1927, **34**, 276).—Variation of the dielectric constant, phase angle, and resistance has been observed when certain natural crystals are exposed to ultra-violet light.
CHEMICAL ABSTRACTS.

Chemical action of X-rays. P. GÜNTHER (Z. angew. Chem., 1928, **41**, 1357—1361).—A review of recent work. A. R. POWELL.

Reaction of excited mercury with oxygen. A. J. LEIPUNSKY and A. W. SAGULIN (Z. physikal. Chem., 1928, B, **1**, 362—368).—An investigation has been made of the oxidation of mercury vapour under the influence of light from the mercury arc, and also by bombardment with electrons emitted by glowing platinum and accelerated by different voltages. Only the line 2537 Å. appears to be photochemically active, and the velocity of reaction increases with increasing pressure of mercury vapour. For any given mercury pressure there is an oxygen pressure at which the velocity is a maximum. This is in agreement with the conception of a chain reaction. The velocity of reaction is not affected by electrons accelerated by a field of less than 5 volts, which is the value of the first resonance potential of mercury. The results show that, contrary to the observations of Noyes (J. Amer. Chem. Soc., 1928, **50**, 49), the reaction is due to excited mercury atoms only, and the primary formation of ozone has not much influence. M. S. BURR.

Formation of ozone by cathode rays. A. L. MARSHALL (J. Amer. Chem. Soc., 1928, **50**, 3178—3197).—The ozonisation of oxygen by high-velocity electrons is a homogeneous gas reaction independent of the nature or extent of the surface exposed. The energy of the electron beam seems to diminish exponentially after penetrating the window of the oxygen cell; half of the ozonisation occurs within a short distance of the window. For low currents in the cathode-ray tube the logarithm of the rate of flow of the oxygen through the cell is a linear function of the yield of ozone for a given exposure. The rate of formation of ozone increases with the pressure, although at high pressures the yield is independent of the pressure. The ozone is also decomposed by the cathode rays, and eventually a steady state is reached, independent of the tube current, in which one ozone molecule is contained in 1700 oxygen molecules. The attainment of a saturation current observed in the experiments of Krüger and Utesch (A., 1926, 136) could not be confirmed, so that the results of these experimenters are regarded as doubtful. S. K. TWEEDY.

Combination of hydrogen and oxygen under the influence of cathode rays. A. L. MARSHALL (J. Amer. Chem. Soc., 1928, **50**, 3197—3204).—Hydrogen peroxide, water vapour, and ozone are formed as primary products, the rate of formation of the first-named being almost independent of the hydrogen and oxygen concentrations, whereas the rates of formation of the last-named vary very considerably. Since, however, the rates of formation of ozone and of water vapour always parallel one another very closely, the same mechanism is probably responsible for both. This conclusion is supported by the fact that the yield of peroxide decreases as the rate of flow is diminished, the decreases being related linearly to the accompanying increases in the yield of water vapour. The gross rate of reaction parallels that observed by Lind (A., 1919, ii, 210) for the same reaction under the influence of α-particles. S. K. TWEEDY.

Chemical effects of cathode rays on oxygen, air, nitric oxide, and carbon dioxide. W. F.

BUSSE and F. DANIELS (J. Amer. Chem. Soc., 1928, **50**, 3271—3286).—In the ozonisation of oxygen, which proceeds independently of the nature of the surface of the containing cell (cf. preceding abstracts), for short exposures the yield is a function of the voltage and current of the cathode-ray tube, the exposure, the distance between the tube and the reaction cell, and the source of the oxygen, but is independent of the time (within limits) during which the ozone remains in the reaction cell and of the moisture content of the oxygen. Equilibrium is attained when about 0·1 mol.-% of ozone is present. One molecule is formed for each ion pair, which is not in agreement with the results of Krüger and Utesch. The M/C ratio, or the number of molecules formed or decomposed per electron passing through the cathode-ray tube, is 100 for the formation of ozone. When air is used, this efficiency falls to about half the value, but nitrogen oxides are also formed in varying yields ($M/C = 13\cdot5$—$16\cdot0$). When nitric oxide is exposed, oxygen, nitrogen, and nitrogen dioxide are formed; M/C is 230 for this decomposition. Carbon dioxide yields carbon monoxide and oxygen (ozone), the M/C ratio being 3. The energy of the rays, determined calorimetrically, varied from 3 to 16 g.-cal. per min. The chemical behaviour of high-voltage electrons is essentially the same as that of α-particles. S. K. TWEEDY.

Irradiated quenching of cadmium resonance radiation. J. R. BATES (Proc. Nat. Acad. Sci., 1928, **14**, 849—852).—Cadmium atoms in the 2^3P_1 state will not activate hydrogen atoms sufficiently to cause them to react with ethylene, whereas mercury atoms in the same state of activation will promote the reaction. Hydrogen was found to quench cadmium resonance radiation just as effectively as it does that of mercury. Hydrogen atoms cannot be formed by these collisions, but there is an increase in the vibrational energy of the hydrogen molecule. It proved difficult to study the temperature coefficient of the reaction between cadmium atoms in the 2^3P_1 state and hydrogen molecules to give hydrogen atoms owing to the large quenching. The work provides some evidence for the consideration that in the case of activation reactions, the thermal activation of reactants is not so important as the activation of some catalytic substance which may be present. A. J. MEE.

Chemical inertia of the rare gases. I. Action of helium on platinum. H. DAMIANOVICH (Anal. Fís. Quím., 1928, **26**, 365—371; cf. A., 1926, 657).—When a discharge from an induction coil was passed between platinum electrodes in a tube containing helium at about 3 mm. pressure a deposit was formed on the tube and a diminution of pressure was observed corresponding with absorption of 14—34 c.c. per g. of platinum deposited. The deposit, which was dark grey, non-metallic, and of characteristic microscopical appearance, decomposed at a measurable rate in a vacuum between 90° and 160° to yield helium and metallic platinum, and probably consisted of platinum containing adsorbed helium or mixtures of this with definite compounds and excess of metal. R. K. CALLOW.

Preparation of cuprous sulphate. J. G. F. DRUCE and G. FOWLES (Chem. News, 1928, **137**, 385—386).—Copper turnings are dropped into concentrated sulphuric acid heated at 200° and when the reaction has ceased the green solution is decanted from any anhydrous cupric sulphate through an asbestos filter into a mixture of equal volumes of anhydrous alcohol and ether or into methyl alcohol. Cuprous sulphate separates in white crystals which rapidly decompose in moist air into copper and cupric sulphate. A. R. POWELL.

Oxidation of silver under dilute solutions of ammonia. K. A. HOFMANN and U. HOFMANN (Ber., 1928, **61**, [B], 2566—2575).—Silver, under aqueous solutions of non-oxidising substances at the ordinary temperature, is much more rapidly oxidised by atmospheric oxygen than is indicated by the literature. Under pure water saturated with oxygen the action on silver is very slight; this effect is not due to the slight solubility of silver oxide since silver is not noticeably oxidised under dilute acetic acid. The oxidisability of silver in presence of dilute ammonia is of a different order of magnitude from that under dilute acid; this is ascribed to the conversion of the oxide into the complex $Ag(NH_3)_2\cdot OH$ and the prevention of the reverse electrochemical reaction. The dissolution of silver in ammonia solutions containing oxygen follows an unexpected course, since the weight of metal dissolved per day depends greatly on the volume of the supernatant liquid and the process comes to a conclusion after some months, long before the solubility of silver oxide in the ammonia has attained the saturation limit. A reverse action leading to re-separation of silver, $Ag_{diss.} \rightleftharpoons Ag_{powder}$, is not possible under the experimental conditions. The possibility that the paralysis of the change is due to the formation of nitrite as in the case of copper is discounted by the observation that the production of nitrite is too small to account for the effect and that ammonium nitrite is stable in ammoniacal solution in presence of silver powder. Utilisation of the oxygen in other directions, such as formation of nitrogen from ammonia, is not involved, since a quantity of air preserved for months over ammoniacal silver oxide still contained 20·6% of oxygen. If the ammonia solution is renewed after the action has come to a pause, the silver is again dissolved but at a much slower rate. The restriction depends on the compound $Ag(NH_3)_2\cdot OH$ and, if this is transformed into the corresponding salt by addition of ammonium nitrate or sulphate, it becomes operative at a much higher concentration than in the absence of such addenda. An adequate explanation of the restriction is found in the assumption of the slow formation of small amounts of silver fulminate or similar products, e.g., Ag_3N or Ag_2NH, which are gradually precipitated by evaporation of ammoniacal silver oxide solutions. Helped by the surface action in the adsorption layer, the amount of silver nitride can finally become so considerable that restriction occurs. Hence inactive silver powder always appears darker than the active material, although foreign matter is present in quantity which can scarcely be detected analytically. The deposit is gradually removed by

the air under aqueous ammonia, but the process is so slow that the surface of the silver powder remains covered as a consequence of fresh deposition of silver nitride from the solution. Confirmation of this hypothesis is found in the observation that additions of chlorides, bromides, and iodides facilitate restriction in increasing sequence corresponding with the solubility of the silver halides and that the mode of action of these addenda agrees with the limitation caused by the silver nitride. H. WREN.

Magnesia–graphite reactions at high temperatures. F. T. CHESNUT.—See B., 1929, 16.

Reduction of tricalcium phosphate by carbon. K. D. JACOB and D. S. REYNOLDS.—See B., 1929, 16.

Stereochemistry of zinc and cadmium. W. WAHL (Förh. III nord. Kemistmötet, 1928, 172—176). —The following complex *salts* of *o*-phenylenediamine and *o*-tolylenediamine with the zinc and cadmium halides have been prepared : $[Cd(o\text{-phen.})_2]Cl_2$; $[Cd(o\text{-phen.})_2]Br_2$ (two isomerides) ; $[Cd(o\text{-tol.})_2]Br_2$; $[Cd(o\text{-tol.})_4]Br_2$; $[Zn(o\text{-phen.})_2]Br_2$; $[Zn(o\text{-phen.})_3]Br_2$; $[Zn(o\text{-phen.})_4]Br_2$; $[Zn(o\text{-tol.})_2]Br_2$; $[Zn(o\text{-tol.})_3]Br_2$. The above salts are all rose-red in colour with the exception of one form of the cadmium di-*o*-phenylenediamine bromide and of the zinc tetra-*o*-phenylenediamine bromide. They usually crystallise well, and can frequently be recrystallised from concentrated aqueous solution, although some decompose when their solutions are heated. The solutions in alcohol are much more stable and can be advantageously employed in preparing the pure salts. Cadmium di-*o*-phenylenediamine bromide also exists in a green modification, crystallising in needles ; the two salts of this type are probably geometrical isomerides, the green compound being the *trans*-form. A similar green modification of zinc tetra-*o*-phenylenediamine bromide has also been prepared. The two zinc triammine salts are octahedral, and correspond with the analogous cobalt and chromium compounds. Those of the above compounds which contain four phenylenediamine groups are of special interest, as they represent a class of complex inorganic salts not hitherto prepared. In these octammine salts the eight valencies can be visualised as directed from the centre of a cube towards the corners : in those octammine compounds containing four bivalent groups united to a central atom two isomerides are possible, the two zinc tetra-*o*-phenylenediamine salts being representatives of this class, and geometrical isomerides. If an asymmetrically placed group be inserted in the diamine ring, eight isomerides are possible, and the above cadmium tetra-*o*-tolylenediamine bromide, which possesses a deep rose-violet colour, is probably one of the *cis*-forms. Direct proof of the hexahedral structure of the above compounds is difficult to obtain, but experimental evidence shows that they cannot be diaminophenazine compounds. Both *m*- and *p*-phenylenediamine give rose-red complex salts with the bromides of zinc and cadmium, the latter having the composition $[Zn(p\text{-phen.})]Br_2$. A similar compound has also been prepared from *p*-phenylenediamine and copper sulphate, the salt formed being sparingly soluble and very stable.

H. F. HARWOOD.

Action of bromine on strontium oxide and its hydrates. H. B. DUNNICLIFF, H. D. SURI, and K. L. MALHOTRA (J.C.S., 1928, 3106—3111).— Bromine was used both in the form of vapour and in the form of its solution in carbon tetrachloride. No reaction occurs with strontium oxide. The monohydrate reacts incompletely to form strontium bromide and hypobromite. Bromine vapour converts strontium hydroxide octahydrate quantitatively into a mixture of bromide and bromate. The same final result is obtained by using bromine in carbon tetrachloride solution, but it can be shown in this case that in the initial stages of the reaction hypobromite is formed which is subsequently decomposed into bromide and bromate. From the relative proportions of bromide and bromate in the final product it appears that some bromate is formed by the direct oxidation of hypobromite by bromine (cf. Dietzel and Schlemmer, A., 1925, ii, 892).

F. J. WILKINS.

Attempts to isolate new fluoborates. A. TRAVERS and MALAPRADE (Compt. rend., 1928, 187, 982—984 ; cf. this vol., 38)—Evidence is provided for the decomposition by heat of potassium fluoborate according to the reactions $2KBF_4=BF_3+BF_3,2KF$ and $BF_3,2KF=BF_3+2KF$, which proceed simultaneously at about 580° and therefore render difficult the isolation of $BF_3,2KF$. Three crystalline compounds, for which the ratios $B/K=1$ and $F/K=3$ were found, were isolated from the action of varying proportions of boric acid on a cold concentrated aqueous solution of potassium hydrogen fluoride. J. GRANT.

Thermal decomposition of aluminium oxide, hydroxide, and nitrate. N. PARRAVANO and G. MALQUORI (Atti II. Cong. Naz. Chim. pura appl., 1926, 1131—1134 ; Chem. Zentr., 1928, ii, 529). —The heating curve of aluminium nitrate nonahydrate shows three arrests : at 73·5° (fusion with conversion into the hexahydrate), at 140° (formation of $4Al_2O_3,3N_2O_5,14H_2O$), and at 200° (conversion into Al_2O_3) ; that of the hexahydrate at 140° and 200° ; the tetrahydrate is converted into the oxide at 180°. The hexahydrate can be prepared by keeping the nonahydrate over phosphorus pentoxide in a vacuum or by repeated treatment with hot 100% nitric acid ; the tetrahydrate by the action of nitrogen pentoxide on the hexahydrate at the ordinary temperature. The curve for aluminium chloride shows a slight arrest at 122° ; conversion into the oxide takes place at 180°. The salt $Al_2(SO_4)_3,18H_2O$ becomes anhydrous at about 105° and affords alumina and sulphur trioxide at about 760°. The thermal dehydration of technical alumina proceeds differently ; the production of definite chemical individuals is postulated.

A. A. ELDRIDGE.

Surface oxidation of aluminium, tungsten, and molybdenum. L. C. BANNISTER (J.C.S., 1928, 3163—3166).—A technique has been developed for the preparation, both chemically and electrochemically, of surface films of oxide on aluminium, tungsten, and molybdenum, which vary gradually in thickness. The optical properties demonstrate clearly that the colours exhibited are set up by interference. Tables are given showing the variation of colour with applied

voltage, the number of coulombs used for formation, and the time of oxidation. Films have been isolated from aluminium by volatilising the metal away in hot gaseous hydrochloric acid. They consist mainly of oxide, with 4% of water and a trace of occluded anion from the electrolyte. F. J. WILKINS.

Separation of pure yttrium from yttrium earths. G. CANNERI (Atti R. Accad. Lincei, 1928, [vi], **8**, 164—167).—Details are given of the separation of yttrium from yttrium earths by the fractional crystallisation of the double carbonates of the elements with sodium. The yttrium so obtained is contaminated with a small percentage of erbium. A final purification is obtained by the fractional precipitation of the crystalline double ferrocyanides with the alkali metals in the presence of a large excess of the alkali metal salt. The presence of the latter eliminates the production of the gelatinous precipitates of the simple ferrocyanides of the yttrium elements and allows of the production of yttrium salts of high purity after four precipitations. F. G. TRYHORN.

Germanium. I. Mode of treatment of germanite, preparation of pure germanium dioxide and of homogeneous germanium tetrachloride. II. Action of carbon tetrachloride on germanium dioxide. L. DEDE and W. RUSS (Ber., 1928, **61**, [B], 2451—2459, 2460—2463).—I. If arsenic is to be removed completely from germanium, it is important that as thorough a separation of the two elements as is possible should be effected in the preliminary treatment of the germanite. This is effected by treatment of the finely-divided mineral with a mixture of nitric acid, sulphuric acid, and water in the volume ratio 50 : 20 : 50 (cf. Keil, A., 1926, 589) whereby germanium dioxide, almost free from arsenic and containing as impurities chiefly lead sulphate and gangue, remains. The residue is mixed with fuming hydrochloric acid (d 1·19) and distilled in an all-glass apparatus in a stream of chlorine, the condensate being collected in a receiver charged with 20% hydrochloric acid. The lower layer of germanium tetrachloride is hydrolysed to the dioxide by water. The precipitated dioxide contains small amounts of chlorine which cannot be removed by decantation with cold or hot water but are evolved as hydrogen chloride by distillation with steam, thus indicating the probable existence of germanium oxychloride. The germanium in the filtrate is precipitated in the presence of 6N-sulphuric acid as the disulphide, which is oxidised to the dioxide by a mixture of nitric acid, sulphuric acid, and water.

The liquid remaining after the preliminary treatment of the germanite (see above) is submitted to electrolysis between a platinum gauze anode and a copper cathode until the deposit on the latter becomes black owing to arsenic. The liquid is concentrated and the germanium dioxide which separates is subjected to treatment with hydrochloric acid and distillation in chlorine as before. The germanium dioxide so prepared is spectroscopically pure.

Germanium dioxide is converted into the tetrachloride by distillation with hydrochloric acid in a current of hydrogen chloride and condensation of the distillate in a receiver cooled by a mixture of ice and salt. The colourless, lower layer of germanium tetrachloride contains hydrogen chloride, which is mainly removed by aspiration of dry air through it at 18° followed by distillation. The product is preserved over anhydrous sodium carbonate and subsequently distilled. It has b. p. 83°/760 mm.

II. Nitrogen charged with the vapour of carbon tetrachloride is passed over germanium dioxide at temperatures between 500° and 865°. Under constant conditions with respect to the rate of passage of the gas, the diminution in the weight of the dioxide divided by the duration of the experiment is regarded as a measure of the rate of reaction. The change occurs with measurable velocity at 500° and the rate increases rapidly with rise of temperature. Intermediate formation of germanium oxychloride is not observed; hexachloroethane, m. p. 184—187°, appears invariably to be formed. In the behaviour of its oxide towards carbon tetrachloride, germanium appears to be allied much more closely to tin than to silicon. H. WREN.

Constitution of sodium plumbate. A. SIMON (Z. anorg. Chem., 1928, **177**, 109—115).—Since sodium plumbate, $Na_2PbO_3,3H_2O$ liberates all three molecules of water simultaneously at 110°, and there is no evolution of oxygen on dehydration, the salt is derived from metaplumbic acid and does not possess the formula $Na_2[Pb(OH)_6]$. This conclusion is supported by the observation that alcohol does not extract sodium hydroxide from the salt. The behaviour of the anhydrous salt at high temperatures (600—800°) is described; at 750° it decomposes into sodium monoxide and lead tetroxide, which rapidly changes to red lead monoxide. The X-ray spectrograph supports the formula $Na_2PbO_3,3H_2O$.
H. F. GILLBE.

Interaction between nitrogen trichloride and nitric oxide. Reactions of compounds with odd electrons. W. A. NOYES (J. Amer. Chem. Soc., 1928, **50**, 2902—2910).—The reaction occurs in a mixed chloroform and carbon tetrachloride solution according to the equations (a) $2NCl_3 = N_2 + 3Cl_2$; (b) $NOCl + NCl_3 = N_2O + 2Cl_2$; (c) $NCl_3 + 2NO = N_2O + NOCl + Cl_2$, respectively, according as the temperature is 0°, —20°, or —80°. Reaction (a) is catalysed by the nitric oxide; reaction (b), which is a subsidiary reaction, and occurs slowly at —80°, is accompanied by the decomposition of one quarter of the nitrogen trichloride into nitrous oxide and chlorine, and by reaction (a); reaction (c) probably occurs in two stages : $NCl_3 + NO = NOCl + NCl_2$, and $NCl_2 + NO = N_2O + Cl_2$, although the intermediate compound could not be isolated. In light petroleum at —130° the reaction is $2NCl_3 + 2NO = 2N_2O + 3Cl_2$. The nitrogen trichloride also reacts with the petroleum and forms hydrogen chloride which serves to catalyse a reaction like (b). An octet structure for nitrous oxide is suggested in which there is a semi-polar union between the nitrogen and oxygen.
S. K. TWEEDY.

Compound of phosphorus pentachloride with bromine. W. A. PLOTNIKOV and S. JAKUBSON (Z. physikal. Chem., 1928, **138**, 243—245).—A reddish-brown *compound*, $PCl_5,5Br_2$, m. p. 25° (decomp.),

separates from a solution of phosphorus penta-chloride and bromine in carbon disulphide on cooling.
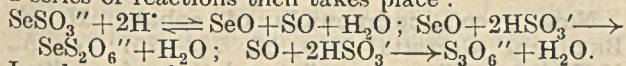R. CUTHILL.

Synthesis of hypophosphoric acid. T. MIŁO-BEDZKI and J. WALCZYŃSKA (Rocz. Chem., 1928, 8, 486—501).—Tetraethyl hypophosphate is obtained by the action of diethyl orthophosphoryl chloride on sodium diethyl phosphite, or of diethoxychloro-phosphine on sodium diethyl orthophosphate. Tetra-ethyl hypophosphate readily dissociates to yield diethyl hydrogen phosphate and metaphosphoric acid. *Tetramenthyl hypophosphite*, prepared in a similar way to the ethyl ester, dissociates with the production of menthene and free hypophosphoric acid.
R. TRUSZKOWSKI.

Hydrogen polysulphides. O. VON DEINES (Z. anorg. Chem., 1928, **177**, 124—128).—On addition of 100 c.c. of $3N$-hydrogen chloride solution to 100 c.c. of sodium thiosulphate solution a flocculent yellow precipitate is formed which in the course of some minutes changes to a yellow oil, consisting of a solution of sulphur in hydrogen persulphide. Pre-cipitated "white" sulphur actually consists of hydrogen persulphide containing a large quantity of sulphur. Polysulphides are also formed by the action of acids on sodium hyposulphite solutions.
H. F. GILLBE.

Sulphurous acid and its salts. VI. [With E. HAUFE.] **Autodecomposition of aqueous hydro-gen sulphite solutions. VII.** [With E. KIRCHEISEN.] **Interaction of hydrogen sulphite and hydro-sulphide. VIII. Inter-relationships of the sul-phur acids.** F. FOERSTER (Z. anorg. Chem., 1928, **177**, 17—41, 42—60, 61—70).—VI. The spontaneous decomposition of hydrogen sulphite solutions, besides being considerably accelerated by the presence of selenium, is autocatalytic, the first products being sulphate and trithionate ions, but not tetrathionate : $4HSO_3' \longrightarrow SO_4'' + S_3O_6'' + 2H_2O$. The slower the re-action the greater is the decomposition of the tri-thionate according to the equation $S_3O_6'' + H_2O \rightleftharpoons SO_4'' + S_2O_3'' + 2H^{\cdot}$. The autocatalytic nature of the main reaction is ascribed to the hydrogen ion, of which the concentration increases more rapidly than is indicated by titration, using methyl-orange as indicator, on account of the disappearance of HSO_3'. The mechanism of the process is as follows : the seleno-dithionate ion, formed rapidly by the action of hydrogen sulphite solution on selenium or on selenious acid, undergoes the decomposition, acceler-ated by the hydrogen ion, $SeS_3O_6'' + H_2O \longrightarrow SO_4'' + SeSO_3'' + 2H^{\cdot}$; in presence of more hydrogen sulphite a series of reactions then takes place :
$SeSO_3'' + 2H^{\cdot} \rightleftharpoons SeO + SO + H_2O$; $SeO + 2HSO_3' \longrightarrow SeS_2O_6'' + H_2O$; $SO + 2HSO_3' \longrightarrow S_3O_6'' + H_2O$.
In absence of selenium the hydrogen sulphite ion decomposes very slowly, according to the equation $4HSO_3' \longrightarrow 2SO_4'' + S_2O_3'' + 2H^{\cdot} + H_2O$; the resulting hydrogen ions in this case also effect autocatalysis, probably through the formation of polythionates.

VII. On mixing solutions containing respectively 2 mols. of hydrogen sulphite and 1 mol. of hydro-sulphide, thiosulphate is formed immediately and in almost theoretical quantity : $2HS' + 4HSO_3' \longrightarrow$

$3S_2O_3' + 3H_2O$; free sulphur and sulphite ion result as by-products in equimolecular quantities. An excess of hydrogen sulphite causes the formation of trithionate and sulphite in addition to thiosulphate, but the primary reaction is so rapid that the secondary effects may be observed only if the hydrosulphide solution be added to the hydrogen sulphite solution ; if the procedure be reversed the excess of hydrogen sulphite remains unchanged. The theory of the reactions involved is discussed, it being assumed that the hypothetical sulphur monoxide plays an important part.

VIII. (Cf. Bassett and Durrant, A., 1927, 843.) On the assumption of the existence in aqueous solution of the equilibrium $H_2SO_2 \rightleftharpoons SO + H_2O$ between sulphoxylic acid and its hypothetical anhydr-ide, the following equations are suggested to account for the formation of certain other of the sulphur acids : (1) $SO + H_2S \longrightarrow 2S + H_2O$, (2) $2SO + H_2O \rightleftharpoons S_2O_3'' + 2H^{\cdot}$, (3) $SO + 2HSO_3' \longrightarrow S_3O_6'' + H_2O$, and (4) $SO + HS_2O_3' \longrightarrow S_5O_6'' + H_2O$. New views on the initial stage of the Wackenroder reaction are put forward, based on the occurrence of the reaction $H_2S + H_2SO_3 \rightleftharpoons S_2(OH)_2 + H_2O$ followed by $S_2(OH)_2 + H_2SO_3 + H_2O \rightleftharpoons 3H_2SO_2$ and $S_2(OH)_2 + H_2S \rightleftharpoons 2H_2O + 3S$. Bassett and Durrant's equation for the formation of trithionic acid, viz., $2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6$, is shown to be improbable, equation (3) being more in accord with the observed facts. H. F. GILLBE.

Decomposition of thiosulphate by hydrogen chloride. O. VON DEINES (Z. anorg. Chem., 1928, **177**, 13—16).—Sulphoxylic anhydride plays an im-portant part in the decomposition of thiosulphate by acids, and the production of hydrogen persulphide has been established. H. F. GILLBE.

Determination of the m. p. of mineral sul-phides and arsenides. L. H. BORGSTRÖM (Förh. III nord. Kemistmötet, 1928, 169—171).—A know-ledge of the m. p. of the ore minerals is of value with regard to the method of origin of such deposits. A number of determinations have been carried out, employing a modification of the usual laboratory m.-p. apparatus, the mineral being heated in a glass or quartz capillary tube immersed in a bath of fused salts contained in a platinum crucible and heated electrically. A Le Chatelier thermo-element is em-ployed to measure the temperature, and this may be inserted directly into the fused salts, no protective tube being necessary. The most suitable salts for the bath are alkali chlorides, sulphates, and nitrates, or mixtures of the two former. An advantage of the method is the small amount of mineral required for a determination. The lowest m. p. are shown by the sulphides of the metalloids, realgar melting at 310°, orpiment at 325°, stibnite at 546°, and bis-muthinite at 718°. The sulphides and arsenides of the metals usually melt between 800° and 1200°, but in some cases decomposition with volatilisation of sulphur or arsenic takes place below the m. p. The majority of the mineral sulpharsenides and sulphantimonides melt between 400° and 600°, but the minerals of the tetrahedrite group melt at 600—700°, and some sulpho-salts of bismuth above 800°. The following minerals of the above class have low

m. p. : dufrenoysite 450°, stephanite 470°, and pyrargyrite 480°, and it is suggested that these minerals may be utilised as "geological thermometers." H. F. HARWOOD.

Corrosive action of sulphur monochloride. E. H. HARVEY.—See B., 1929, 16.

Molybdates and tungstates. Binary systems Li_2MoO_4–MoO_3, Na_2MoO_4–MoO_3, K_2MoO_4–MoO_3, Li_2WO_4–WO_3, Na_2WO_4–WO_3, K_2WO_4–WO_3, Li_2MoO_4–Na_2MoO_4, Li_2WO_4–Na_2WO_4, Li_2MoO_4–K_2MoO_4. F. HOERMANN (Z. anorg. Chem., 1928, 177, 145—186).—The simple molybdate and tungstate of lithium separate from aqueous solution and from fusions as anhydrous trigonal crystals, whereas the potassium salts, which are also anhydrous, crystallise in the monoclinic system; the dihydrated sodium salts form rhombic–bipyramidal crystals. Thermal analysis of the systems Li_2MoO_4–MoO_3 and Na_2MoO_4–MoO_3 indicates the existence of di-, tri-, and tetramolybdates; in the case of potassium the trimolybdate alone is formed. The salts $Li_2O,2MoO_3$, $Na_2O,2MoO_3$, and $K_2O,3MoO_3$ crystallise in the rhombic system. The rhombic ditungstates of lithium and sodium melt without decomposition, and are probably isomorphous with the corresponding molybdates; potassium ditungstate does not appear to exist. Tetratungstates of lithium and sodium, and tri- and tetra-tungstates of potassium, exist. The following m. p. have been determined :

Li_2O,MoO_3, 705° ; $Li_2O,2MoO_3$, (532°) ;
$Li_2O,3MoO_3$, (549°) ; $Li_2O,4MoO_3$, (568°) ;
Na_2O,MoO_3, 687° ; $Na_2O,2MoO_3$, 612° ;
$Na_2O,3MoO_3$, (528°) ; $Na_2O,4MoO_3$, (515°) ;
K_2O,MoO_3, 926° ; $K_2O,3MoO_3$, 571° ;
Li_2O,WO_3, 742° ; $Li_2O,2WO_3$, 745° ;
$Li_2O,4WO_3$, (800°) ; Na_2O,WO_3, 700° ;
$Na_2O,2WO_3$, 738° ; $Na_2O,4WO_3$, (784°) ;
K_2O,WO_3, 921° ; $K_2O,3WO_3$, (660°) ;
$K_2O,4WO_3$, (930°) ; $Li_2MoO_4,3Na_2MoO_4$, (484°) ;
$Li_2WO_4,3Na_2WO_4$, (511°).

Figures in parentheses are incongruent m. p.
H. F. GILLBE.

Reduction of tungsten by hydrogen. Mechanism of formation of crystals of tungsten of different sizes. G. A. MEIERSON (J. Russ. Phys. Chem. Soc., 1928, 60, 1217—1228).—The growth of crystals of tungsten does not commence below 1200° if the powdered metal be heated in a stream of dry hydrogen. Should the latter contain moisture, growth commences at 1050°, and is accompanied by loss in weight of the sample. These effects are due to the formation of tungsten dioxide, which is volatile at 1050°. This, on being reduced, deposits tungsten on the crystals at the further end of the combustion tube. Similarly, the formation of large crystals of tungsten in the reduction of tungstic anhydride is due to the volatility of the oxides WO_3 and W_2O_5, which assumes measurable proportions at 850° and 900°, respectively. Where tungsten is prepared by the reduction of the trioxide, the magnitude of the crystals of the latter has no influence on that of the product. It is similarly possible to prepare large crystals of dioxide by slow reduction of trioxide at an appropriate temperature. R. TRUSZKOWSKI.

New fluorides, especially chlorine fluoride. O. RUFF [with J. FISCHER, F. LUFT, E. ASCHER, F. LAASS, and H. VOLKMER] (Z. angew. Chem., 1928, 41, 1289—1292).—Electrolysis in a copper vessel at 125° of fused ammonium hydrogen fluoride gives a good yield of nitrogen trifluoride which may be purified by fractional distillation at −160°. *Nitrogen trifluoride* is a colourless gas, condensing to a colourless liquid, b. p. −119°, f. p. −210°; it is relatively stable, is not decomposed by an electric spark, but yields a mixture of nitric oxide and nitrogen peroxide when sparked with steam. *Chlorine fluoride*, ClF, is found among the products of the reaction of slightly moist chlorine and fluorine; it is a colourless gas which condenses to a faintly yellow liquid, b. p. −110°, f. p. −150°. Some evidence of the formation of oxygen fluoride or of a hydroxyfluorine compound has been obtained by the fractional distillation of the gases obtained from the interaction of fluorine and water vapour. A. R. POWELL.

Existence of an oxide of bromine. B. LEWIS and H. J. SCHUMACHER (Z. physikal. Chem., 1928, 138, 462).—Experiments on the kinetics of the reaction between bromine and ozone show the presence of some intermediate compound, probably a bromine oxide. In order to test this view, an attempt was made to isolate the product by mixing a small amount of bromine and liquid ozone, and allowing to evaporate in a flask. A thick white deposit of a substance thought to be bromine oxide was formed on the walls of the vessel, but owing to explosion it could not be kept under observation for a sufficient length of time to reach any definite conclusion.
A. J. MEE.

Ferromagnetic ferric oxide. E. F. HERROUN and E. WILSON (Proc. Physical Soc., 1928, 41, 100—111).—A review of recent work.

Reaction between sodium nitroprusside and sulphides. G. SCAGLIARINI and P. PRATESI (Atti R. Accad. Lincei, 1928, [vi], 8, 75—81).—Stable, homogeneous, crystalline compounds of the type $M_4[Fe(CN)_5NOS]$ have been obtained by the interaction of the sulphides of potassium, sodium, lithium, and rubidium, with sodium nitroprusside in absolute methyl alcohol. Electro-titrimetric evidence is adduced for the view that the reaction proceeds in two stages :

$$[Fe^{III}(CN)_5N^{II}O]'' + HS' = \left[Fe^{II}(CN)_5N^{III}{<}^O_{SH}\right]'''$$
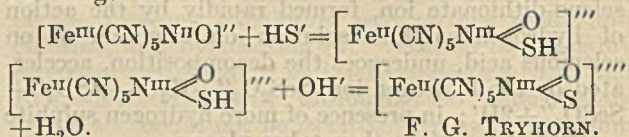
$$\left[Fe^{II}(CN)_5N^{III}{<}^O_{SH}\right]''' + OH' = \left[Fe^{II}(CN)_5N^{III}{<}^O_S\right]''''$$
$+ H_2O$.
F. G. TRYHORN.

New green compounds of cobalt. II. A. BERNARDI (Gazzetta, 1928, 58, 743—757; cf. A., 1927, 636).—When very dilute solutions of cobaltous salts and sodium hydroxide react in the cold, the blue basic salts which are first precipitated are rapidly converted into green compounds, which are stable both in solution and in the dry state. The formation of these green compounds depends on the proportions of cobaltous salt and sodium hydroxide used. With cobaltous chloride a green compound is formed only when the mol. ratio $NaOH : CoCl_2,6H_2O$

lies within the limits 0·02—0·44. Cobaltous sulphate and nitrate behave similarly but within still narrower limits. The green compounds are not formed in absence of oxygen, but appear when air is bubbled through the solution, and their formation is probably dependent on the oxidation of the cobalt atom from the bivalent state to a higher state. The compounds are of variable composition, which cannot be accounted for on the usual valency principles, and they are considered to be " adsorption compounds."
O. J. WALKER.

Quantitative spectroscopic analysis of alloys. T. NEGRESCO (J. Chim. Phys., 1928, **25**, 343—362; cf. A., 1928, 501, 929).—The conditions for using spark and arc spectra in the quantitative analysis of binary alloys are described, and precautions as to times of exposure, voltage, and development of plates are given. Two lines, one for each of the metals of the alloy, very close together are selected and their intensities compared either by eye or by a micro-photometer. As the proportion of one metal increases relatively to the other, it is found that the line of this metal is first less intense and finally becomes more intense than the neighbouring line of the second metal. Comparison is made with the photographs recording the results of a set of standard alloys, whereby the percentage of the constituents is determined. The accuracy of the method depends on the constancy of the physical conditions employed and also on the nature of the alloy. Examples of the analysis of Sn–Bi, Pb–Bi, Cu–Si, Fe–Si, Cu–Co, and Zn–Cd alloys are given. J. J. Fox.

Sensitivity of spectral lines. T. NEGRESCO (J. Chim. Phys., 1928, **25**, 363—407; cf. preceding abstract).—The sensitivity of any spectral line in a given source of emission in an alloy depends solely on its intensity in the pure metal examined under the same conditions. The effect of diminishing the proportion of an element in a mixture is studied and it is concluded that all the spectral lines excited by any particular method diminish in intensity and finally disappear, the last line to vanish being the most intense of the particular spectrum. These last lines are the true " raies ultimes," a definition which differs from that given by de Gramont for these lines. The divergence from de Gramont's conclusions is discussed in detail and sources of error in the results of various observers are indicated. It is shown that in spectra of sources of emission excited by smaller energy, e.g., flames and arcs, the most sensitive lines are emitted by the neutral atom (arc lines); in those of sources excited by greater energy, e.g., spark spectra, the most sensitive lines are given by ionised atoms (spark lines). In both cases the order of sensitivity of the series is sharp, principal, diffuse, Bergmann.
J. J. Fox.

Apparatus for rapid sedimentation analysis. C. J. VAN NIEUWENBURG and W. SCHOUTENS.—See B., 1929, 1.

Wood's metal as cathode in electrolysis. H. A. J. PIETERS (Chem. Weekblad, 1928, **25**, 706—707; cf. Paweck and Weiner, A., 1928, 143).—The determination is carried out by finding the increase in weight of a washed and dried quantity of the alloy after electrolysis; the alloy is kept liquid during electrolysis. The method is most suitable for determination of copper, cadmium, zinc, mercury, nickel, and cobalt present as sulphates. S. I. LEVY.

Fajans' method of titration. H. A. J. PIETERS (Chem. Weekblad, 1929, **26**, 6—9).—The use of colour change indicators in titrations in which precipitates are obtained has been investigated. In addition to the fluorescein derivatives employed by Fajans for the silver halide titration, Victoria-violet, chrome-green G, bromophenol-blue, and bromocresol-purple are found to give satisfactory results, both for simple titrations and for determination of chloride and iodide together. Titrations of lead salts with soluble oxalates, ferrocyanides, and phosphates can also be effected by the same method. Close study of the conditions for reaction is necessary in each case. S. I. LEVY.

Micro-analysis and technical methods of investigation. R. LUCAS and F. GRASSNER (Mikrochem., 1928, **6**, 116—132).—A description of the application of micro-analytical methods to technical problems with special reference to the determination of sulphur, halogens, carbon, hydrogen, nitrogen, and phosphorus in organic materials, electro-analysis, and colorimetric methods. J. S. CARTER.

Spot analysis. W. P. MALITZKY (Mikrochem., 1928, **6**, 157—160).—A reply to Feigl (A., 1928, 382).
J. S. CARTER.

Gas analysis apparatus. H. A. BAHR (Chem. Fabr., 1929, 13—15).—Improvements in the construction and manipulation of absorption pipettes are described. A rapid and accurate form of Orsat apparatus, especially suited for the analysis of gases containing hydrogen and methane, is described.
J. S. CARTER.

Hydrogen-ion colorimeter. R. B. H. GRADWOHL (J. Lab. Clin. Med., 1927, **12**, 694—701).—The illuminating box slides along a row of glass ampoules containing the selected sterile buffer of known p_H value. CHEMICAL ABSTRACTS.

" Salt error " of indicators in the colorimetric determination of p_H. I. M. KOLTHOFF (J. Physical Chem., 1928, **32**, 1820—1833).—A calculation of the salt correction of indicators on the basis of the Debye–Hückel equation has been attempted. When the ionic strength of the solution is considerably greater than that of the ordinary buffer solutions, the calculated values are higher than the experimental. Furthermore, indicators of the same type vary considerably. The salt corrections for many indicators in citrate solutions and in the presence of neutral salts have been experimentally determined and referred to the hydrogen electrode at 18° as standard. The average salt corrections of the various phthaleins at an ionic strength between 0·1 and 0·0025 are tabulated. The salt correction is also dependent on the properties of the buffer solution. Methyl-orange and methyl-red show small salt errors under different conditions and hence are suitable indicators in the colorimetric determination of p_H. Their behaviour is explained by their hybrid character.
L. S. THEOBALD.

Colorimetric determination of hydrogen-ion concentration in weakly-buffered solutions. E. OEMAN (Papier-Fabr., 1929, **27**, 27—30).—The p_H values of unbuffered solutions are accurately determined by plotting the p_H values observed as a function of the number of drops of solution of indicator present and extrapolating to zero concentration of indicator. The slope of the curve may be decreased, and the accuracy of the determination consequently increased, by using as indicator a mixture of the indicator proper and one of its salts.
J. S. CARTER.

Titration of strong acids combined with ammonia or organic amines. Titration of ammonium salts, amino-salts, and amino-acids. C. P. A. KAPPELMEIER (Rec. trav. chim., 1928, **47**, 1064—1071).—The method depends on the fact that phenolphthalein paper which has been reddened with ammonia or with an organic amine is rapidly decolorised when warmed owing to the dissociation of the compound of phenolphthalein with the ammonia or amine, whereas the red colour produced by dilute alkalis is stable for a considerable period. The total acid content of a solution containing sulphuric acid and ammonium sulphate may be determined by titrating with dilute sodium hydroxide solution until a piece of phenolphthalein paper which has been dipped in the solution does not lose its colour when warmed. The method can give results accurate to within $\pm 0.3\%$ of the total acid content and is illustrated by titration results for solutions of strong acids containing ammonia and nicotine. It may also be used for the determination of the nitrogen content of ammonium or amino-salts. O. J. WALKER.

Universal indicator which gives the spectrum colours for a p_H range of 3—11·5. H. W. VAN URK (Pharm. Weekblad, 1928, **65**, 1246—1249).—The indicator is prepared by dissolving 0·1 g. of methyl-orange, 0·04 g. of methyl-red, 0·4 g. of bromothymol-blue, 0·32 g. of naphtholphthalein, 0·5 g. of phenolphthalein, and 1·6 g of cresolphthalein in 70% alcohol, and diluting to 100 c.c. S. I. LEVY.

Use of potassium iodate in back titration for the determination of the hypochlorite content of solutions. J. R. LEWIS and R. F. KLOCKOW (J. Amer. Chem. Soc., 1928, **50**, 3243—3244).—Hypochlorite solutions may be analysed by adding excess of a suitable reducing agent and titrating back with potassium iodate, exactly as described for determining hydrogen peroxide (Jamieson, " Volumetric Iodate Methods," 1926). When sodium arsenite is used as reducing agent small amounts of nitrate or chlorate may be present, but chlorates must be absent when sodium thiosulphate or iodide solutions are used.
S. K. TWEEDY.

Detection of " chloramine-T," and its differentiation from hypochlorites. H. W. VAN URK (Chem. Weekblad, 1929, **26**, 9—10).—Various colour tests by means of which " chloramine-T " may be distinguished are described; the most suitable is the behaviour towards reduced indigo-carmine solution, the yellow colour of which is discharged by the bleaching action of hypochlorites, but changed to blue by the oxidising action of the chloroamine.

The thalleioquinine reaction is not given by the chloroamine, but is recommended as a more delicate and suitable test for hypochlorites than the starch–iodide test. S. I. LEVY.

Sensitive spot reaction for fluoride. F. PAVELKA (Mikrochem., 1928, **6**, 149—151).—The method depends on the fact that the colour of a zirconium alizarin lake is destroyed by hydrofluoric acid. The test-papers are prepared by moistening filter-paper with a solution of basic zirconium chloride to which an excess of an alcoholic solution of alizarin has been added. The dried papers are moistened with a drop of 50% acetic acid and a drop of the suspected solution is added. In presence of 0·01 mg. of fluorine a yellow stain appears on the originally red paper. Sulphates, oxalates, and phosphates interfere. With insoluble fluorides the powdered material is shaken with 5 c.c. of dilute hydrochloric acid containing 0·5—1·0 g. of borax and a drop of the resulting mixture taken for the test. About 0·06 mg. of calcium fluoride may be detected thus. Alternatively, the fluoride may be treated with silica and sulphuric acid and the moistened test-paper held in the vapours.
J. S. CARTER.

Determination of sulphur in copper alloys containing tin. H. LEYSAHT.—See B., 1929, 22.

Volumetric determination of sulphate ion. Z. MINDALEV (Z. anal. Chem., 1928, **75**, 392—395).—The neutral sulphate solution (10 c.c.) is treated with 10 c.c. of alcohol and 2—3 drops of a cold saturated solution of potassium iodide. The solution is then titrated with $0.1N$-lead nitrate solution added slowly with vigorous agitation until a faint yellow colour persists. When these conditions are rigidly adhered to, concordant results very slightly below the theoretical are obtained. A. R. POWELL.

Determination of selenium in sulphuric acid. Z. REICHINSTEIN.—See B., 1929, 15.

Refractometric analysis of solutions of pure compounds. F. URBAN and V. W. MELOCHE (J. Amer. Chem. Soc., 1928, **50**, 3003—3009).—Tables are given which enable the concentrations of solutions of telluric acid, selenious acid, and potassium ferrocyanide to be determined from observations in an immersion refractometer. S. K. TWEEDY.

Detection of phosphoric acid in minerals and rocks. H. LEITMEIER (Mikrochem., 1928, **6**, 144—148).—The sensitive phosphomolybdic acid–benzidine reaction may be applied to the detection of phosphates in minerals etc. A little of the powdered material on a filter-paper or a scratch on a porcelain plate is treated in the manner described (Feigl, A., 1928, 1107). The localisation of phosphates in minerals may be determined by pressing a filter-paper moistened with nitric acid–molybdate solution against a section. This paper is then brought into contact with a second paper moistened with benzidine solution and finally held in ammonia vapour. The blue regions correspond with the positions of the phosphatic constituents. J. S. CARTER.

Analysis of phosphorite. A. V. KRASNOVSKI (J. Chem. Ind. Moscow, 1928, **5**, 408—409).—The

insoluble residue is determined by boiling 5 g. with 50 c.c. of aqua regia. In the determination of dissolved silica, nitric acid is employed. The filtrate is diluted to a definite volume; a portion containing <0.1 g. P_2O_5 is used for the determination of phosphate by Woy's method (the molybdate precipitate being kept for 2—3 hrs. in a warm place and at least 12 hrs. at the ordinary temperature before filtration) and another for determining alumina, iron, calcium, and magnesium. This portion is evaporated nearly to dryness and treated on a water-bath with 1 g. pieces of tin and a few c.c. of fuming nitric acid to eliminate phosphoric with metastannic acid. The iron and alumina are determined together by Blum's method; the filtrate is diluted to 300 c.c., and the calcium precipitated twice as oxalate from solutions containing acetic and hydrochloric acids, respectively. Magnesium is determined by Schmitz's method, and moisture and loss on ignition by the usual methods. The determination of fluorine requires examination.
CHEMICAL ABSTRACTS.

Volumetric determination of arsine. H. KUBINA (Z. anal. Chem., 1929, **76**, 39—48).—Two titrimetric methods for the determination of arsine are described. According to the first method the gas is introduced into an evacuated absorption vessel containing an excess of a standard solution of bromate and a considerable excess of bromide. After acidification the contents are agitated and oxidation to arsenic acid occurs. An excess of a standard solution of arsenious salt is added and the back titration carried out with the bromate solution. Each c.c. of $0.1N$-solution of bromate required during the absorption corresponds with 0.280 c.c. of arsine at 0° and 760 mm.

In the second method the absorbing medium is an acid solution of iodine monochloride, the iodine liberated according to the equation, $AsH_3 + 8ICl + 4H_2O = AsO_4''' + 4I_2 + 8Cl' + 11H^+$, being titrated with a solution of potassium iodate in the presence of a cyanide (Lang, A., 1925, ii, 713). Each c.c. of $0.1N$-solution of iodate corresponds with 0.187 c.c. of arsine at 0° and 760 mm. J. S. CARTER.

Decomposition of silicates by strontium salts for the determination of alkali metals. J. KAVINA (Chem. Listy, 1928, **22**, 289—294).—The alkali metal content of silicates can be determined with satisfactory accuracy using a fusion mixture consisting of 1 part of ammonium chloride to 6 parts of strontium carbonate. R. TRUSZKOWSKI.

Determination and separation [of sodium and potassium]. A. THÜRMER (Chem.-Ztg., 1928, **52**, 974—975).—Alcohol (96—99%) is suitable for the separation of sodium and potassium perchlorates. Sodium may be determined in the filtrate by removal of solvent and perchloric acid at 80° and 180°, respectively. In accurate work the resulting sodium perchlorate may be fused with sodium carbonate and potassium nitrate and chloride determined volumetrically or gravimetrically. If the alkali metals are initially present as sulphates precipitation of potassium as the salt $KNa_2Co(NO_2)_6$ should be effected by addition of excess of sodium cobaltinitrite. Sodium and potassium chlorides are appreciably volatile at a bright red heat. J. S. CARTER.

Determination of potassium. L. GALIMBERTI (Atti II Cong. Naz. Chim. pura appl., 1926, 1396—1397; Chem. Zentr., 1928, ii, 589).—The method depends on the precipitation of potassium sodium cobaltinitrite, reduction therewith of permanganate solution, addition of oxalate, and titration of the excess. It is applicable in presence of considerable quantities of sodium chloride or magnesium sulphate.
A. A. ELDRIDGE.

Indirect detection and determination of alkali sulphates in certain other metallic sulphates. A. WØHLK (Dansk Tidsskr. Farm., 1928, **2**, 315—319).—The method obviates the necessity for using hydrogen sulphide. The sulphate (1 g.) is dissolved in water (150 c.c.) and a slight excess of a 4% solution of barium hydroxide is added. The whole is boiled for 10 min., the volume being kept constant, and then filtered. Phenolphthalein (0.5 c.c. of a 1% solution) is added to the filtrate, and carbon dioxide passed in until the red colour disappears. The liquid is boiled again until the hydrogen carbonates are decomposed and the red colour returns. After thorough cooling the solution is filtered, 15 drops of methyl-red are added to the filtrate, and the liquid is then titrated with $0.1N$-acid until the pink colour of methyl-red appears. If only a qualitative test is desired the solution can be titrated directly, but for quantitative purposes it must first be evaporated to 50 c.c. and refiltered if necessary. Blank determinations require about 0.5—0.9 c.c. of $0.1N$-hydrochloric acid for the titration, and the method permits the detection of 1% of alkali sulphate. It is necessary that the sulphates under examination should conform with the requirements of the pharmacopœia as regards freedom from chloride, ammonia, etc.
H. F. HARWOOD.

Nephelometric determination of barium sulphate. J. KŘEPELKA and A. KALINA (Chem. Listy, 1928, **22**, 545—550).—At concentrations of 0.3—1.0 mg. Ba per litre the mean error of nephelometric determinations of the sulphate is 0.5%. The suspension should not be kept longer than 30 min. after preparation; the addition of glycerol to 10% by volume greatly augments the stability of these suspensions. The limiting percentage concentrations of other salts which may be present without affecting the accuracy of this method are: sodium 0.15, hydrogen 0.30, magnesium 0.003, zinc or cadmium 0.006, mercury 0.04, and aluminium chloride 0.002. All these ions, with the exception of magnesium, provoke coagulation of the suspension at higher concentrations than the above, leading to excessively high results, whilst magnesium has a protective influence, so that the results are low.
R. TRUSZKOWSKI.

Radium and geology. C. S. PIGGOT (J. Amer. Chem. Soc., 1928, **50**, 2910—2916).—A method of determining the radium content of rocks is outlined very briefly. Preliminary experiments on granites indicate that radium is associated more with those minerals of high than with those of low sp. gr.; it is particularly associated with the micas. A possible method of determining directly the lead derived from uranium by means of the mass-spectrograph is given (cf. Aston, A., 1927, 806). S. K. TWEEDY.

Determination of zinc as zinc pyrophosphate in the presence of much sodium chloride. L. DEDE (Ber., 1928, 61, [B], 2463—2465; cf. this vol., 43).—The precipitate obtained by the addition of ammonium phosphate to a solution of a zinc salt containing sodium and ammonium chlorides is a mixture of zinc ammonium and zinc sodium phosphate; the proportion of the former can be increased by increasing the relative amount of ammonium chloride, but, contrary to Finlay and Cumming (J.C.S., 1913, 103, 1004), homogeneous zinc ammonium phosphate can only be thus precipitated if the solution contains less than 3% of sodium chloride. If this is not the case, the solution is concentrated until sodium chloride commences to separate, cooled, and saturated with dry hydrogen chloride. The precipitated sodium chloride is removed and washed with highly concentrated hydrochloric acid. After removal of the bulk of the acid from the filtrate by evaporation, the zinc is precipitated as zinc ammonium phosphate in the residue which has been neutralised cautiously by ammonia.   H. WREN.

Rapid electrolytic deposition of cadmium and zinc and their separation by regulation of the voltage. E. BRENNECKE (Z. anal. Chem., 1928, 75, 321—371).—The deposition potential of zinc from acid sulphate solutions 0·1—0·5N in free acid using rotating coppered platinum gauze cathodes is 2·7—2·8 volts whilst that of cadmium is 2·28—2·34 volts, but the deposition potential of zinc on cadmium-plated electrodes under the same conditions is 2·92—3·0 volts. The deposition of cadmium from sulphate, acetate, or cyanide solutions is never complete, a fraction of a mg. always remaining in the electrolyte; nevertheless the results obtained for cadmium are invariably high under the conditions usually recommended, owing to oxidation of the surface of the deposit by oxidising agents in the ether used for washing prior to weighing. The use of amalgamated cathodes does not ensure complete precipitation of the cadmium nor does it prevent oxidation. Amalgamated copper electrodes cannot be used for the deposition of zinc from solutions containing ammonium sulphate as ammonium amalgam is formed and the cathode disintegrates, but good results are obtained by deposition from feebly acid acetate solutions using a coppered platinum cathode. For the separation of cadmium from zinc 100 c.c. of the solution are treated with 10—12 c.c. of 2N-sulphuric acid and electrolysed at 2·8 volts for 5—10 min., then at 2·7 volts for 25—35 min. to deposit the cadmium; the solution is then neutralised with ammonia, reacidified with acetic acid, treated with 4 g. of sodium acetate, and electrolysed for 10 min. with 1—2 amp. to deposit the zinc. The results are good by a compensation of errors as the cadmium deposit contains traces of zinc and the zinc deposit traces of cadmium.   A. R. POWELL.

Determination of lead by means of 8-hydroxyquinoline. V. MARSSON and L. W. HAASE (Chem.-Ztg., 1928, 52, 993—995).—The hot acetate solution of lead is treated with 30—60 c.c. of a hot solution of 8-hydroxyquinoline (saturated cold), then with dilute ammonia until feebly alkaline, stirred vigorously, and set aside over-night in a cold place. The precipitate is collected in a porous filter crucible, washed with cold water, dried at 105°, and weighed; it contains 41·85% Pb. As the solubility of the compound in cold water is about 4·5 mg./litre in the presence of excess of the precipitant, the method is unsuitable for the determination of minute quantities of lead, e.g., in drinking water. For the separation of copper from lead the copper is precipitated by means of dibromo-8-hydroxyquinoline in hot dilute hydrochloric acid solution and the lead from the filtrate as described above.   A. R. POWELL.

Colorimetric determination of thallium. C. STICH (Pharm. Ztg., 1929, 74, 27).—For the determination of thallium in rat-poisons etc. about 2 g. of material are ashed and the residue is dissolved in dilute sulphuric acid. Thallium is determined colorimetrically as sulphide in alkaline solution.
                                J. S. CARTER.

New salts of nitrosophenylhydroxylamine and their application in microchemical analysis. A. MARTINI (Mikrochem., 1928, 6, 152—156).—The micro-crystalline forms of the *cuprammonium, uranyl, calcium, strontium, barium,* and *cadmium* salts of nitrosophenylhydroxylamine (cupferron) are described and photomicrographs are given. The crystal forms of the barium and uranyl salts are sufficiently characteristic for the detection of these cations. The calcium, strontium, and cadmium salts are, however, very similar. Cadmium should therefore be confirmed by treatment with sodium bromide and brucine acetate (A., 1927, 953), and calcium confirmed by conversion into calcium selenite, using a saturated solution of sodium selenite.   J. S. CARTER.

Analysis of bauxite and refractories of high alumina content. G. E. F. LUNDELL and J. I. HOFFMAN.—See B., 1929, 19.

Determination of manganese in the presence of silica. C. NEWCOMB (Analyst, 1928, 53, 644—645).—If the ordinary procedure is followed in the colorimetric determination of manganese by permanganate in acid solution in presence of silica it is impossible to extract all the manganese as it is tenaciously adsorbed by the silica. If the ash, fused with alkali carbonate, is dissolved in water and the solution poured into more than sufficient acid to neutralise it, a colloidal solution results; the adsorption then taking place is not in a form that interferes with the oxidation, and a clear pink solution is finally obtained.   D. G. HEWER.

Detection of iron as an impurity in reagents by the thiocyanate test. H. W. VAN URK (Chem. Weekblad, 1928, 25, 703—704, 704—706).—The delicacy of the test is influenced by presence of salts. The influence of sodium sulphate has been examined; the test in this case is not more sensitive than the sulphide test, although it can be made sufficiently accurate for examination of the "reagent quality" salt. The presence of chlorides and nitrates is not harmful. The influence of salts is shown to be due to their effect on the hydrogen-ion concentration; by adjustment of this, the otherwise strong effect of salts of weak acids can be completely eliminated.   S. I. LEVY.

Stability of ferrous sulphate solutions and their use in standardising permanganate. J. A. N. FRIEND and E. G. K. PRITCHETT (J.C.S., 1928, 3227—3232).—Addition of sulphuric acid in concentrations up to $2N$ greatly increases the resistance of ferrous sulphate solutions to oxidation in air; further increase in acid concentration has little effect. If the precautions described are taken, the results of standardising permanganate with solutions of ferrous sulphate prepared by dissolving iron in sulphuric acid agree to within 0·1% with those obtained by the oxalate method.   F. J. WILKINS.

Standard method for examination of [alkali] ferrocyanides. H. MOLL (Chem. Weekblad, 1928, 25, 657—658).—The method selected at the April conference at Berlin (titration against standard zinc sulphate solution) is described in detail.
S. I. LEVY.

Determination of molybdenum. H. A. DOERNER (U.S. Bur. Mines. Inf. Circ., 1928, No. 6079, 2 pp.; also Bull., No. 212).—The sample is dissolved in aqua regia, the solution evaporated with sulphuric acid, and lead sulphate removed; calcium etc. is removed by addition of ammonia solution and sodium carbonate (3 g.) and digestion. Any precipitate produced in the filtrate by tartaric acid and hydrogen sulphide is removed. The alkaline sulphide solution is then acidified and molybdenum disulphide collected. This is dissolved in aqua regia, and lead molybdate precipitated in a properly buffered solution.   CHEMICAL ABSTRACTS.

Determination of molybdenum by reduction of molybdic acid with zinc. J. KASSLER (Z. anal. Chem., 1928, 75, 457—466).—About 10 g. of zinc in the form of coarse powder are added to 250 c.c. of the warm solution of molybdic acid containing 30 c.c. of 1 : 1 sulphuric acid and 5 c.c. of 1 : 1 hydrochloric acid. If sufficient chloride is present addition of hydrochloric acid is unnecessary. When reduction is effected (about 15 min.) the whole is filtered, conveniently through glass wool covered with a layer of glass beads, and titrated with a solution of potassium permanganate. Precautions must be taken to minimise oxidation between reduction and titration.

To determine molybdenum in steels etc. the solution obtained after dissolution in hydrochloric acid, oxidation with chlorate, and removal of excess of chlorine is neutralised and transferred to a litre flask containing an excess of alkali. After dilution to 1000 c.c., 250 c.c. of filtered solution are neutralised with 1 : 1 sulphuric acid and a further 30 c.c. added. The solution is boiled and a few c.c. of permanganate solution are added to oxidise organic matter before addition of zinc. If present, vanadium must be reduced by sodium sulphite or ferrous salt before precipitation with alkali. Tungsten and nitrates interfere. The determination of molybdenum in presence of tungsten will be described shortly.
J. S. CARTER.

Analytical chemistry of tungsten. I. Berzelius' method for determination of tungsten as mercurous tungstate. V. I. SPITZIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1229—1235, and Z. anal. Chem., 1928, 75, 433—440).—The use of mercurous nitrate without the addition of nitric acid gives complete precipitation of mercurous tungstate from neutral tungstate solution, without the necessity of any further treatment of the precipitate, such as addition of alkali. Where precipitation takes place from acid solution even the subsequent addition of alkali does not bring about quantitative separation of tungsten trioxide, owing probably to the formation of soluble mercury metatungstates and of free tungstic acid under the influence of the acidity of the medium.
R. TRUSZKOWSKI.

Analytical chemistry of tungsten. II. Quantitative analysis of tungsten compounds in the dry way. V. SPITZIN and L. KASCHTANOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1333—1349, and Z. anal. Chem., 1928, 75, 440—457).—Sodium tungstate is heated in a platinum boat at 650—700° in a current of pure dry hydrogen for 30 min., and then at 900° for 1 hr.; the tube is then cooled, and again heated at 900° for a further 30 min. The residue in the boat now consists only of tungsten. The preliminary heating at 650° is necessary in order to avoid fusion of acid tungstates, which would interfere with their further reduction. The sodium content is determined similarly by heating in a current of dry hydrogen chloride at 500—550° for 2—8 hrs., when the residue consists of sodium chloride, the tungsten having been volatilised as oxychloride. Tungsten bronzes, of the general formula $x(R_2O),y(WO_3),WO_2$, where R represents one equivalent of an alkali or alkaline-earth metal, are quantitatively converted into tungstates by heating at 400—500°; alternatively, when heated in a current of hydrogen chloride the dioxide is converted into oxychloride : $3WO_2+4HCl=W+2WO_2Cl_2+2H_2O$, the residual tungsten, after roasting and volatilisation in hydrogen chloride, affording a measure of that originally present. Metallic tungsten is best analysed for oxides by heating in a current of dry hydrogen chloride, when the oxides are converted into volatile oxychlorides as follows : $3W_2O_5+10HCl=W+5WO_2Cl_2+5H_2O$, with a corresponding loss in weight of the sample.   R. TRUSZKOWSKI.

Zirconium. II. Detection of potassium by zirconium sulphate in the presence of ammonium ions. R. D. REED and J. R. WITHROW (J. Amer. Chem. Soc., 1928, 50, 2985—2987; cf. A., 1928, 858). —The sensitiveness of zirconium sulphate as a reagent for the detection of potassium is unimpaired by the presence of ammonium ions.   S. K. TWEEDY.

Determination of small quantities of antimony in the form of stibine. J. GRANT (Analyst, 1928, 53, 626—632).—A rapid electrolytic method for determining antimony in solutions containing up to 8 mg. in 10 c.c. of liquid consists in removal of the antimony (from solution in $0·5N$-hydrochloric acid) as stibine by a swift current of hydrogen, which, as a stream of bubbles, impinges on the point of an inverted cone lead cathode. The stibine is thus removed from the cell before it decomposes. The actual apparatus is an improved form of the electrolytic Marsh type. The antimony in the deposit is determined by a colorimetric method for amounts from 2 to 0·01 mg., and by matching with standard stains for smaller quantities. Any arsenic present is

deposited with the antimony, but since arsenic is sparingly soluble in hydrochloric acid the colorimetric method suggested need not be modified. The deposit is dissolved in 1 c.c. of concentrated hydrochloric acid, diluted with 3 c.c. of water and 1 c.c. of a clear, saturated solution of hydrogen sulphide, and the colour matched against that produced from a known volume of a dilute standard solution of tartar emetic. D. G. HEWER.

Determination of palladium by means of 6-nitroquinoline. S. C. OGBURN, jun., and A. H. RIESMEYER (J. Amer. Chem. Soc., 1928, 50, 3018—3022).—Boiling palladium chloride solution is precipitated with a hot, saturated, aqueous solution of 6-nitroquinoline. The precipitate is ignited in air and then in hydrogen and, after cooling (preferably in carbon dioxide), the residue of palladium is weighed. Any other platinum metal may be present. The precipitate is $Pd(C_9H_6O_2N_2)_2$. S. K. TWEEDY.

Electric arc in gases at low pressures. F. H. NEWMAN (Phil. Mag., 1928, [vii], 6, 811—817).—The cold electrode arc previously described (A., 1926, 1069) has been modified by the incorporation of water-cooling of the electrodes and the provision of a large reservoir to minimise pressure changes due to the liberation of gases from the electrodes and walls of the containing vessel. The starting of the arc is facilitated by the initial electric discharge through two effects. First, local heating of impurities in the cathode surface gives rise to thermionic emission and, secondly, the gases are modified so as to be more easily ionised than when in the normal state.
A. E. MITCHELL.

Simple modifications of the Kohlrausch bridge for the potentiometric measurement of alternating current resistance. E. DENINA (Annali Chim. Appl., 1928, 18, 529—540).—Descriptions are given of : (1) a simple modification of the Kohlrausch bridge which gives directly the value of a resistance as the mean of two readings ; (2) an improved method for elimination of the influence of the contact resistances, and (3) an arrangement for compensating for the capacitance of electrolytic cells.
T. H. POPE.

Microphotometer for comparative measurements of density on X-radiogram spots. K. V. VASILEV (Trans. Inst. Econ. Min. Met. Moscow, 1928, No. 34, 10—19).—Two similar microscopes are used for the examination of the film and a photographic wedge, which is adjusted until the images are indistinguishable. The central portion of the image is that of the spot ; its extent depends on the silvered area in the Lummer cube.
CHEMICAL ABSTRACTS.

Method of obtaining X-radiograms. K. V. VASILEV (Trans. Inst. Econ. Min. Met. Moscow, 1928, No. 34, 45—58).—The specimen is mounted in a circular hole in the centre of the film. The plane of the film includes the axis of the beam. The reflected rays are recorded as radial streaks originating at the centre of the film. CHEMICAL ABSTRACTS.

Microphotometer for the study of spectrograms. I. J. GWINN (Proc. Iowa Acad. Sci., 1927, 34, 279).—The light is focussed by means of a vertical

system of microscope lenses on to a bismuth–silver thermocouple. Measurements of length are made with a micrometer screw. CHEMICAL ABSTRACTS.

Gas circulating pump. G. BARR (J.C.S., 1928, 3293—3295).—A pump is described for the circulation of gas in a closed system at pressures near that of the atmosphere. F. J. WILKINS.

Apparatus for micro-gas analysis. C. H. PRESCOTT, jun. (J. Amer. Chem. Soc., 1928, 50, 3237—3240).—An apparatus is described, designed quantitatively to analyse about 0·3 c.c. of gas for carbon dioxide and monoxide, hydrogen, and nitrogen, all reagents being used in solid form.
S. K. TWEEDY.

Stirrer for gas absorption. A. F. BENNING (Proc. Indiana Acad. Sci., 1927, 37, 263—264).—Two short tubular arms are sealed to a tubular shaft near the end, the 4-way junction being constricted and a hole provided at a convenient point in the lower part of the shaft, so that gas is drawn down and mixed with the liquid. A high speed of revolution is necessary. CHEMICAL ABSTRACTS.

Laboratory devices. Vacuum stirrer, pressure alternator, and a gauge for measuring low pressure of permanent gases in condensable vapours. R. K. TAYLOR (J. Amer. Chem. Soc., 1928, 50, 2937—2940).—The stirrer is used for freeing liquids from dissolved gases. By means of the pressure alternator, which automatically applies alternately a pressure of 1 atm. and a pressure less than 1 atm. by a desired amount, the liquid is continually washed over a column of beads. The gauge is a modified form of McLeod's gauge.
S. K. TWEEDY.

Miscometer. J. HOUSTON (Analyst, 1929, 54, 30 ; cf. B., 1926, 930).—The measuring device consists of a burette instead of a hollow stopper connected through the top with the air suction, and with a stopcock at the bottom which allows the samples to be drawn in in turn. These are mixed by turning the stopcock to connect the burette with the second chamber in such a way that air is drawn through the mixture. By manipulating the top stopcock (connecting to air-suction and to the second chamber) the mixed sample is drawn into the second chamber, the small burette opening out from this fills up, and the remainder of the sample flows out from a bottom outlet tube by gravity. The stopcocks on each side of the measuring chamber are then closed and the measured sample is drawn out from the small burette.
D. G. HEWER.

Shaker for the Van Slyke blood-gas apparatus. H. F. PIERCE (J. Lab. Clin. Med., 1928, 13, 1048—1049).

Apparatus for the distillation of urea-nitrogen. L. C. MURPHY and R. C. JENKINS (J. Lab. Clin. Med., 1928, 13, 1049—1051).

Separator for continuous fractional distillation under reduced pressure. R. DELABY and R. CHARONNAT (Bull. Soc. chim., 1928, [iv], 43, 1287—1288).—The actual receiver is connected by means of a stopcock with a lower portion fitted with outlet tube and stopcock for distillate. This lower portion

may, by suitable manipulation of stopcocks, be isolated, opened to the air to permit removal of liquid, and re-introduced into the evacuated system without interrupting the distillation. J. S. CARTER.

Laboratory rectifying column. M. J. MARSHALL (Ind. Eng. Chem., 1928, **20**, 1379).—The vapour passes up a lagged column filled with beads and out through a small, wide side-tube connected with a vertical condenser. The reflux ratio can be adjusted to any value up to total reflux by operating a small stopcock fitted in the side tube close to the column; a certain fraction is drawn off through the cock and the excess overflows into the fractionation column. Hold-up of reflux liquid is avoided.
E. H. SHARPLES.

Self-adjusting burette. R. C. HOCKETT (J. Chem. Education, 1928, **5**, 1131—1132).—The burette is automatically filled to the zero mark by means of a stopcock in the side arm. CHEMICAL ABSTRACTS.

Rapid calibration of burettes. Z. MINDALEV (Z. anal. Chem., 1928, **15**, 390—392).—Three burettes are joined to one another by means of T-pieces and rubber tubes below the graduation marks. The first burette serves as a reservoir and the second as a standard for calibrating the third. The volume occupied by 2 c.c. in the second burette is accurately ascertained by weighing, and this volume is marked off in the usual way. By repeatedly transferring this weighed 2 c.c. of water from the standard to the third burette the latter is progressively calibrated and can then be used as a standard for calibrating any number of burettes on the same principle.
A. R. POWELL.

Standardised ground-glass apparatus. J. FRIEDRICHS (Chem. Fabr., 1929, 5—6).—Apparatus with interchangeable ground-glass connexions includes reaction flasks for the treatment of one liquid by another, miscible or non-miscible, of a solid by a liquid, Soxhlet extractors, flasks for the generation of gases, etc. It is possible, e.g., to perform an extraction and distil off the solvent without transferring the liquid from one flask to another. C. IRWIN.

Temperature regulator for Carius furnaces. G. B. HEISIG (J. Amer. Chem. Soc., 1928, **50**, 3388).—Regulation of the temperature of gas-heated Carius furnaces is facilitated by using a thermostatic control of the type fitted to gas cookers. H. E. F. NOTTON.

Drying oven. F. HAHN (Chem.-Ztg., 1928, **52**, 975).—A convenient form of a small aluminium drying oven, which may be supported by a retort stand, is described. The principal feature is that the door is not hinged, but leans against the sloping front. No jolt is then given to the oven on opening.
J. S. CARTER.

Determination of Engler viscosities. S. ERK (Chem. Fabr., 1928, 715—716, and Chem.-Ztg., 1928, **52**, 995).—An error is introduced if the volume of liquid is determined by pouring from the flask and draining for 1 min., as viscous liquids will drain more slowly than water. With a liquid of 121° Engler the error is 5·6%. A clean, dry flask should be used, graduated by filling. In the case of determinations at temperatures above atmospheric the water-bath should not be heated during the determination to counteract a fall in the reading of the thermometer immersed in the oil which is running out. The temperature of the water-bath should be kept constant.
C. IRWIN.

Turbidimeter. W. EWALD (Instruments, 1928, **1**, 371—375).—Two pencils of rays from the same source, which have passed respectively through the turbid solution and an adjustable turbid wedge, are reflected on to a divided field, equalised, and the scale reading is recorded. CHEMICAL ABSTRACTS.

[Filtering] apparatus with fused-in porous glass plates. G. F. HÜTTIG (Chim. et Ind., 1928, **20**, 1034—1038).—Filters of 25 c.c. capacity made from fritted glass plates fused into ordinary laboratory glass were examined for loss in weight through contact with water, hot dilute hydrochloric acid, and solutions of ammonia, sodium hydroxide (hot), and lead nitrate. In no case was the loss in weight greater than 0·3 mg. except with sodium hydroxide, when 4—8 mg. were lost, the amount depending on the size of pores. The rapidity with which precipitates can be dried on these filters, the loss in weight on heating to 400°, and the increase in weight of a dried filter by absorption of atmospheric moisture were also examined. In their properties these filters compare very favourably with the Gooch and Brunck types. In analytical work care should be taken to choose a filter having pores smaller than the particles being filtered, as otherwise subsequent complete removal of the solid from the filter plate is difficult. H. INGLESON.

Apparatus for testing filtering and decolorising media. A. LINSBAUER and J. VAŠÁTKO.—See B., 1929, 5.

Attachment for bottles used for storage of standard solutions. A. G. LIPSCOMB (Analyst, 1928, **53**, 645).—In order to prevent contamination by carbon dioxide or concentration of the solution being stored, a glass jacket, through the top of which is sealed a tube expanded into three bulbs, is fixed through the cork of the store bottle. The lowest bulb opens into the jacket, and down the centre of the bulbs is a narrower tube, sealed into the lower end of the jacket and passing into the store bottle, and with its upper end sealed through the wall of the centre bulb tube and opening into the top of the jacket. A suitable liquid, such as sodium hydroxide solution, for that solution in store, is poured down the bulb tube; the incoming air is thus freed from carbon dioxide and takes up water vapour to the correct extent. D. G. HEWER.

Micro-determination of mol. wt. by the ebullioscopic method. A. RIECHE [with F. QUERBERITZ] (Chem.-Ztg., 1928, **52**, 923—924).—The advantages and disadvantages of the apparatus of Sucharda and Bobranski (A., 1927, 849) are discussed. The use of the authors' apparatus (A., 1926, 1118) with solvents of higher b. p. is described. F. R. ENNOS.

Atomiser for flame coloration. H. EMDE (Chem.-Ztg., 1928, **52**, 1003).—A simple device for the introduction of atomised spray from a salt solution into the air supply of a Bunsen burner is described.
J. S. CARTER.

Geochemistry.

Occurrence of free sulphuric acid in groundwater. E. SCHROEDTER (Chem. Erde, 1928, 4, 70—75).—Analyses of the soils taken at various depths on the moors near Danzig show the presence of small amounts of free sulphuric acid.   L. J. SPENCER.

Action of sulphurous gases at high temperatures on basic glasses and rocks and a probable origin of sulphated thermal waters. A. PORTEVIN (Compt. rend., 1928, **187**, 1148—1150).—Sulphurous gases, even when dilute, attack basic rocks and glasses superficially at 900° with the formation of a water-soluble deposit consisting principally of sodium sulphate with traces of calcium, potassium, and magnesium sulphates. The dissolution of such deposits in warm springs during the early post-volcanic period is a probable explanation of the origin of alkaline sulphated thermal waters.   J. GRANT.

Bearing of base exchange on the genesis of petroleum. E. McK. TAYLOR (J. Inst. Petroleum Tech., 1928, **14**, 825—840).—The properties of sodium and calcium clays are described. The p_H values and replaceable calcium and sodium have been determined for samples of shale from Rumania and the West Indies. Under the conditions imposed by a sodium clay roof, oils, fats, waxes, and allied substances, fatty acids which may have been formed by the previous decomposition of oils and fats, and glycerol are decomposed by bacteria, glycerol yielding methane. A theory of the genesis of petroleum involving the formation of sodium clays by base exchange, and the subsequent bacterial decomposition of contiguous organic matter, is advanced.
C. W. GIBBY.

Blue rock salt. F. C. GUTHRIE (Nature, 1929, **123**, 130).—That blue rock salt has a slightly greater energy content than the colourless variety is shown by the facts that it glows, with loss of the blue colour, when suddenly heated at 350°, and that it has a slightly smaller negative heat of dissolution.
A. A. ELDRIDGE.

Asphaltite from the Philippine Islands. E. T. HODGE (Philippine J. Sci., 1928, **37**, 263—272).—The chemical and physical properties of a sample of asphaltite from the Philippine Islands are described, and show that it lies between manjak and grahamite. Its genesis is discussed.   C. W. GIBBY.

Microscopic characteristics of the oxides of manganese and of the natural manganites. J. ORCEL and S. PAVLOVITCH (Compt. rend., 1928, **187**, 1295—1297).—The optical characteristics and behaviour towards etching reagents of a number of anisotropic and isotropic natural manganites and oxides of manganese are tabulated. Neukirchite, ebelmenite, and brostenite are considered to be mixtures of polianite and psilomelane, braunite also being associated with the last-named. Vredenburgite is a mixture of braunite, hæmatite, and polianite.   J. GRANT.

Minerals of the apatite group. G. CAROBBI [with S. RESTAINO] (Atti II Cong. Naz. Chim. pura Appl., 1926, 1156—1181; Chem. Zentr., 1928, ii,

531).—A pyromorphite from Braubach (Nassau) contained lanthanum, neodymium, samarium, yttrium, europium, gadolinium, dysprosium, erbium, ytterbium, and cerium (rare-earth oxides about 0·05%). Pyromorphite from Leadhills (Lanarkshire) contained these elements (0·02% of oxides), except samarium and ytterbium; Cr_2O_3 0·1 (probably as chromate), MnO 0·001, CaO 0·16%, SrO and BaO traces, were also present. Mimetite from Santa Eulalia (Chihuahua, Mexico) contained Cr_2O_3 0·07, MnO 0·008, ZnO 1·37, CaO 0·29, BaO and SrO 0·009%, Cu none. Experimental evidence for the existence of pyromorphites, vanadinites, and mimetites in which rare-earth elements isomorphously replace lead has been obtained.   A. A. ELDRIDGE.

Phosgenite of Monteponi. F. RODOLICO (Atti R. Accad. Lincei, 1928, [vi], **8**, 171—174).—Twinned crystals of phosgenite, d 6·05, are described, in one of which numerous regular pits occurred. These pits were square in shape with edges parallel to the angles between the planes (001) and (111), and were formed by the facets of a very obtuse bipyramid sometimes truncated and terminating in a square. An analysis of this phosgenite gave PbO 81·73, Cl 13·06, CO_2 7·91, Ag 0·01, less O for Cl 2·99%.   F. G. TRYHORN.

Betafite from Sludianka, E. Siberia. G. TSCHERNIK (Bull. Soc. Franç. Min., 1927, **50**, 485—489; Chem. Zentr., 1928, ii, 335).—Betafite, black octahedra, often combined with dodecahedra, d 4·82—4·93, contained: MgO 0·13, CaO 3·93, PbO 0·10, MnO 0·15, FeO 1·20, Fe_2O_3 2·25, Al_2O_3 0·24, ceria earths 1·61, yttria earths 13·11, UO_3 26·37, ThO_2 1·30, SnO_2 0·37, TiO_2 16·51, SiO_2 0·59, Nb_2O_5 37·36, Ta_2O_5 1·46, H_2O 2·47%.   A. A. ELDRIDGE.

Laumontite of Toggiano. P. GALLITELLI (Atti R. Accad. Lincei, 1928, [vi], **8**, 82—87).—Two types of laumontite occur associated with the datolite of Toggiano, the one of a rather fibrous structure, with a pearly lustre, the other granular and whitish. Goniometric analyses have been made of these two varieties, which contain, respectively, SiO_2 50·78, 51·43; Al_2O_3 21·09, 22·30; BeO 0·47, 0·40; CaO 12·13, 12·47; H_2O 15·34, 13·74. When heated, laumontite loses water continuously, but there is some evidence of an arrest point between 250° and 300°, leading to the conclusion that there is probably some difference in the nature of the water lost below 300° and that given up at higher temperatures.
F. G. TRYHORN.

Chemical and spectrographic investigations on crocoite from Tasmania and wulfenite from Bleiberg. G. CAROBBI (Annali Chim. Appl., 1928, **18**, 485—494).—A Tasmanian crocoite contains (%): Ce_2O_3 0·003; La_2O_3 etc. 0·026; Y_2O_3 etc. 0·008; CaO 0·10; SrO, BaO traces, and wulfenite from Bleiberg: Cr_2O_3 0·47; Fe_2O_3, Al_2O_3, and rare earths (less than 0·001) 0·07; CaO, BaO, SrO 0·34; the rare-earth metals include Ce, La, Nd, Sm, Y, Er (cf. A., 1926, 811; 1927, 1164).   T. H. POPE.

Oxidation products derived from sphalerite and galena. P. F. BOSWELL and R. BLANCHARD

(Econ. Geol., 1927, **22**, 419—453).—Sphalerite and galena may dissolve without generation of, or attack by, iron-bearing solutions, thus leaving no limonite. CHEMICAL ABSTRACTS.

Fushun coal and its geological significance. C. IWASAKI (Tech. Rep. Tôhoku, 1928, **8**, 99—126). —Analyses and microscopic sections of different coals from the Fushun colliery, Manchuria, are given, and the geological significance of the latter is discussed. C. W. GIBBY.

Composition of coal—its rational analysis. W. FRANCIS and R. V. WHEELER.—See B., 1929, 5.

Chemical weathering in northern Norway. E. BLANCK, F. GIESECKE, and H. KEESE (Chem. Erde, 1928, **4**, 76—87).—Analyses are given of fresh and weathered rocks (granite and schist) and of the covering soil on the island of Hindö (cf. A., 1928, 612). L. J. SPENCER.

Dolomitisation in the Bryozoa reefs of the Zechstein of Thuringia. E. KÖHLER (Chem. Erde, 1928, **4**, 42—64).—Many (105) partial analyses are given of the rock taken from different parts of the " coral " reefs in the limestones. They show varying amounts of magnesia from traces up to that required for pure dolomite. L. J. SPENCER.

So-called kaolinisation of granite under a humus cover in the Black Forest. E. BLANCK and H. KEESE (Chem. Erde, 1928, **4**, 33—41).— Analyses of the bleached rock show an increase in silica and a diminution in alumina and alkalis. Kaolin is not formed from felspar under these conditions. L. J. SPENCER.

Composition of phonolite from the Heldburg near Koburg. H. JUNG (Chem. Erde, 1928, **4**, 23— 26).—A detailed chemical analysis of this rock differs appreciably from that of Hilger (1890). L. J. SPENCER.

Earth cementation by iron and manganese or by alumina and lime. M. HELBIG (Chem. Erde, 1928, **4**, 12—22).—Analyses are given of the cementing material in German pebble beds of recent origin. The material is the product of weathering. L. J. SPENCER.

South European red earths. H. HARRASSOWITZ (Chem. Erde, 1928, **4**, 1—11).—Red earths beneath the humus-bearing soil of the Black Forest contain in the hydrochloric acid extract a higher silica/alumina ratio, namely 2·5—2·98, than those from farther south. The ratio is as low as 0·17—0·5 in the red earth from Lake Garda in Italy. The latter, like the " terra rossa " of the Karst region, contains free alumina. The " terra rossa " rests on pure limestones, and the red colour is not confined to the Mediterranean type of weathering. L. J. SPENCER.

Minerals. V.—VIII. H. COLLINS (Chem. News, 1928, **137**, 242—244, 276—278, 338—341, 402—404).

Presence of the rare-earth elements in the sun. C. E. ST. JOHN and C. E. MOORE (Astrophys. J., 1928, **68**, 93—108).—Lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, and ytterbium, in the ionised state, are probably present in the sun. A. A. ELDRIDGE.
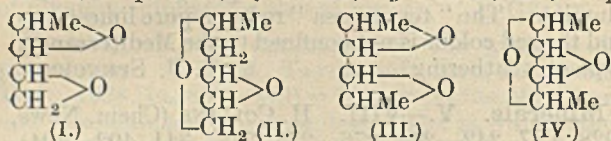
Organic Chemistry.

Synthesis of methane from mixtures of carbon monoxide and hydrogen at a nickel surface. H. A. BAHR and T. BAHR (Ber., 1928, **61**, [B], 2465— 2469).—Observations are recorded of the passage of a mixture of carbon monoxide and hydrogen (1 : 3) over nickel carbide, Ni_3C, prepared at 250° and stabilised by preservation in nitrogen. The first step in the production of methane is the decomposition of carbon monoxide with production of nickel carbide, $3Ni + CO \longrightarrow Ni_3C + O$. As secondary changes, the carbide is hydrogenated to methane with re-formation of nickel, $Ni_3C + 2H_2 = CH_4 + 3Ni$, and the oxygen, derived from carbon monoxide, is converted into water or carbon dioxide. As long as nickel carbide is present, the production of methane occurs chiefly according to the equation $2CO + 2H_2 = CH_4 + CO_2$, which is succeeded by the reaction $CO + 3H_2 = CH_4 + H_2O$ in proportion as the contact becomes decarbonised. H. WREN.

Allyl transformations and additive compounds of erythrenic hydrocarbons. III. C. PRÉVOST (Ann. Chim., 1928, [x], **10**, 356—438).—Mainly experimental details of work already published (A., 1928, 1211). The most probable stereochemical formulæ for the various derivatives are deduced and tabulated together with a large amount of physical data, the following of which appears to be new (or revised). $\Delta^{\alpha\gamma}$-Pentadiene yields a solid tetrabromide, m. p. 114° (best obtained from the *trans*-hydrocarbon), together with a liquid, b. p. 121—131°/3 mm., d_4^{18} 2·3195, n_D^{18} 1·5915; $\Delta^{\beta\delta}$-hexadiene yields the known tetrabromide, m. p. 185°, together with two *tetrabromides*, m. p. 108° and 162°, and a mixture of liquid tetrabromides, b. p. 128—133°/3 mm., d_4^{16} 2·1990, n_D^{16} 1·5831, those having m. p. 95—97° and 64—65° (Griner, A., 1893, i, 241) never being obtained. $\beta\gamma$-Dibromo-$\Delta^{\alpha\gamma}$-pentadiene (A., 1926, 496) has d_4^{22} 1·8225, n_D^{22} 1·5630; $\gamma\delta$-*dibromo*-$\Delta^{\beta\gamma}$-*pentadiene* (not quite pure), b. p. 83—86°/12 mm., d_4^{22} 1·6700, n_D^{22} 1·5400, with excess of bromine yields $\beta\gamma\delta\varepsilon$-*tetrabromo*-$\Delta^{\gamma}$-*hexene*, m. p. 112—113°; $\Delta^{\alpha\gamma}$-pentadi-inene, b. p. 54—56°, d_4^{21} 0·7375, n_D^{21} 1·4431, the hexa- and heptadi-inenes being obtained only as their *silver* derivatives; α-*phenyl*-$\Delta^{\alpha\gamma}$-*pentadi-inene*, m. p. 22·45°, b. p. 129°/20 mm., d_4^{18} 0·9745, n_D^{18} 1·6368 (optical properties described), adds only 2 mols. of bromine, yielding two *tetrabromides*, m. p. 127—131° and 98°, and with aqueous-alcoholic mercuric chloride yields the *compound* $CPhCl:C(HgCl)·C(OEt):CHMe$. $\Delta^{\alpha\gamma}$-Pentadiene dibromides have b. p. 70°/11 mm., d_4^{18} 1·6992, n_D^{18} 1·5247, and b. p. 85—86°/11 mm., d_4^{15} 1·7482, n_D^{15} 1·5523; the latter yield two diacetates, b. p. 112·5°/11 mm., d_4^{24} 1·0446, n_D^{23} 1·4398 (cf. A., 1926, 496),

and b. p. 104—105°/13 mm., d_4^{21} 1·0386, n_D^{21} 1·4365 (the latter being probably the *diacetate* of Δγ-*pentene-αβ-diol*). The dibromide fraction, b. p. 87—88°/ 12 mm., on hydrolysis yields three *glycols*, b. p. 109°/ 14 mm., d_4^{17} 1·0147, n_D^{17} 1·4633; b. p. 127°/14 mm., d_4^{17} 1·0234, n_D^{17} 1·4730, and b. p. 93°/14 mm., d^{20} 1·0082, n^{20} 1·4575. From Δ$^{\beta\delta}$-hexadiene are obtained the diacetates, b. p. 117—118°/14 mm., d_4^{21} 1·0247, n_D 1·4460 (65—70%), and b. p. 106—109°/14 mm., d_4^{21} 1·0210, n_D^{21} 1·4390, (35—30%), of trans-Δγ-*hexene-βε-diol*, b. p. 117—118°/11 mm., d_4^{21} 0·9865, n_D^{21} 1·4660, and Δ$^\delta$-*hexene-βγ-diol*, b. p. 99—100°/11 mm., d_4^{21} 0·9838, n_D^{21} 1·4614, respectively. By the action of an excess of finely-powdered potassium hydroxide on an ethereal solution of the appropriate glycol saturated with bromine the following substituted *erythrene oxides* are obtained : I, b. p. 146°, d_4^{17} 1·0813, n_D^{17} 1·4382; II, b. p. about 145° : a mixture of the stereoisomerides of III, b. p. 161°, d_4^{21} 1·0312, n_D^{21} 1·4375; IV, b. p.

$$\begin{array}{cccc} \text{CHMe} & \text{CHMe} & \text{CHMe} & \text{CHMe} \\ \text{CH} & \text{CH}_2 & \text{CH} & \text{CH} \\ \text{CH} & \text{CH} & \text{CH} & \text{CH} \\ \text{CH}_2 & \text{CH} & \text{CHMe} & \text{CHMe} \\ & \text{CH}_2 & & \\ \text{(I.)} & \text{(II.)} & \text{(III.)} & \text{(IV.)} \end{array}$$

151°, d_4^{21} 1·0373, n_D^{21} 1·4350. These by hydration yield *erythritols*, *methylerythritol*, m. p. 109·5°, s-*dimethylerythritol*, m. p. 172° (corr.) (not identical with the isomeride obtained by Wagner, A., 1889, 226). αζ-Dibromo-Δ$^{\beta\delta}$-hexadiene (A., 1927, 337) yields a mixture, b. p. 129—131°/12 mm., d_4^{21} 1·0700, n_D^{21} 1·4760, of the *diacetates* of Δ$^{\alpha\gamma}$-hexadiene-εζ-diol and Δ$^{\alpha\delta}$-hexadiene-γζ-diol, and the diacetate, m. p. 25°, d_4^{21} 1·0762, n_D^{21} 1·4850 (supercooled), of Δ$^{\beta\delta}$-hexadiene-αζ-diol. Spontaneous decomposition of βε-dibromo-βε-dimethyl-Δγ-hexene (A., 1927, 748) yields (?) α-*bromo-βε-dimethyl-Δ$^{\beta\delta}$-hexadiene*, b. p. 64—67°/3 mm., d_4^{18} 1·2230, n_D^{18} 1·5522, converted into the *acetate*, b. p. 77—79°/3 mm., d^{18} 0·9570, n_D^{18} 1·4890, hydrolysed to βε-*dimethyl-Δ$^{\beta\delta}$-hexadien-α-ol*, b. p. 77—78°/4 mm., d_4^{17} 0·9197, n_D^{17} 1·5095, which is reduced catalytically to βε-dimethylhexan-α-ol. J. W. BAKER.

New tautomeric phenomena in the allylic series. C. PRÉVOST (Compt. rend., 1928, **187**, 1052—1054).—Δ$^\alpha$-Penten-γ-ol (I) and Δ$^\beta$-penten-α-ol (II) are mesomeric at the ordinary temperature, but towards 360° some transformation of I into II takes place. A pseudo-isomeric bromide corresponding with II is formed from either alcohol, but the action of phosphorus trichloride on I yields two chlorides corresponding with I, b. p. 93°, d^{23} 0·8966, n^{23} 1·4224, and II, b. p. 109·5°, d^{23} 0·9095, n^{23} 1·4347, respectively. These are mesomeric, becoming desmotropic above 175°. By the action of sodium acetate on these chlorides only the acetate corresponding with II could be isolated, but sodium ethoxide with either chloride yielded a mixture of the mesomeric γ-*ethoxy-Δ$^\alpha$-pentene*, b. p. 102°, d^{23} 0·7768, n^{23} 1·3986, and α-*ethoxy-Δ$^\beta$-pentene*, b. p. 123°, d^{23} 0·7930, n^{23} 1·4099. Some conclusions with regard to synionism (cf. A., 1926, 131; 1927, 851; 1928, 152, 614) are deduced.

B. W. ANDERSON.

[Preparation of nitro- and chloronitro-olefines.] E. SCHMIDT (Ber., 1928, **61**, [B], 2613; cf. Schmidt and Rutz, A., 1928, 1352).—Substitution of the hydrogen atom in the system C:CH·NO$_2$ by chlorine with formation of the system C:CCl·NO$_2$ causes a depression of the exaltation. H. WREN.

Dodecane-αμ-diol and linear true diacetylenes, $C_{13}H_{20}$ and $C_{20}H_{34}$. R. LESPIEAU (Bull. Soc. chim., 1928, [iv], **43**, 1189—1193).—The action of chloromethyl ether on magnesium pentamethylene bromide gives a *methyl ether*, Me·[CH$_2$]$_5$·OMe, b. p. 124—125°, d^{19} 0·7897, n_D 1·4065, some αμ-dimethoxydodecane, b. p. 182°/35 mm., m. p. 13—14° (Chuit, A., 1926, 499) (αμ-dibromododecane, m. p. 38·5—39°, and dodecane-αμ-diol, m. p. 80—81° [acetyl derivative, m. p. 36·5—37·5°], are described), and, mainly, the dimethyl ether of heptamethylene glycol, converted by hydrobromic acid into heptamethylene bromide, b. p. 124—125°/12 mm., d^{10} 1·529, n_D 1·065. The magnesium derivative of the latter with αβ-dibromo-Δ$^\beta$-propene yields (1) a fraction, b. p. 90°/13 mm., containing β-bromo-Δ$^\alpha$-n-decene, (2) and chiefly βμ-*dibromo-Δ$^{\alpha\mu}$-tridecadiene*, b. p. 180°/16 mm., d^{26} 1·274, n_D 1·497; (3) βτ-*dibromo-Δ$^{\alpha\tau}$-eicosadiene*, b. p. 249—252°/11 mm., d^{21} 1·120, n_D 1·4915, and (4) a liquid fraction, b. p. 300—350°/11 mm. With alcoholic potassium hydroxide the tridecadiene is converted into Δ$^{\alpha\mu}$-*tridecadi-inene*, b. p. 115·5°/12 mm., m. p. −3° to −2°, d^{21} 0·8262, n_D 1·454, and the eicosadiene into the *hydrocarbon*, CH:C·[CH$_2$]$_{16}$·C:CH, m. p. 54—56°, the liquid fraction, b. p. 340°/11 mm., affording a similar (impure) product, m. p. 70—75°. Both acetylenes give silver derivatives (cf. A., 1925, i, 225), and further support for the true diacetylene structure of this compound is afforded by the conversion of the undecadi-inene obtained by the action of alcoholic potassium hydroxide on the reaction product of epidibromohydrin on dimagnesium pentamethylene bromide, with magnesium ethyl bromide and carbon dioxide into Δ$^{\alpha\lambda}$-*undecadi-inene-αλ-dicarboxylic acid*, m. p. 111·5—112·5°, giving on hydrogenation behenolic acid, m. p. 110·5—111·5°. R. BRIGHTMAN.

Carbohydrates and polysaccharides. H. HIBBERT. XVIII. [With M. G. STURROCK.] *p*-Nitrobenzylidene glycols and glycerols. XIX. [With N. M. CARTER.] Structural, geometrical, and optical isomerism of *p*-nitrobenzylideneglycerols and their derivatives. (J. Amer. Chem. Soc., 1928, **50**, 3374—3376, 3376—3388).—XVIII. p-*Nitrobenzylidene ethylene ether*, m. p. 90·5°, and *trimethylene ether*, m. p. 111·5°, are formed from p-nitrobenzaldehyde and the appropriate glycol at 100° in presence of a little sulphuric acid. The reaction between the aldehyde and glycerol is favoured by removing the resulting water under reduced pressure. The product is separated by fractional crystallisation into nearly equal amounts of αγ-p-*nitrobenzylideneglycerol* (I), m. p. 88° when freshly prepared, changing to 98°, and αβ-p-*nitrobenzylideneglycerol* (II), b. p. 177—179°/0·3 mm. (*benzoate*, m. p. 178°).

XIX. Although the separation of the stereoisomerides of I and II, the presence of which is indicated by the change in the m. p. of I, has not been effected, the four isomeric methyl ethers, benzoates, and p-nitrobenzoates theoretically obtainable from I and II have been prepared. Methylation of I yields a mixture from which grey, m. p. 139°, and white,

m. p. 106°, isomeric *methyl αγ-p-nitrobenzylideneglyceryl ethers* are separated. These are both formed from β-methyl glyceryl ether and *p*-nitrobenzaldehyde in presence of sulphuric acid at 120°. α-Methyl glyceryl ether and *p*-nitrobenzaldehyde give similarly a mixture of yellow, m. p. 47°, and white, m. p. 42°, geometrically isomeric α-*methyl βγ-p-nitrobenzylideneglyceryl ethers*, which were also isolated with some difficulty from the methylation product of II. Benzoylation of the freshly-prepared acetal, I, in pyridine affords yellow *αγ-p-nitrobenzylideneglyceryl benzoate*, m. p. 204°, but the samples of m. p. 98° yield, in addition, a white *isomeride*, m. p. 159°, A greenish-yellow *αβ-p-nitrobenzylideneglyceryl benzoate*, m. p. 115°, apparently isomeric with that described above, is prepared similarly. Yellow, m. p. 208°, and white, m. p. 202°, isomeric *αγ-p-nitrobenzylideneglyceryl p-nitrobenzoates*, and yellow, m. p. 117—118°, and white, m. p. 110°, isomeric *αβ-p-nitrobenzylideneglyceryl p-nitrobenzoates* were isolated by manual separation. The pure acetals I and II in presence of a trace of hydrogen chloride at 130° pass into an equilibrium mixture containing 1 part of I and 5 parts of II.

H. E. F. NOTTON.

[**Configuration of pentaerythritol. II. Optically active dipyruvic acid pentaerythritols.**] J. KENNER (Ber., 1928, **61**, [*B*], 2470—2471).—In connexion with the work of Böeseken and Felix (A., 1928, 1213), it is pointed out that chemical methods such as those used by the authors are not suitable for the examination of the Weissenberg principle. H. WREN.

Symmetrical ethers of the alcohols, CH$_2$X·CH(OH)·CH$_2$X' **and** CH$_2$X·CH(OH)·CH$_2$·OR. L. BLANCHARD (Bull. Soc. chem., 1928, [iv], **43**, 1194—1204).—*αγ*-Dichloropropyl β-*p*-toluenesulphonate, unlike the methyl sulphonate (cf. A., 1927, 853), does not react with dichlorohydrin at 140—190°. With 1 mol. of sulphuryl chloride the dichlorohydrin gives 65% of *αγ-dichloropropyl chlorosulphonate*, b. p. 113—114°/13 mm., d^{20} 1·592, n 1·48325, decomposed above 160°, yielding trichloropropane, probably from the addition of hydrogen chloride to αγ-dichloropropylene first formed; with 4—5 mols. of dichlorohydrin at 130—140°, sulphuryl chloride affords *αγ-dichloropropyl β-ether*, b. p. 141—142°/13 mm., d^{15} 1·388. Chlorosulphonic acid and dichlorohydrin yield *αγ-dichloropropyl hydrogen sulphate*, crystalline (*sodium* salt), but when this is heated with potassium cyanide the nitrile is not obtained. α-*Chloro-γ-bromopropyl chlorosulphonate* decomposed on re-distillation, yielding dichlorobromopropane and α-*chloro-γ-bromopropyl β-ether*, b. p. 175—177°/ 20 mm., d^{15} 1·806 (yield 85%). *Sodium α-chloro-γ-bromopropyl sulphate* is described, but the chlorosulphates of dibromohydrin and chloroiodohydrin appear to be too unstable to react further with the hydrin. Attempts to obtain the corresponding ethers by the action of sulphuryl chloride on epichlorohydrin, "epimethyline" (γ-methoxypropane αβ-oxide), and "epiethyline" failed. "*Epiamyline*," b. p. 79—81°/20 mm., at 120—130° gives a liquid of b. p. 190—220°/20 mm., possibly di(chloroamyline) ether. R. BRIGHTMAN.

Influence of poles and polar linkings on course pursued by elimination reactions. III.

Decomposition of dialkylsulphones. G. W. FENTON and C. K. INGOLD (J.C.S., 1928, 3127—3130). —In agreement with the theory that dialkylsulphones should decompose similarly to quaternary ammonium hydroxides (Hanhart and Ingold, A., 1927, 650) into an olefine and an alkylsulphinic acid, it is found that diethylsulphone, m. p. 71°, decomposes in the presence of a concentrated solution of potassium hydroxide at 200° into ethylene and ethanesulphinic acid; *ethyl-n-octylsulphone*, m. p. 68° (prepared by oxidation of ethyl *n*-octyl sulphide, b. p. 102—103°/11 mm., with nitric acid), and potassium hydroxide at 200° gave ethylene and *n*-octanesulphinic acid (*ferric* salt) but no *n*-octene or ethanesulphinic acid, whilst *di-n-octylsulphone*, m. p. 76° (prepared by oxidation of *n*-octyl sulphide, b. p. 180°/10 mm., with nitric acid, d 1·49), was unaffected by heating under reflux with 90% potassium hydroxide. A. I. VOGEL.

Esters of α-bromopropionic and α-bromoiso-butyric acids. V. DEULOFEU (Anal. Fís. Quím., 1928, **26**, 315—319).—By the action of the bromides of the acids on an excess of the corresponding anhydrous alcohols, the following esters have been prepared in yields of 40—54% : iso*propyl α-bromopropionate*, b. p. 163—165°; *allyl α-bromopropionate*, b. p. 173—177°; n-*butyl α-bromopropionate*, b. p. 192—196°; n-*propyl α-bromoisobutyrate*, b. p. 92—96°/42 mm.; iso*propyl α-bromoisobutyrate*, b. p. 91—94°/55 mm.; *allyl α-bromoisobutyrate*, b. p. 90—93°/42 mm. The esters are oily liquids, denser than water. The allyl esters have pungent and the others fruity odours.

R. K. CALLOW.

Acids derived from chlorohydrins with two β-substituents. E. TROELL (Ber., 1928, **61**, [*B*], 2497—2503).—Ethyl dimethylglycidate is converted into the corresponding sodium salt and transformed by the calculated amount of hydrogen chloride into *β-chloro-α-hydroxy-β-methylbutyric acid*, m. p. 80·6—81·3°; attempts to prepare salts from it give the metallic chloride and a malodorous, neutral compound which gradually reacts with alkali hydroxide. Decomposition of the acid in aqueous, alkaline solution is not a simple bimolecular change. *β-Chloro-α-hydroxy-β-phenylbutyric acid*, m. p. 82° (decomp.), is analogously prepared. If benzophenone is condensed with ethyl monochloroacetate and the product is distilled, an ester, b. p. 202°/12 mm., is obtained regarded by Pointet (A., 1909, i, 234) as ethyl diphenylglycidate,

$$\frac{CPh_2}{O}{>}CH·CO_2Et.$$ It must, however, be considered

as *ethyl ββ-diphenylpyruvate*, since the acid derived from it forms a *phenylhydrazone*, m. p. 189° (decomp.); isomerisation occurs during distillation of the ester.
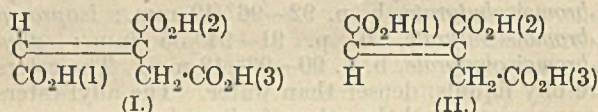
H. WREN.

Esters of α-bromoisovaleric acid. V. DEULOFEU (Bull. Soc. chim., 1928, [iv], **43**, 1229—1230).— *Propyl α-bromoisovalerate*, b. p. 115°/36—38 mm. iso*propyl α-bromoisovalerate*, b. p. 104°/33 mm., and *allyl α-bromoisovalerate*, b. p. 117—118°, have been obtained from α-bromoisovaleryl bromide in 38—41% yield. R. BRIGHTMAN.

Mesoxalates from nitrogen tetroxide and esters of malonic acid. E. GILMAN and T. B. JOHNSON (J. Amer. Chem. Soc. 1928, **50**, 3341—

3348).—Ethyl malonate and nitrogen tetroxide in presence of metallic sodium at 0° yield 90% of the theoretical amount of ethyl mesoxalate (I) (cf. Curtiss, A., 1911, i, 518). β-Chloroethyl malonate, prepared by an improved method (cf. Bennett, A., 1925, i, 883), is similarly converted into greenish-yellow β-*chloroethyl mesoxalate* (II), b. p. 148°/3 mm. (oily *hydrate*); and β-*bromoethyl malonate*, b. p. 153°/1 mm., from ethylene bromohydrin and malonic acid in presence of hydrogen chloride, is converted into yellow β-*bromoethyl mesoxalate*, b. p. 155°/0·8 mm. (oily *hydrate*). The hydrochloride of β-diethylaminoethyl alcohol and malonyl chloride afford in chloroform β-*diethylaminoethyl malonate dihydrochloride*, m. p. 145° (decomp.), from which the free *base* (III), b. p. 163°/4·5 mm., is liberated by sodium hydrogen carbonate. This reacts violently with nitrogen tetroxide, yielding an unstable oil from which none of the desired mesoxalate can be separated. The pharmacological effects of compounds I, II, and III are described.   H. E. F. Notton.

Aconitic acids. I. Stereochemistry of aconitic acids. R. Malachovski and M. Maslovski (Ber., 1928, **61**, [B], 2521—2525).—Aconitic acid occurs in two geometrical isomerides, the ordinary acid, m. p. 194—195°, being the more stable *trans*-form (I). The cis-*acid* (II), m. p. 125°, is prepared by

$$\begin{array}{cc} \text{H} \quad\quad \text{CO}_2\text{H(2)} & \text{CO}_2\text{H(1)} \quad \text{CO}_2\text{H(2)} \\ \text{C}=\!\!=\!\!=\text{C} & \text{C}=\!\!=\!\!=\text{C} \\ \text{CO}_2\text{H(1)} \quad \text{CH}_2\cdot\text{CO}_2\text{H(3)} & \text{H} \quad\quad \text{CH}_2\cdot\text{CO}_2\text{H(3)} \\ \text{(I.)} & \text{(II.)} \end{array}$$
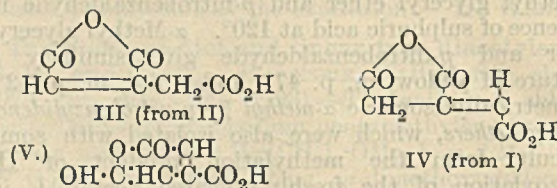
hydrolysis of the so-called " anhydro-acid." It is readily transformed into the *trans*-acid when melted or moderately warmed in aqueous solution. It adds bromine more readily than the *trans*-acid. Its *sodium*, *barium*, and *copper* salts are described. It is converted by dehydrating agents exclusively into the anhydro-acid, the isomeric hydroxyanhydro-acid not being produced even transitorily. The anhydro-acid is therefore the actual anhydride of *cis*-aconitic acid. Thorpe's " labile acid " does not appear to be a definite individual. Hydrolysis of the hydroxyanhydro-acid, however performed, yields solely somewhat impure *trans*-aconitic acid. In most of its properties, the " labile " acid differs but little from ordinary aconitic acid. The hydroxyanhydro-acid must be regarded as the true anhydride of *trans*-aconitic acid. The structure of aconitic acid is not symmetrical and its α- and γ-carbon atoms are not equivalent. The production of a single methyl-aconitic acid by introduction of a methyl group at the α- or γ-carbon atom is readily explained by the hypothesis that a transformation into the more stable form occurs as a secondary process.
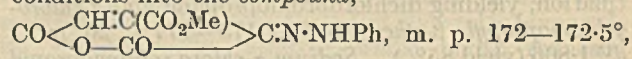
The following new data are recorded : *trans*-aconitic acid, m. p. 194—195° (corr.); the hydro-acid, m. p. 78—78·5° (corr.) [also +0·5C_6H_6].   H. Wren.

Aconitic acids. II. Constitution and mode of formation of aconitic anhydrides. R. Malachovski, M. Giedroyc, and Z. Jerzmanovska (Ber., 1928, **61**, [B], 2525—2538).—Aconitic acid is converted by technical acetyl chloride into the so-called " anhydro-acid," m. p. 78·5°, and by acetic anhydride or acetyl chloride free from phosphorus trichloride into the hydroxyanhydro-acid, m. p. 135°. These com-
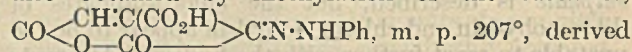
pounds are the anhydrides of the *cis*- and *trans*-aconitic acid (cf. preceding abstract).

$$\begin{array}{cc} \underset{\text{III (from II)}}{\overset{\displaystyle\text{CO}\quad\text{CO}}{\overset{\displaystyle\diagdown\,\text{O}\,\diagup}{\text{HC}=\!\!=\!\!=\text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}}}} & \underset{\text{IV (from I)}}{\overset{\displaystyle\overset{\text{O}}{\overset{\diagdown}{}}}{\begin{array}{l}\text{CO}\quad\text{CO H}\\ \text{CH}_2\!\!-\!\!\text{C}=\!\!=\text{C}\\ \quad\quad\quad\text{CO}_2\text{H}\end{array}}} \end{array}$$

$$\underset{\text{(V.)}}{\quad}\quad \begin{array}{c} \text{O}\cdot\text{CO}\cdot\text{CH} \\ \text{OH}\cdot\text{C}\!:\!\text{HC}\cdot\text{C}\cdot\text{CO}_2\text{H} \end{array}$$

To the *cis*-anhydride the structure III is readily assigned, since it gives dark colorations resembling those of citraconic anhydride when mixed with dimethylaniline or quinol in ether (cf. Easterfield and Sell, J.C.S., 1892, **61**, 1009). The decision between IV and V for the *trans*-anhydride is less easy, the main reason which has hitherto led to a preference for IV being the isomerisation of the compound by phosphorus pentachloride to the *cis*-anhydride. For the elucidation of the problem the six possible monomethyl esters of the aconitic acids have been prepared. α-*Monomethyl dihydrogen* cis-*aconitate* (in II, Me at 3), m. p. 101—102° (corr.), is prepared by treating the *cis*-anhydride with ethereal diazomethane, thus giving the *anhydro*-ester, $C_7H_6O_5$, b. p. 140—150°/2—8 mm., m. p. 37—38°, d_4^{20} 1·3318, n_D^{20} 1·48350, which is subsequently hydrolysed. Treatment of the cis-anhydride with methyl alcohol yields a mixture of γ-*methyl dihydrogen* cis-*aconitate* (in II, Me at 1), m. p. 126—127° (corr.) (characterised by conversion by acetic anhydride into the ester, m. p. 102°), and β-*methyl dihydrogen* cis-aconitate (in II, Me at 2), m. p. 102—104° (corr.). The *trans*-esters are prepared by isomerisation of the *cis*-derivatives in direct sunlight or in the light of the quartz lamp in presence of bromine. α-*Methyl dihydrogen* trans-*aconitate* (in I, Me at 3), m. p. 136—137° (corr.), β-*methyl dihydrogen* trans-aconitate, (in I, Me at 2), m. p. 144—144·5° (corr.), and γ-*methyl dihydrogen* trans-*aconitate* (in I, Me at 1), m. p. 154·5—155° (corr.), are described. As expected, the α-*trans*-ester is not affected by acetic anhydride, whereas the γ-*trans*-ester is relatively easily converted into the anhydro-ester, m. p. 102°. Unfortunately, the behaviour of the *trans*-anhydride towards methyl alcohol affords no clue to the structure, since the sole isolable product is the α-*trans*-ester which can be derived from IV or V. The following method is more successful. The β-*cis*-ester is converted by treatment with acetic acid and acetic anhydride followed by coupling with diazotised aniline under very precise conditions into the *compound*,

$$\text{CO}\!\!<\!\!\overset{\displaystyle\text{CH:C}\cdot\text{CO}_2\text{Me})}{\underset{\displaystyle\text{O—CO}}{}}\!\!>\!\!\text{C:N}\cdot\text{NHPh, m. p. 172—172·5°,}$$

also obtained by methylation of the *substance*,

$$\text{CO}\!\!<\!\!\overset{\displaystyle\text{CH:C}\cdot\text{CO}_2\text{H})}{\underset{\displaystyle\text{O—CO}}{}}\!\!>\!\!\text{C:N}\cdot\text{NHPh, m. p. 207°, derived}$$

from the *trans*-anhydride and diazotised aniline. The applicability of structure V to the *trans*-anhydride is confirmed further by the observation that the β-*trans*-ester is converted by mild treatment with acetic anhydride into *methyl 6-hydroxy-2-pyrone-4-carboxylate* (trans-*anhydro-ester*), m. p. 90—91°, which yields *methyl 6-methoxy-2-pyrone-4-carboxylate*, m. p. 76·5—78°, obtained also by the action of diazomethane in acetone on the *trans*-anhydride. An unstable *tri-bromo*-derivative is obtained by the action of bromine

on the *trans*-anhydride. The relationship of the aconitic acids and their anhydrides is most probably shown by the scheme :
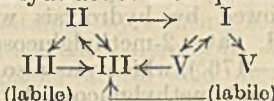
$$\text{II} \longrightarrow \text{I}$$
$$\text{III} \rightarrow \text{III} \leftarrow \text{V} \quad \text{V}$$
$$\text{(labile)} \qquad \text{(labile)}$$

Quantitative investigation of the transformation of the *trans*-anhydride shows the process to be particularly favoured by phosphorus trichloride. Pure acetyl chloride scarcely affects transformation, whereas acetic anhydride and in particular acetic acid have a somewhat more pronounced effect. The action of acetyl chloride or acetic anhydride on *trans*-aconitic acid proceeds simultaneously in two directions, leading to the *cis*- and *trans*-anhydrides, respectively, the production of which occurs independently of the temperature in the ratio 4 : 5. The practical yields are displaced further towards the *cis*-side by secondary changes. H. WREN.

Carbazylic acids : ammonia analogues of carboxylic acids. E. F. CORNELL (J. Amer. Chem. Soc., 1928, **50**, 3311—3318).—The following reactions are adduced to show that the relationship of the acid amidines (carbazylic acids) and nitriles (acid anammonides) to ammonia is similar to that of the carboxylic acids and anhydrides to water (cf. A., 1913, i, 959). Salts of carbazylic acids are formed from metallic amides and amidines or nitriles in liquid ammonia. The following are described : *potassium*, CMe(:NH)·NHK, and *sodium ammonoacetates*, *potassium*, *sodium*, and *calcium ammonopropionates* ; *potassium* and *sodium ammono-n-butyrates*, *potassium ammono-n-valerate*, *ammonoisohexoate*, *ammonopalmitate*, *ammonosuccinate*, and *ammono-p-toluate* ; *potassium*, *sodium*, *silver* (cf. Pinner, A., 1878, 491), *calcium*, *cupric*, and *cuprous ammonobenzoates*, and the *compound* NNa(CPh:NH)$_2$. Hydrogen cyanide and cyanogen react anomalously with potassamide in liquid ammonia, forming potassium cyanide, and a mixture of potassium cyanide and potassium cyanamide, respectively. In liquid ammonia at 200°, benzonitrile yields with potassium hydroxide benzamide, and with ammonium chloride, a little benzamidine. Propionitrile is similarly converted into potassium propionamide and propionamidine. Dry distillation of a potassium carbazylate, NH:CR·NHK, with potassamide yields potassium cyanamide, ammonia, and the hydrocarbon RH. Alkyl carbazylates may be formed and ammonolysed by methods similar to those employed for aquo-esters. The additive product from benzonitrile and magnesium phenyl bromide is converted by liquid ammonia into benzophenoneimine. H. E. F. NOTTON.

Catalytic hydrogenation under reduced pressure. II. Selective reduction in a vacuum of citral, geraniol, and limonene. R. ESCOURROU (Bull. Soc. chim., 1928, [iv], **43**, 1204—1214).— Hydrogenation at 190° under reduced pressure in presence of nickel of citral, b. p. 108—112°/12 mm., n_D^{18} 1·48846, containing about 90% of the terpinolenic form, affords inactive citronellal, b. p. 207—208°, n_D^{18} 1·4591 (semicarbazone, m. p. 80—81°). Under ordinary pressure at 180° the same product is obtained, but at 300° dimethyloctanol, saturated hydrocarbons, and a cyclic product, b. p. 215° (cf. Enklaar, A., 1908,

i, 664, 934). Similarly, Java geraniol, b. p. 114—115°/12 mm., n_D^{11} 1·47628, d^{11} 0·908, in presence of platinum oxide at 130°/50 mm. is converted into *r*-citronellol, b. p. 214—215°, 107—108°/12 mm., n_D^{13} 1·4513 (allophanate, m. p. 112·5—113·5°) ; at 150°/90 mm. in presence of nickel almost the same product, b. p. 213—215°, n_D^{13} 1·45037, d^{13} 0·850 (allophanate, m. p. 111—111·5°), is obtained (cf. A., 1925, i, 772), these properties agreeing with those of natural citronellol and not those of Barbier and Bouveault's rhodinol. Under 20 mm., *d*-limonene, b. p. 175—176°, d^{14} 0·847, n_D^{23} 1·4717, $[\alpha]_D^{14}$ +116·1°, containing about 80% of limonene, 12% of terpinolene, and 8% probably of α-terpinene, is hydrogenated only to the extent of about 10%, as shown by the bromine value, the rotatory power being unaltered ; hydrogenation is complete only at 150—200 mm. Ozonisation of the product indicates the presence of 88% of the limonene or dipentene form and only 3—4% of terpinolene. These results, which may be attributed to partial isomerisation of the terpinolene into dipentene, or into α-terpinene, which then undergoes reduction and partial isomerisation to β-terpinene, indicate that pure limonene has not been obtained (cf. Braun and Lemke, A., 1923, i, 813).
R. BRIGHTMAN.

" Normal " structure of aldoses and ketoses. H. KILIANI (Z. angew. Chem., 1929, **42**, 16—17).— Polemical (cf. Leibowitz, *ibid.*, 1926, **39**, 1147).
J. W. BAKER.

Structure of normal monosaccharides. V. Lyxose. E. L. HIRST and J. A. B. SMITH (J.C.S., 1928, 3147—3154).—α-Methyl-lyxoside when treated with methyl iodide and silver oxide gave *trimethylmethyl-lyxoside*, b. p. about 70°/0·02 mm., n_D^{14} 1·4460, $[\alpha]_{5461}^{20}$ +10° in water, which with 6% aqueous hydrochloric acid at 100° yielded *trimethyl-lyxose*, b. p. 90°/0·05 mm., n_D^{15} 1·4629, m. p. 79°, $[\alpha]_D^{20}$ —22° in water. Direct methylation of lyxose with methyl sulphate also gave *trimethylmethyl-lyxoside*, b. p. 70°/0·02 mm., n_D^{14} 1·4471, $[\alpha]_D^{20}$ —6° in methyl alcohol, containing some of the β-isomeride ; hydrolysis with 6% aqueous hydrochloric acid gave an 80% yield of trimethyl-lyxose, m. p. 79°, $[\alpha]_D^{20}$ —22°. Oxidation of trimethyl-lyxose with bromine water yielded *trimethyl-δ-lyxonolactone*, b. p. 105°/0·02 mm., n_D^{18} 1·4620, $[\alpha]_D^{19}$ +35·5° (initial value) and —9·3° (equilibrium value) in water (*phenylhydrazide*, m. p. 180—181°), which by further oxidation with nitric acid (*d* 1·42) and esterification of the resultant product with 3% methyl-alcoholic hydrogen chloride furnished methyl trimethoxyglutarate, b. p. about 100°/0·1 mm., n_D^{20} 1·4353, $[\alpha]_D^{20}$ —39° in methyl alcohol, $[\alpha]_D^{20}$ —31° in water, in 76% yield [corresponding trimethoxyglutaramide, m. p. 230° (decomp.), and the methylamide, m. p. 171—172° ; in both cases the yields were more than 70%]. Trimethylmethyl-lyxoside on oxidation with nitric acid (*d* 1·42) gave methyl trimethoxyglutarate, n_D^{20} 1·4355, $[\alpha]_D^{20}$ —34° in water, which with methylalcoholic ammonia furnished trimethoxyglutaramide, m. p. 230° (decomp.), $[\alpha]_D^{20}$ —49° in water, in 88% yield. From these results the authors assign the pyranose structure to α-methyl-lyxoside and hence also to lyxose. These conclusions are in disagreement with those of Phelps and Hudson (A., 1926, 501), who assign a butylene-oxide formula to α-methyl-lyxoside and its derivatives. A. I. VOGEL.

Detection of lævulose in presence of other carbohydrates. L. EKKERT (Pharm. Zentr., 1928, **69**, 805—806).—A *résumé* of the reactions of lævulose is given. Treatment of 0·01—0·03 g. of lævulose with 3—5 drops of 2N-potassium hydroxide solution followed by the addition of 0·5—1·0 g. of solid potassium or sodium hydroxide results in the formation of a blood-red band round the solid alkali and after several minutes the whole liquid assumes a blood-red colour. Other carbohydrates similarly treated behave as follows : arabinose, xylose, maltose, galactose, and dextrin, yellow colour within 1 min.; rhamnose and lactose, lemon-yellow within 1 min.; dextrose, yellow after 2 min.; mannose, yellow after 1 min.; sucrose and glycogen, colourless after 15 min.   A. I. VOGEL.

Action of trimethylamine and other bases on acetobromocellobiose. G. ZEMPLÉN and Z. BRUCKNER (Ber., 1928, **61**, [*B*], 2481—2486; cf. A., 1928, 741).—Reinvestigation of the action of alkali hydroxide on the product derived from acetobromocellobiose and trimethylamine (*loc. cit.*) has shown the base evolved to be di- and not tri-methylamine. Support for the conception that the new compound is *hepta-acetylcellobiosidodimethylamine* (I),

(I.)
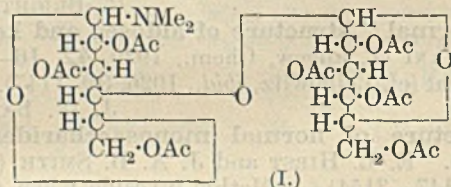
m. p. 198—199° (decomp.), $[\alpha]_D^{25}$ —10·51° in chloroform, is found in the observation that it is more readily prepared from acetobromocellobiose and trimethylamine in chloroform at the ordinary temperature, whereby also tetramethylammonium bromide is produced. The same base (together with dimethylamine hydrobromide) is obtained from acetobromocellobiose and dimethylamine. Acetobromocellobiose and triethylamine yield only hepta-acetylcellobiose and the mother-liquors are free from diethylamine. The latter base and acetobromocellobiose afford *hexa-acetylcellobiosen*, m. p. 125—126°, $[\alpha]_D^{20}$ —19·78° in chloroform (for nomenclature see Maurer and Mahn, A., 1927, 751). Piperidine and acetobromocellobiose give *hepta-acetylcellobiosidopiperidine*, $C_{31}H_{45}O_{17}N$, m. p. 115—120° (decomp.), $[\alpha]_D^{18}$ —15·28° in chloroform, which appears to absorb two atoms of bromine in chloroform but permits the isolation only of a *monobromo*-compound, m. p. 132—133° (decomp.).   H. WREN.

Glucosides. I. Formation of glucosides from 3 : 4 : 6-triacetylglucose 1 : 2-anhydride. W. J. HICKINBOTTOM (J.C.S., 1928, 3140—3147).— 3 : 4 : 6-Triacetylglucose 1 : 2-anhydride (I) (cf. Brigl, A., 1922, i, 1117), most conveniently prepared by the action of dry ammonia on a suspension of dry, finely-powdered 3 : 4 : 6-triacetylglucosyl chloride in dry benzene for 3 hrs., reacts with ethyl alcohol with the formation of 3 : 4 : 6-tri-acetyl-β-ethylglucoside, m. p. 121°, $[\alpha]_D$ +14·4° in ethyl alcohol, which with methyl iodide and silver oxide yielded a *triacetylmethyl-*

(I.)

β-*ethylglucoside*, m. p. 95—96°, $[\alpha]_D$ +5·0° in alcohol. Deacetylation by means of alcoholic ammonia, followed by hydrolysis with aqueous hydrochloric acid, gave 2-methylglucose (*phenylhydrazone*, m. p. 175—176°), which was also prepared from 3 : 4 : 6-tri-acetyl-β-methylglucose by methylation with silver oxide and methyl iodide followed by deacetylation and hydrolysis. Methyl alcohol and I yielded 3 : 4 : 6-tri-acetyl-β-methylglucoside, m. p. 95—97°, $[\alpha]_D$ +19° (cf. Brigl, *loc. cit.*), which on acetylation in pyridine yielded tetra-acetyl-β-methylglucoside, m. p. 101—103°, whilst *iso*propyl alcohol and I furnished 3 : 4 : 6-triacetyl-β-*iso*propylglucoside, which with acetic anhydride in pyridine solution gave 2 : 3 : 4 : 6-*tetra-acetyl*-β-iso*propylglucoside*, m. p. 134—135°, $[\alpha]_D$ —23·4° in alcohol. The interaction between benzyl alcohol and I at 100° afforded 3 : 4 : 6-triacetylbenzyl-glucoside, which was converted by alcoholic ammonia into β-benzylglucoside, m. p. 119°, $[\alpha]_D$ —49°; acetyl-ation of the latter yielded 2 : 3 : 4 : 6-tetra-acetyl-β-benzylglucoside, m. p. 98—99°, $[\alpha]_D$ —44° in alcohol (lit. m. p. 96—101°, $[\alpha]_D$ —48°). When I is heated with menthol at 90—100° for 30 hrs. 3 : 4 : 6-triacetyl-menthylglucoside, m. p. 144° (sintering at 141°), $[\alpha]_D$ —10·6° in benzene, is formed; this furnished β-menthylglucoside with aqueous-alcoholic potassium hydroxide (cf. Fischer and Bergmann, A., 1917, i, 467). The interaction between 3 : 4 : 6-triacetyl-glucose anhydride and phenol proceeded less readily than with primary and secondary alcohols; combination was effected in the presence of excess of phenol by heating at 100° for 20 hrs. and 2 : 3 : 4 : 6-tetra-acetyl-α-phenylglucoside, m. p. 112°, $[\alpha]_D$ +162° in alcohol (lit. m. p. 115°, $[\alpha]_D$ +164·9° in benzene), was produced which yielded *α-phenylglucoside hydrate*, m. p. 155—160°, $[\alpha]_D$ +157° in alcohol, with alcoholic ammonia. The results are regarded as affording independent evidence for the formula I originally assigned to the triacetylglucose anhydride by Brigl (*loc. cit.*). A comparison is made between the chemical reactions of α-glucosan (Pictet and Castan, A., 1920, i, 594) and 3 : 4 : 6-triacetylglucose anhydride, and doubts are cast on the structure of the former.   A. I. VOGEL.

Phloridzin and quercitrin. G. ZEMPLÉN, Z. CSÜRÖS, Á. GERECS, and S. ACSÉL (Ber., 1928, **61**, [*B*], 2486—2497).—The synthesis of phloretin from purely synthetic materials is effected in the following manner. β-Phenylpropionic acid is converted by heating with lead thiocyanate into β-phenylpropionitrile, b. p. 132—135°, transformed by nitric acid (d 1·48) at 5° into β-p-*nitrophenylpropionitrile*, m. p. 79·5°, and thence successively into β-p-*aminophenylpropionitrile* and β-p-*hydroxyphenylpropionitrile*. The last compound is converted by phloroglucinol and hydrogen chloride through the ketimine hydrochloride into phloretin, $(OH)_3C_6H_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot OH$. Unsuccessful attempts are recorded to condense p-hydr-oxyphenylpropionitrile with the tetra-acetyl derivative of phlorin (obtained from acetobromoglucose and phloroglucinol) and to synthesise phloridzin from phloretin and acetobromoglucose under conditions similar to those leading to the isolation of tetra-acetylphlorin or in presence of quinoline. Glucoside production from free phloretin is rendered difficult by

the ability of acetobromoglucose to react with three different hydroxyl groups and thus furnish a number of isomerides. A phloretin derivative containing a single hydroxyl group is obtained by treating *hepta-acetylphloridzin*, $[\alpha]_D$ —41·33° in chloroform, with hydrogen bromide and glacial acetic acid at the atmospheric temperature, whereby acetobromoglucose and *triacetylphloretin*,

$OAc·C_6H_4·CH_2·CH_2·CO·C_6H_2(OH)(OAc)_2[1:2:4:6]$,

m. p. 188—189°, are produced. The compound last mentioned could not be caused to react with acetobromoglucose, with production of phloridzin.

Quercitrin is converted by acetic anhydride and sodium acetate into *quercitrin hepta-acetate*, $[\alpha]_D^{24}$ —165·6° in chloroform, hydrolysed by hydrogen bromide in glacial acetic acid to *tetra-acetylquercetin* and acetobromorhamnose. The acetyl derivative reacts with acetobromoglucose in the presence of silver oxide and quinoline, giving the acetyl derivative of a quercetin glucoside, presumably acetyl*iso*quercitrin. The production of the glucoside is placed beyond doubt, but its isolation has not been effected. H. WREN.

Triacetylstarch and its mol. wt. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1928, **3**, 276—285).—Treatment of starch (soluble Merck) with excess of acetic anhydride at about 70° in presence of a saturated aqueous solution of zinc chloride gives a 90% yield of a *triacetylstarch* (I), decomp. slowly above 270° after sintering at 258°, $[\alpha]_D^{18}$ +170·2° in chloroform (cf. Pregl, A., 1902, i, 135; Bergmann and Knehe, A., 1927, 342). Hydrolysis of I with sodium ethoxide in toluene gives a phosphate-free soluble starch re-acetylated to I. Cryoscopic determinations of the mol. wt. of I in ethylene dibromide, bromoform, camphor, acetic acid, and phenol, and ebullioscopic determinations in acetic acid, chloroform, and acetone give values ranging from 82 to 8050, but in neutral solvents the value appears to be about 5000, thus demonstrating that the molecule is at least $(C_6H_7O_5Ac_3)_{18}$ (cf. Pictet, A., 1926, 387).
H. BURTON.

Constitution of flax cellulose. G. W. RIGBY (J. Amer. Chem. Soc., 1928, **50**, 3364—3370; cf. Hess and Messmer, A., 1922, i, 988).—Pure cellulose, isolated from flax fibres by the method recommended for cotton cellulose (B., 1923, 825), yields on exhaustive methylation and hydrolysis (cf. Denham, J.C.S., 1921, **119**, 77; Irvine, *ibid*., 1923, **123**, 518) only βγζ-trimethylglucose and a little of the dimethyl derivative. Under the conditions employed by Haworth and Hirst (J.C.S., 1921, **119**, 197) cellobiose octa-acetate is obtained in equal yield from both flax and cotton celluloses. Graded acetolysis of flax cellulose by Irvine's method (A., 1926, 823) yields a mixture of trisaccharide and anhydrotrisaccharide acetates identical with the mixture obtained by this author from cotton cellulose. These and other chemical and physical properties are quoted to show the complete identity of the unit structures of flax and cotton celluloses. H. E. F. NOTTON.

Acetylation of beech wood. O. HORN (Ber., 1928, **61**, [*B*], 2542—2545).—Treatment of beech wood with acetic anhydride containing 0·25% of sulphuric acid gives an acetylated wood (yield 150%) possessing unchanged woody structure and, apart from its lighter colour, resembling externally the original wood. It does not give the customary colour reactions for lignin; appreciable amounts of substance cannot be removed from it by treatment with organic solvents. A single acetylation gives a product containing 42·2% of acetyl. About 90% of the lignin present in the original wood is found in the acetylated product; hemicelluloses appear to be mainly removed during the acetylation, which does not cause sensible alteration of the methoxyl content. Treatment of the acetylated wood alternatively with chlorine and sodium sulphite followed by potassium permanganate or by Schmidt's chlorine dioxide method leaves 76% of nearly homogeneous cellulose triacetate. The acetylation of beech wood is therefore precisely similar to that of pine (cf. Fuchs, A., 1928, 743; Suida and Titsch, *ibid*., 1227).
H. WREN.

Influence of poles and polar linkings on course pursued by elimination reactions. II. Mechanism of exhaustive methylation (*continued*). C. K. INGOLD and C. C. N. VASS (J.C.S., 1928, 3125—3127). —Theory predicts (Hanhart and Ingold, A., 1927, 650) that in the decomposition of quaternary ammonium compounds $CHR_1R_2·CR_3R_4·NMe_3·OH \longrightarrow CR_1R_2:CR_3R_4 + NMe_3 + H_2O$ (A) or $CHR_1R_2·CR_3R_4·NMe_3 + MeOH$ (B) the suppression of (A) in favour of (B) should (i) be governed by R_1 and R_2 much more than by R_3 and R_4, (ii) should increase tending towards constancy, with increasing R_1 and R_2, and (iii) should be greater when R_1R_2CH-, or any part thereof, is branched than when the corresponding group or part is unbranched but isomeric. Prediction (ii) is here verified, the values for percentage olefine (reaction A) being ($R_2=R_3=R_4=H$); and $R_1=Et$, 95%; Pr^a, 84%; Bu, 79%; *n*-amyl, 77%; *n*-hexyl, 76%; *n*-heptyl, 74%; *n*-octyl, 75%, the constant value being 75%. Prediction (iii) is verified by comparison of *n*-butyl and *iso*butyl, 72%. The results differ from these previously described by von Braun (A., 1911, i, 610). Benz-*n*-amylamide has m. p. 31—32°, b. p. 205—210°/18 mm. (cf. von Braun and Sobecki, A., 1911, i, 128). A. I. VOGEL.

Reaction between sugars and amino-acids. H. VON EULER and E. BRUNIUS (Annalen, 1928, **467**, 201—216).—Cryoscopic determinations on mixtures of dextrose and glycylglycine in aqueous solution at p_H 6·0—9·2 show that condensation increases rapidly with increasing p_H. This is contrary to the findings of Waldschmidt-Leitz and Rauchalles (A., 1928, 672), but is similar to the reaction between dextrose and glycine (A., 1926, 822). The decolorisation of methylene-blue solution by a mixture of dextrose and glycylglycine at p_H 9·1 is rather slower than with a mixture of dextrose and glycine. This last mixture decolorises methylene-blue still more rapidly at p_H 10·5 (cf. A., 1928, 1118). A mixture of lævulose and glycine begins to decolorise methylene-blue at p_H 9·1; at p_H 10·3 reduction is more rapid.
H. BURTON.

Amino-acid methionine; constitution and synthesis. G. BARGER and F. P. COYNE (Biochem. J., 1928, **22**, 1417—1425).—The amino-acid, $C_5H_{11}O_2NS$, isolated by Mueller (cf. A., 1923, i, 869, 963) is shown to be *γ-methylthiol-α-aminobutyric acid*

N

(*methionine*) by the following synthesis. β-*Methylthiol-propaldehydediethylacetal*, b. p. 89°/14 mm., 96°/20 mm., was prepared by passing methyl mercaptan into alcoholic sodium ethoxide solution and adding β-chloro-propaldehyde acetal. Hydrolysis of the acetal yielded β-*methylthiolpropaldehyde*, b. p. 60°/12 mm., which was converted into α-*amino-γ-methylthiolbutyronitrile*, and finally on boiling the nitrile with hydrochloric acid α-*amino-γ-methylthiolbutyric acid*, m. p. 281° (decomp.), was obtained. The α-*naphthylcarbamido*-derivative, m. p. 181—182°, was obtained. The thiohydantoin and the picrolonate prepared from the synthetic product were identical with the corresponding deriv-atives from natural methionine.

The synthesis of methionine by Erlenmeyer's method failed. The following compounds were prepared. *Methylthiolacetaldehydediethylacetal*, b. p. 188—190°/760 mm.; *methylthiolacetaldehyde*; *methylthiolethyl-idenehydantoin*, SMe·CH$_2$·CH:C$<$ $^{NH·CO}_{CO·NH}$, m. p. 156° (from which methionine could not be obtained by reduction); β-*methylthiolpropionic acid*, b. p. 235—240°/760 mm.; β-*methylsulphonepropionic acid*, b. p. 200°/4 mm.   S. S. ZILVA.

Specific action of erepsin and trypsin-kinase. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1928, **10**, 179—187).—The *carbamide* derivatives, in which the free amino-group of the polypeptide is replaced by the carboxylamide group, of *dl*-leucyl-glycine, glycyl-*dl*-valine, and leucylglycylglycine (pre-pared by the action of ammonia on the corresponding carbethoxy-derivative), are not hydrolysed by either erepsin or trypsin-kinase, but suffer fission when treated with an extract of pancreas powder. Similarly, the phenylurethanes of *dl*-leucylglycylglycine and *dl*-leucyl-glycine are much more readily hydrolysed with pancreas extract than with trypsin-kinase. The specific action of erepsin, trypsin, and trypsin-kinase on various polypeptides containing *l*-leucine has been investigated. *l*-Leucylglycyl-*l*-leucine, glycyl-*l*-leucyl-glycyl-*l*-leucine, dl-*leucylglycyl*-l-*leucylglycine*, m. p. 256°, dl-*leucylglycylglycyl*-l-*leucine*, and *l*-leucylglycyl-*l*-leucylglycyl-*l*-leucine are all hydrolysed by erepsin and trypsin-kinase, whilst *glycyl*-dl-*leucylglycine*, m. p. 216° (decomp.), *dl*-leucyl-*dl*-leucylglycylglycine, *l*-leucylpentaglycylglycine, di-(*l*-leucyltriglycyl)-*l*-leucylpentaglycylglycine, and tri-(*l*-leucyltriglycyl)-*l*-leucylpentaglycylglycine are attacked only by erepsin. *l*-Leucyltetraglycylglycine is hydrolysed by erepsin and slowly by trypsin-kinase, but not by trypsin. Thus, seemingly, trypsin-kinase has an affinity for the carboxyl group of leucine which is absent when the glycine residue is at the end of the chain (but cf. Waldschmidt-Leitz and others, A., 1928, 446, and Abderhalden and Fleischmann, *ibid.*, 1043). Neither *dl*-leucyl-γ-aminobutyric acid nor its *phenyl-urethane*, m. p. 166°, is hydrolysed by erepsin or trypsin-kinase. Whilst glycyl-*d*-α-aminobutyric acid is hydrolysed by erepsin, the corresponding *l*-com-pound is unattacked. *Chloroacetyl*-dl-*leucylglycine*, m. p. 141°, and α-*bromoisohexoylglycyl*-l-*leucylglycine*, m. p. 180°, are prepared.   J. W. BAKER.

Specific action of erepsin and trypsin-kinase; their behaviour with polypeptides and their

derivatives in which β-aminobutyric acid re-places an α-amino-acid, and the action of *N*-alkali on these compounds. E. ABDERHALDEN and R. FLEISCHMANN (Fermentforsch., 1928, **10**, 195—212; cf. Abderhalden and Köppel, A., 1928, 1042).—The *phenylurethanes* of di-(*d*-valyl-*d*-alanyl)-*l*-cystine, decomp. 175°, di-(*l*-leucylglycyl)-*l*-cystine, decomp. 190°, diglycylglycine, m. p. 214—216° (the substance, m. p. 184°, described by Curtius and Wüstenfeld, A., 1904, i, 833, as this derivative being some other compound) (α-*naphthylurethane*, decomp. 225°), and tri- and tetra-glycylglycine, both decomp. above 220°, have been prepared, and the effect of the substitution of the amino-group on the action of erepsin and trypsin-kinase has been investigated. The first two derivatives are not attacked by erepsin ($p_{\rm H}$ 7·8) at 37° (although the parent polypeptides are readily hydrolysed), but are hydrolysed by trypsin-kinase ($p_{\rm H}$ 8·3) at 37°. All are hydrolysed by *N*-sodium hydroxide at 37°. No hydrolysis occurs if the $p_{\rm H}$ value is increased from 8·1 to 9·2. None is hydrolysed by erepsin and only tetraglycylglycine phenylurethane is attacked by trypsin-kinase. By usual methods tetraglycylglycine is converted successively into d-α-*bromoisohexoyltetraglycylglycine*, decomp. above 220°, [α]$_{\rm D}^{20}$ +12·21°, and *l*-*leucyltetraglycylglycine*, decomp. above 220°, [α]$_{\rm D}^{20}$ +9·41°. The latter suffers 80% hydrolysis in 3 hrs. with *N*-sodium hydr-oxide at 37°, and is attacked by trypsin-kinase but not by erepsin (cf. Abderhalden and Schwab, preceding). The influence of the presence of a β-aminobutyric acid group was investigated with the following compounds : *dl*-leucyl-β-aminobutyric acid (I) (*phenylurethane*, m. p. 188°; *benzoyl* derivative, m. p. 182°); dl-*leucyl-*dl-*leucyl-β-aminobutyric acid* (II), m. p. 240° (*phenyl-urethane*, m. p. 212°) (prepared from dl-α-*bromoiso-hexoyl*-dl-*leucyl-β-aminobutyric acid*, m. p. 172°); β-*aminobutyryl*-dl-*leucine* (III), m. p. 265—268° (decomp.) (prepared from β-*chlorobutyryl* chloride, b. p. 40—41°/12 mm., 65—67°/40 mm., through β-*chloro-butyryl*-dl-*leucine*, m. p. 132°); β-*aminobutyrylglycine* (IV), m. p. 248° (from β-*chlorobutyrylglycine*, m. p. 122°); β-*aminobutyryldiglycylglycine* (V), m. p. 230° (decomp.) (from β-*chlorobutyryldiglycylglycine*, m. p. 195°); β-*aminobutyryltriglycylglycine* (VI), decomp. 249° (from β-*chlorobutyryltriglycylglycine*, m. p. 227°); β-*aminobutyryl-β-aminobutyric acid* (VII) (from β-*chlorobutyryl-β-aminobutyric acid*, m. p. 142°); and β-*aminobutyryl*-l-*leucyltetraglycylglycine* (VIII) (from β-*chlorobutyryl*-l-*leucyltetraglycylglycine*, de-comp. above 215°). Neither I nor its *benzoyl* derivative is attacked by *N*-sodium hydroxide, whilst the *phenylurethane* suffers hydrolysis; II is un-attacked, whilst its phenylurethane is readily hydro-lysed; III, IV, and VII are not acted on, whilst V, VI, and VIII are hydrolysed. None of these compounds is affected by erepsin, but with trypsin-kinase VIII is hydrolysed, whilst V and VI are not attacked. Trypsin does not act on the amino-group but on the carboxyl group, so that if the terminal amino-acid is not one which occurs naturally (*e.g.*, a β-amino-acid) no attack is possible.
    J. W. BAKER.

Hydrolysis of polypeptides and their deriv-atives with erepsin, trypsin-kinase, and *N*-alkali.

E. ABDERHALDEN and O. HERRMANN (Fermentforsch., 1928, **10**, 145—158).—The hydrolysis of a number of synthetic polypeptides and their derivatives with N-sodium hydroxide, erepsin, and trypsin-kinase has been investigated quantitatively. By usual methods are obtained dl-α-aminobutyrylglycine (I) (*phenylurethane*, m. p. 203°; o-*nitrotoluene*-p-*sulphonyl*, m. p. 170—172°, p-*nitrobenzoyl*, m. p. 188—189°, and m-*nitrobenzoyl*, m. p. 204°, derivatives); dl-α-*bromopropionyl*-dl-α-*aminobutyrylglycine*, m. p. 173°; dl-*alanyl*-dl-α-*aminobutyrylglycine* (II), m. p. 225° (*phenylurethane*, m. p. 208—210°) dl-*valylglycine*, m. p. 245°; dl-α-*bromopropionyl*-dl-*valylglycine*, m. p. 202°; dl-*alanyl*-dl-*valylglycine* (III), m. p. 248° (*phenylurethane*, m. p. 218°; *naphthalene-2-sulphonyl* derivative, m. p. 198°); l-leucyl-l-phenylalanine+ d-leucyl-d-phenylalanine (IV), m. p. 260° (*phenylurethane*, m. p. 183°), and l-leucyl-d-phenylalanine+ d-leucyl-l-phenylalanine (V), m. p. 220° (cf. Leuchs and Suzuki, A., 1904, i, 867) (*phenylurethane*, m. p. 193°; o-*nitrotoluene*-4-*sulphonyl* derivative, m. p. 75°); glycyl-dl-phenylalanine (VI), m. p. 260° (decomp.) [*phenylurethane*, m. p. 208°; *naphthalene-2-sulphonyl*, m. p. 100° (decomp.), and *benzoyl*, m. p. 172°, derivatives]; dl-α-*bromoisovaleryl*-dl-*phenylalanine*, m. p. 135°, which by treatment with ammonia yields, not the dipeptide, but an unsaturated *substance*, m. p. 260° (decomp.). By treatment in $0.1M$-solution with N-sodium hydroxide at 37°, I, II, and III are hydrolysed more slowly than their phenylurethanes; IV, V, and VI, and the naphthalene-2-sulphonyl derivative of the last are not hydrolysed, whilst their phenylurethanes and the benzoyl derivative of VI suffer hydrolysis. Thus in all cases the phenylurethanes (this group remaining combined with the amino-acid after fission of the polypeptide) are more readily hydrolysed by alkali than are the parent substances. With erepsin (p_H 7·8 at 37°) fission of the unsubstituted polypeptide occurs in each case, but none of the derivatives is attacked. Conversely, with trypsin-kinase the parents are unattacked, whilst the derivatives suffer enzymolysis in each case. J. W. BAKER.

Influence of the substitution of the free amino-group of polypeptides by various groups on their fission by N-alkali, erepsin, and trypsin-kinase. E. ABDERHALDEN, E. RINDTORFF, and A. SCHMITZ (Fermentforsch., 1928, **10**, 213—232).— dl-Leucylglycine is more readily attacked by N-sodium hydroxide at 37° than is its phthaloyl derivative, m. p. 119—120°, whilst methyl-dl-leucylglycine is very resistant to attack. The *trichloroacetyl* derivative, m. p. 172—173°, eliminates trichloroacetic acid under these conditions. Similarly, *methyldiglycylglycine*, m. p. 139—140° (decomp.), is slightly more resistant to attack by N-sodium hydroxide than is the parent diglycylglycine. Erepsin (p_H 7·8) at 37° attacks dl-leucylglycine, but its acyl derivatives and methyl-diglycylglycine are not affected. On the contrary, all the derivatives of dl-leucylglycine with the exception of the methyl compound are hydrolysed by trypsin-kinase (p_H 8·3) at 37°. Ethyl oxalyldi-d-glutamate is readily hydrolysed by N-sodium hydroxide at 37° with fission of oxalic acid, whilst

ethyl succinyl-d-*glutamate* is hydrolysed only very slowly. Neither derivative is hydrolysed by erepsin, whilst trypsin-kinase attacks the former but not the latter. From glycyl-dl-leucine are prepared its *naphthalene-2-sulphonyl*, m. p. 123° (attacked by N-sodium hydroxide only with difficulty); *phenylurethane*, m. p. 177° (much more readily hydrolysed by N-sodium hydroxide than the parent dipeptide); *chlorobenzoyl*, m. p. 190°, and *butyryl*, m. p. 182° (both attacked by alkali at a velocity intermediate between that of the phenylurethane and the parent polypeptide), derivatives, and *oxalylglycyl*-dl-*leucine ethyl* ester, m. p. 163° (readily hydrolysed by alkali). Unlike the parent glycyl-dl-leucine, all these derivatives are unattacked by erepsin, whilst trypsin-kinase, which has no action on the parent dipeptide, hydrolyses them all. From glycyl-dl-*valine*, m. p. 240° (decomp.) (prepared from *chloroacetyl*-dl-*valine*, m. p. 129·5— 130·5°), are prepared its *phenylurethane*, m. p. 155°, *dichloroacetyl*, m. p. 151·5—152°, and *benzoyl*, m. p. 135—136°, derivatives, all of which are more readily hydrolysed by N-sodium hydroxide than is the parent dipeptide. The dichloroacetyl group is rapidly eliminated by the action of alkali to regenerate the parent dipeptide and not as *dichloroacetylglycine*, m. p. 125—126°, which was synthesised, and is itself rapidly hydrolysed by alkali at 37°. The phenylurethane is attacked by trypsin-kinase but not by erepsin. These results confirm the view that a free amino-group is essential for attack by erepsin, whilst trypsin-kinase, which does not attack the original polypeptide containing a free amino-group, is able to attack the derivatives in which this group is substituted with a biologically foreign group (*e.g.*, acyl but not methyl). J. W. BAKER.

Action of N-alkali, erepsin, and trypsin-kinase on polypeptides containing d-alanine. E. ABDERHALDEN and J. J. DELGADO Y MIER (Fermentforsch., 1928, **10**, 251—255).—d-Alanyl-d-alanine (I) (*phenylurethane*, m. p. 176°; *naphthalene-2-sulphonyl* derivative, m. p. 158—159°) and d-*alanyl*-d-*alanyl*-d-*alanine* (II), m. p. 245°, $[\alpha]_D^{20}$ −15·1° (prepared from d-*alanine anhydride*, m. p. 297°, $[\alpha]_D^{20}$ −28·7°, through d-α-*bromoisopropionyl*-d-*alanyl*-d-*alanine*, m. p. 148°), are both hydrolysed by N-sodium hydroxide at 37°, II more rapidly than I. Under the same conditions the phenylurethane of I is completely hydrolysed in 3 hrs. to d-alanine and its phenylurethane, whilst its naphthalene-2-sulphonyl derivative is only slowly attacked. Erepsin (p_H 7·8) hydrolyses I more rapidly than II, but neither is attacked by trypsin-kinase. J. W. BAKER.

Action of N-alkali, erepsin, and trypsin-kinase on polypeptides containing β-alanine. E. ABDERHALDEN and F. REICH (Fermentforsch., 1928, **10**, 173—178).—Glycyl-β-alanine, decomp. 230° (Miyamichi, Chem. Zentr., 1927, i, 1428), dl-α-*bromoisohexoyl*-β-*alanine*, m. p. 69—72°, and dl-*leucyl*-β-*alanine*, m. p. 202—204° (*phenylurethane*, m. p. 160—162°), are prepared by the usual methods. With N-sodium hydroxide at 37° glycyl-β-alanine is readily hydrolysed and dl-leucyl-β-alanine is almost unchanged after 48 hrs., whilst its phenylurethane is rapidly

attacked. In every case fission occurs with erepsin or trypsin-kinase. J. W. BAKER.

Action of N-alkali, erepsin, and trypsin-kinase on polypeptides containing dl-α-aminoisovaleric acid. E. ABDERHALDEN, P. SAH, and E. SCHWAB (Fermentforsch., 1928, **10**, 264—273).—By the usual methods the following have been prepared : dl-valylglycine (copper salt ; phenylurethane, m. p. 188—190° ; naphthalene-2-sulphonyl derivative, m. p. 195°); dl-α-bromoisovalerylglycylglycine, m. p. 145—146° ; dl-valylglycylglycine, m. p. 240° (copper salt ; benzoyl, m. p. 155°, and naphthalene-2-sulphonyl, m. p. 190°, derivatives ; phenylurethane, m. p. 216—217°); chloroacetyl-dl-valylglycine, m. p. 141° ; glycyl-dl-valylglycine, m. p. 239° (phenylurethane, m. p. 197—198° ; naphthalene-2-sulphonyl derivative, m. p. 148°). With N-sodium hydroxide at 37° only those polypeptides in which the glycine component contains a free aminogroup (glycyl-dl-valine, glycyl-dl-valylglycine) suffer hydrolysis. All the phenylurethanes are attacked, but, contrary to the view previously held that the naphthalene-2-sulphonyl group exerted a stabilising influence against alkaline hydrolysis, all these derivatives suffer hydrolysis, although in two cases the parent polypeptides are unattacked. dl-Valylglycine, dl-valylglycylglycine, and glycyl-dl-valylglycine are all hydrolysed by erepsin, but not by trypsin-kinase, whilst the phenylurethane of the second is hydrolysed by the latter but not by the former enzyme.

J. W. BAKER.

Action of N-alkali, erepsin, and trypsin-kinase on dl-αε-dileucyl-dl-lysine. E. ABDERHALDEN and H. SICKEL (Fermentforsch., 1928, **10**, 302—304). —dl-αε-Dileucyl-dl-lysine, an amorphous powder, decomp. 160°, is prepared by usual methods from dl-αε-dibromoisohexoyl-dl-lysine. It is rapidly hydrolysed by N-sodium hydroxide at 37—40°. Erepsin and trypsin-kinase both hydrolyse it, the latter more readily than the former. J. W. BAKER.

Behaviour of αδ-di-(dl-leucyl)-dl-ornithine and its phenylurethane with N-alkali, erepsin, trypsin-kinase, pepsin and hydrochloric acid, and arginase. E. ABDERHALDEN and H. SICKEL (Fermentforsch., 1928, **10**, 188—194).—dl-Ornithine (obtained by hydrolysis of dl-δ-benzoylornithine ; Fischer and Zemplén, A., 1909 i, 303) condenses with dl-α-bromoisohexoyl bromide to yield αδ-di-(dl-α-bromoisohexoyl)-dl-ornithine, m. p. 126—128° (together with a small amount of a benzoylated monosubstituted substance, m. p. 165°), converted by alcoholic ammonia into αδ-di-(dl-leucyl)-dl-ornithine, +H₂O, sintering at 95°, decomp. 150° (phenylurethane, sintering 98°, m. p. 130°). The rate of hydrolysis with N-sodium hydroxide at 37—40° is greater for the phenylurethane derivative than for the parent tripeptide, but neither suffers fission with erepsin or trypsin-kinase, nor is the tripeptide attacked by pepsin in 0·1N-hydrochloric acid or by arginase. J. W. BAKER.

Accurate method for the analysis of carbamide. (MISS) M. TAYLOR (J. Amer. Chem. Soc., 1928, **50**, 3261—3265).—The use of carbamide as a reference substance in migration and other experiments is suggested. An accurate method of analysis of carbamide solutions is described, depending on the hydrolysis of the substance under pressure in presence of a small excess of standard hydrochloric acid.

S. K. TWEEDY.

High-molecular condensation products of carbamide and formaldehyde. H. SCHEIBLER, F. TROSTLER, and E. SCHOLZ (Z. angew. Chem., 1928, **41**, 1305—1309).—Carbamide and freshly-distilled, neutral formaldehyde solution react, giving hydroxymethylcarbamide (I), m. p. 110°, which on treatment with aqueous acetic acid gives both an insoluble substance, $(NH_2 \cdot CO \cdot N{:}CH_2)_{12}, H_2O$, and a soluble product, $(NH_2 \cdot CO \cdot N{:}CH_2)_{12}, AcOH$ (cf. van Laer, A., 1921, i, 499). Treatment of I first with acetic acid and then with bromine affords the compound $(NH_2 \cdot CO \cdot N{:}CH_2)_3, Br_2$, obtained also from the above complexes. s-Dihydroxymethylcarbamide, m. p. 133° (cf. Einhorn and Hamburger, A., 1908, i, 141), is converted by the acetic acid–bromine treatment into the compound (II), $(OH \cdot CH_2 \cdot NH \cdot CO \cdot N{:}CH_2)_3, Br_2$, which after prolonged action passes into the substance (III), $[CO(N{:}CH_2)_2], Br_2$. When formaldehyde and carbamide are condensed in presence of a small amount of ammonia hydroxymethylmethylenecarbamide, $(OH \cdot CH_2 \cdot NH \cdot CO \cdot N{:}CH_2)_3, H_2O$, is obtained. This is converted by the bromine treatment into II.

The product prepared from technical formaldehyde and carbamide is hydrolysed by 20% hydrochloric acid to ammonium chloride, whilst prolonged treatment with hot acetic acid gives, in addition to formaldehyde and methylamine, a water-soluble substance, hydrolysed by phosphoric acid to formaldehyde, carbon dioxide, ammonium salts, and acetic acid. It is converted by the bromine treatment into III, and with a mixture of acetic acid and anhydride yields a chloroform-soluble substance, $[CO(N{:}CH_2)_2], Ac_2O$, convertible by bromine into III.

s-Dimethylcarbamide and formaldehyde give hydroxymethyl derivatives and not condensation products, thus indicating that the methylenecarbamide residues are correctly represented as $(NH_2 \cdot CO \cdot N{:}CH_2)$ (cf. van Laer, loc. cit. ; Dixon, J.C.S., 1918, **113**, 238).

H. BURTON.

Carbylamines. M. PASSERINI (Mem. R. Accad. Lincei, 1927, [vi], **2**, 377—398).—A résumé of work previously published (A., 1921, 743, to 1927, 149). The author discusses the reactions of carbylamines with organic acids, aldehydes, and ketones in presence of acids, hydrates of chloro-aldehydes, phenol and naphthols, and pernitroso-derivatives.

E. W. WIGNALL.

Dichloromethylarsine. E. V. ZAPPI and V. DEULOFEU (Bull. Soc. chim., 1928, [iv], **43**, 1230—1232).—Dichloromethylarsine, b. p. 130—132°, is obtained in 83% yield (53% after purification) by decomposing sodium cacodylate with hydrochloric acid (d 1·19), filtering, evaporating, and then distilling in a current of dry hydrogen chloride.

R. BRIGHTMAN.

New syntheses of organic selenium compounds. Q. MINGOIA (Gazzetta, 1928, **58**, 667—673 ; cf. A., 1927, 134).—The action of acetyl chloride on magnesium bromohydroselenide yields selenoacetic acid, $CH_3 \cdot COSeH$, which has a penetrating, irritating odour and was obtained as ammonium salt, but this is highly unstable and rapidly undergoes partial change

into selenium and ammonium acetate. With salts of the heavy metals, this ammonium salt gives coloured precipitates, which decompose to form the corresponding black selenides.

Ethoxyselenoformic acid, OEt·COSeH, prepared by the interaction of magnesium bromohydroselenide and ethyl chloroformate, rapidly decomposes into its *anhydride*, b. p. 125—127°, of nauseating odour, carbon monoxide, selenium, and alcohol.

Ethyl iodide and magnesium bromohydroselenide readily react, giving ethylselenomercaptan and magnesium bromoiodide. The action of acetaldehyde or benzaldehyde on magnesium bromohydroselenide, to yield selenoacetaldehyde, m. p. 136° (Vanino and Schinner, A., 1915, i, 117, gave 139°), or seleno-benzaldehyde, m. p. 203—205° (Vanino and Schinner, *loc. cit.*), is described.　　　T. H. POPE.

Valency. XII. Isomeric derivatives of di-ethyl telluride. F. L. GILBERT and T. M. LOWRY (J.C.S., 1928, 3179—3189).

—α-Diethyltelluronium di-iodide, m. p. 57° (α-*tetraiodide*, m. p. 98°), yields an α-base, which is converted into a β-base (β-*di-iodide*, m. p. 42°, β-*dibromide*, solidifying at −12°, β-*di-chloride*, m. p. −10°), when an aqueous solution is evaporated to dryness at 100°/15 mm. in a stream of nitrogen. The α- and β-salts differ in their behaviour towards alkali; with aqueous ammonia the α-di-iodide gives an α-*monoxyiodide*, $[O(TeEt_2)_2]I_2$, m. p. 104—106°, whilst the β-di-iodide gives a *triethyltelluronium iodide*. Mercury diphenyl and the α-di-iodide react in chloroform solution to give an additive *compound*, $(TeEt_2I_2)_2,HgPh_2$, m. p. 94°; mercury di-*p*-tolyl does not react with α-dimethyl- or α-diethyl-telluronium di-iodide. The absorption spectra of the iodides in *cyclo*hexane exhibit the twin maxima of the " iodoform band " and the bromides exhibit only a step-out. Conductivity measurements show that the β-base has a higher conductivity than the α-base, whereas potentiometric titrations indicate that the β-base is stronger than the α-base during the first half of the process of neutralisation; the curve for the β-base is inflected after half neutralisation and the two curves cross (cf. A., 1928, 1098), proving that the β-base is weaker than the α-base after half neutralisation.
　　　　　　　　　　　　A. I. VOGEL.

Side reactions in the preparation of magnesium alkyl halides. H. GILMAN and R. E. FOTHERGILL (J. Amer. Chem. Soc., 1928, 50, 3334—3341; cf. Fuson, A., 1926, 604, 1237; Gomberg and Bachmann, A., 1927, 245).

—The yields of (*a*) ethylene, hydrogen, methane, and ethane; (*b*) ethylene, hydrogen, ethane, and butane, and (*c*) α-butylene and *n*-butane, formed under varying conditions in the preparation of (*a*) magnesium methyl iodide, (*b*) magnesium ethyl bromide, and (*c*) magnesium *n*-butyl bromide, have been determined. The results are in agreement with the view that the production of the Grignard reagent, MgRX, is preceded by the formation of the free radical, R·, from which the by-products, R·R, RH, and R(−H) are derived. Similarly, the decomposition of magnesium methyl iodide by means of dilute sulphuric acid yields in addition to methane traces of hydrogen, ethylene, and probably other hydrocarbons. These side-reactions constitute pos-

sible sources of error in the analysis of Grignard reagents and in the determination of active hydrogen by the Zerevitinov method.　　　H. E. F. NOTTON.

Factors influencing yields of magnesium *tert.*-butyl and *tert.*-amyl chlorides, and preparation of acids from them and carbon dioxide. H. GILMAN and E. A. ZOELLNER (Rec. trav. chim., 1928, 47, 1058—1063; cf. A., 1928, 401).

—Magnesium *tert.*-amyl chloride is best prepared by the slow addition of *tert.*-amyl chloride (0·1 mol.) to finely-divided magnesium (0·1 atom) and ether (0·7 mol.), with stirring, the ether being maintained in ebullition. Details are also given for the preparation of αα-di-methylpropionic (55—63%) and αα-dimethyl-*n*-butyric acids (about 54%) from the requisite Grignard reagent and dry carbon dioxide at 0—8°.
　　　　　　　　　　　　H. BURTON.

Chlorination of *p*-cymene. W. QUIST (Förh. III nord. Kemistmötet, 1928, 194).

—*p*-Cymene when chlorinated under varying conditions behaves essentially in the same way as simpler hydrocarbons under similar treatment. It differs, however, from these in that even when treated with chlorine under the most favourable conditions for obtaining compounds substituted in the side-chain the yield of these is small, chlorination of the heated material even in direct sunlight giving rise largely to products substituted in the carbon nucleus, together with considerable quantities of a viscous material, which is difficultly volatile in steam. Chlorination in acetic or formic acid solution also gave rise to nuclear monosubstitution products. The complete conversion of *p*-cymene into the technically important ω-chloromethyl derivative would thus appear to present considerable difficulties.
　　　　　　　　　　　　H. F. HARWOOD.

Stereoisomerism of disulphoxides and related substances. III. Pairs of aromatic disulphoxides. E. V. BELL and G. M. BENNETT (J.C.S., 1928, 3189—3192).

—Oxidation of aromatic disulphoxides, $C_2H_4(SAr)_2$, Ar being phenyl, *p*-tolyl, and benzyl, and $C_6H_4(SR)_2$, R being methyl or benzyl, with 25% hydrogen peroxide in glacial acetic acid solution gave in every case a pair of diastereoisomeric disulphoxides which were separated by fractional crystallisation, and were differentiated by their m. p., crystalline forms, and solubilities. Both forms give the parent disulphide on reduction, the alternative structure of a monosulphone being thereby excluded. Thus s-*diphenylthiolethane*, m. p. 69° (prepared by condensation of thiophenol with ethylene dibromide in the presence of potassium hydroxide), gave an α-*disulphoxide*, m. p. 166° (decomp.), and a β-*disulphoxide*, m. p. 123° (decomp.); s-di-p-*tolylthiolethane*, m. p. 81°, gave an α-*disulphoxide*, m. p. 173—174° (decomp.), and a β-*disulphoxide*, m. p. 126—127° (decomp.); dibenzylthiolethane gave an α-*disulphoxide*, m. p. 209°, and a β-*disulphoxide*, m. p. 192° (cf. Fromm and others, A., 1913, i, 44); l : 3-dimethyl-thiolbenzene (*mercurichloride*, m. p. 108°) gave an α-*disulphoxide*, m. p. 147°, and a β-*disulphoxide*, m. p. 102° (cf. Zincke and Krüger, A., 1913, i, 44); l : 3-dibenzylthiolbenzene gave an α-*disulphoxide*, m. p. 133°, and a β-*disulphoxide*, m. p. 123° (cf. Zincke and Krüger, *loc. cit.*); l : 4-dimethylthiol-

benzene gave an α-disulphoxide, m. p. 183° [mercuri-chloride, m. p. 216° (decomp.)], and a β-*disulphoxide*, m. p. 136° [mercurichloride, m. p. 188° (decomp.)] (cf. Zincke and Frohneberg, A., 1909, i, 643). No crystalline bromide or hydrochloride of the disulph-oxides could be isolated.   A. I. VOGEL.

Effect of specific compound formation between substrate and enzyme on the hydrolysis of poly-peptides. E. ABDERHALDEN and H. BROCKMANN (Fermentforsch., 1928, **10**, 159—172).—Colamine (β-hydroxylethylamine) reacts with *dl*-α-bromoprop-ionyl bromide to yield dl-α-*bromopropionylcolamine*, m. p. 78·5°, converted by ammonia into dl-*alanyl-colamine*, m. p. 78—79° (best isolated through its *picrate*, m. p. 105—108°). Chloroacetanilide, m. p. 138°, is converted by ammonia into glycylaniline, +2H₂O, m. p. 62—63° [*picrate*, m. p. 186° (decomp.)], and a *substance*, m. p. 144·5°, probably (NHPh·CO·CH₂)₂NH, which condenses with dl-α-bromopropionyl bromide to yield a *substance*, m. p. 244—245° (uncorr.). Similarly are obtained *dl*-α-bromopropionylaniline, m. p. 101°; dl-*alanylaniline*, b. p. 190—196°/15—16 mm. (*picrate*, m. p. 175°), which reacts with chloroacetyl chloride to yield *chloroacetyl*-dl-*alanylaniline*, m. p. 156°, converted by ammonia into *glycyl*-dl-*alanylaniline*, m. p. 80° [*picrate*, m. p. 186° (decomp.)], and a *substance*, m. p. 207—208°, probably (NHPh·CO·CHMe·NH·CO·CH₂)₂NH; dl-*alanylglycylaniline*, m. p. 124—125° [*picrate*, m. p. 198° (decomp.)]. Similarly from diphenylamine is obtained dl-*alanyldiphenylamine*, m. p. 86°. All these sub-stances with the exception of the last are attacked by intestinal erepsin at 37° (p_H 8·0), whilst trypsin (p_H 8·5) is without action (cf. Waldschmidt-Leitz and others, A., 1927, 345; Grassmann and Dyckerhoff, A., 1928, 672). With *N*-sodium hydroxide at 37°, *dl*-alanyl-glycine, *dl*-alanylglycylaniline, glycylaniline, and glycyl-*dl*-alanylaniline suffer hydrolysis. Erepsin is thus effective if the substrate contains a free amino-group, but no free carboxyl group, whilst in the absence of the latter trypsin has no action. All m. p. are corrected.   J. W. BAKER.

Influence of certain substituent groups in the aniline molecule on the formation of carbyl-amines. M. PASSERINI and G. BANTI (Gazzetta, 1928, **58**, 636—640).—The presence in the aniline molecule of the carboxyl, hydroxyl, nitro-, or arsinic group prevents the formation of carbylamine by treatment with potassium hydroxide and chloroform, a halogen atom limits such formation, whilst a ketonic group exhibits no hindering effect. Thus, anthranilic acid gives formylanthranilic acid; *p*-aminophenol gives formyl-*p*-aminophenol; *p*-nitroaniline remains unchanged, as does sodium *p*-aminophenylarsinate; *p*-aminoacetophenone gives p-*carbylaminoacetophen-one*, b. p. 80—81°/30 mm., and diphenylformamidine; *o*-bromoaniline yields a small proportion of a liquid having the odour of carbylamine.   T. H POPE.

Compounds of tetryl with hydrocarbons. N. N. EFREMOV and A. M. TICHOMIROVA (Ann. Inst. Anal. Phys. Chem., 1928, 4, 92—117).—Fusion curves are constructed for binary mixtures of tetryl with various other substances. Unstable equimolecular *compounds* are formed with naphthalene, m. p. 86·4°,

acenaphthene, m. p. 92·4°, phenanthrene, m. p. 73·2°, fluorene, m. p. 77·5°, and retene, m. p. 95·2°. With picramide, 2 : 4-dinitroaniline, picryl chloride, 2 : 4 : 6-trinitroanisole, 2 : 4 : 6-trinitro-*m*-xylene, and camphor the formation of compounds or solid solutions was not observed. The addition of the above substances to tetryl causes a considerable depression of m. p.
                    R. TRUSZKOWSKI.

Degradation of quaternary ammonium salts. I. T. S. STEVENS, E. M. CREIGHTON, A. B. GORDON, and M. MacNICOL (J.C.S., 1928, 3193—3197).—With the object of protecting a secondary amino-group by a more easily removable radical than benzyl, quater-nary phenacylammonium salts have been prepared by refluxing the base with bromoacetophenone in benzene or alcohol, and isolating the resulting bromide, or converting it into the iodide. The following are described : *Phenacylphenyldiethylammonium iodide*, m. p. 133°; *phenacyl-β-phenylethyldimethylammonium bromide*, m. p. 191°; *diphenacyldimethylpiperazinium dibromide*, m. p. 222—225° (decomp.); *hydro-hydrastinine phenacyliodide*, m. p. 190°. These all readily lose the phenacyl radical on reduction in aqueous solution by sodium amalgam,

With *phenacylbenzyldimethylammonium bromide* (I), m. p. 167—168°, sodium amalgam reduction is abnormal; a *base*, C₁₇H₁₉ON (II), is formed, identical with the product obtained by the action of sodium hydroxide. This base is not a product of loss of a methyl group, since its methobromide (see below) is not identical with I, but gives phenyl styryl ketone with hot alkali. It is shown by synthesis from ω-*bromo*-ω-*benzylacetophenone* (m. p. 57—59°; obtained by bromination of benzylaceto-phenone in carbon tetrachloride) and dimethylamine hydrochloride, in presence of sodium methoxide, to be ω-*dimethylamino*-ω-*benzylacetophenone*, m. p. 77—79° [*picrate*, m. p. 147—149°; *methobromide* (+0·5EtOH), m. p. 195—197°]. Reduction of I by zinc and sulphuric acid furnishes a crude base, of which the picrate, m. p. 173—174°, is identified with benzyltrimethylammonium picrate (lit. 168—169°).
                    E. W. WIGNALL.

Action of carbon disulphide on benzidine in presence of metallic oxides. B. CECCHIETTI and U. SARTI (Gazzetta, 1928, 58, 758—760).—The preparation by Krulla (A., 1913, i, 1174) of a com-pound (NHPh·CS·S)₂Sn suggested that it might be possible to prepare a compound of the type (NHR·CS·)₂; actually such a *compound*, (NH₂·C₆H₄·C₆H₄·NH·CS·)₂, is formed when benzidine is heated in alcoholic solution with carbon disulphide and stannous oxide. The product can be diazotised and coupled with β-naphthol, when the *substance* (OH·C₁₀H₆·N₂·C₆H₄·C₆H₄·NH·CS·)₂, decomp. 210°, is obtained.   E. W. WIGNALL.

Action of allylthiocarbimide on benzidine. B. CECCHIETTI and U. SARTI (Gazzetta, 1928, 58, 760—763).—When benzidine and excess of allylthio-carbimide are heated together under reflux, a dark product is formed from which a grey substance, (C₃H₅·NH·CS·NH·C₆H₄·)₂, m. p. 243°, is obtained (cf. Schiff, A., 1878, 669). If the reaction mixture contains a large excess of allylthiocarbimide, and

is strongly heated, a different product, 4 : 4'-*dithio-carbimidodiphenyl*, m. p. 203°, is obtained, without evolution of hydrogen sulphide; this is identical with the substance obtained by Jaffé (A., 1894, i, 418) by heating benzidine with thiocarbonyl chloride under pressure. E. W. WIGNALL.

Diphenyl and its derivatives (and dinaphthyls). Scission into optical antipodes of compounds without asymmetric atoms. II. L. MASCARELLI (*Gazzetta*, 1928, **58**, 627—630).—When converted into its salts with various optically active acids, 2 : 2'-diamino-αα'-dinaphthyl (cf. Mascarelli and Brusa, A., 1914, i, 267) shows definite indications of scission into two optical antipodes, but 1 : 1'-diamino-ββ'-dinaphthyl exhibits no such indications. This behaviour is in accord with the theory, since with the αα-disubstituted derivatives, rotation of the two naphthyl nuclei round their joining axis cannot be hindered by the presence of the two adjacent amino-groups (cf. Mills and Elliott, A., 1928, 748; Kuhn and Albrecht, *ibid.*, 1015). T. H. POPE.

Reduction of nitro-compounds by aromatic ketols. II. Some *o*-, *m*-, and *p*-azoxy-compounds. H. B. NISBET (J.C.S., 1928, 3121—3124). —The method previously described (A., 1927, 1063) is successful in the reduction of *p*-nitro-compounds; with *o*- and *m*-nitro-compounds the yields are inferior, owing to difficulty in isolation of the azoxy-compounds. The following are prepared (benzoin being used for each reduction): *p*-azoxybenzylideneacetophenone; *o*- and *m*-*isomerides* of the latter, m. p. 141—142° (sintering at 135°), and 156—157°, respectively; 2-*o*-, 2-*m*-, and 2-*p*-*azoxystyryl-3-methylchromones*, m. p. 202°, 275·5°, and 289°, respectively; *o*-, *m*-, and *p*-*azoxybenzylidene-p-bromoanilines*, m. p. 299°, 120°, and 218°, respectively; *m*-*azoxybenzylidene-p-toluidine*, m. p. 150° (sintering at 135°); *ethyl p*-*azoxybenzoate*; and 2-*nitro-3-azoxytoluene*, m. p. 164°. 2-*o*-, 2-*m*-, and 2-*p*-*Nitrostyryl-3-methylchromones*, m. p. 161°, 212°, and 238°, respectively, were prepared by condensation of 2 : 3-dimethylchromone with the appropriate nitrobenzaldehyde (cf. Heilbron and others, J.C.S., 1923, **123**, 2565), and *m*-*nitrobenzyl-idene-p-bromoaniline*, m. p. 84°, by condensation of *m*-nitrobenzaldehyde and *p*-bromoaniline.

It was not found possible to isolate *o*-azoxybenzyl-idene-*p*-toluidine, *m*- or *p*-azoxybenzoates, *o*- or *m*-azoxybenzonitrile, α-azoxynaphthalene, or azoxy-benzene itself, but nitrobenzene was found to give with benzoin, anisoin, and furoin, 30—40%, 80%, and 90% yields of benzil, anisil, and furil, respectively. E. W. WIGNALL.

Metallic complexes [co-ordination compounds] of *o*-amino- and *o*-hydroxyazo-derivatives. G. B. CRIPPA [with F. VICINI, G. LEVI, and A. MANGANO] (*Gazzetta*, 1928, **58**, 716—726; cf. Crippa and Venturini, A., 1927, 1180).—The following compounds are described, all the metallic compounds being of the general type [X·C₁₀H₆·N:NR]₂M : p-*acetophenoneazo-β-naphthol*, m. p. 180° (*oxime*, m. p. 234—235°; *phenylhydrazone*, m. p. 165°; *semicarbazone*, m. p. above 300°), giving a *nickelo*-compound, m. p. above 300°, a *cupri*-compound, m. p. above 300°, and a *cobalto*-compound (?), m. p. 275°. The corresponding *methyl*

ether, m. p. 134—135° [*oxime*, m. p. 250°; *phenyl-hydrazone*, m. p. 87—88°; *semicarbazone*, m. p. 210°], and *ethyl ether*, m. p. 102° (*oxime*, m. p. 161—162°; *phenylhydrazone*, m. p. 64°; *semicarbazone*, m. p. 190°), form no such metallic compounds, nor does benzene-azo-β-naphthol or *p*-phenolazo-β-naphthylamine.

Nickelo- and *cupri*- (and in three cases *cobalto*-) compounds of the following are described: *p*-phenol-azo-β-naphthol, *o*-, *m*-, and *p*-nitrobenzeneazo-β-naph-thol, *o*-, *m*-, and *p*-nitrobenzeneazo-β-naphthylamine. β-Naphtholazobenzene-*p*-sulphonic acid forms a *nickel* salt, C₃₂H₂₂O₈N₄S₂Ni, and an *ammonium-cupri*-derivative, [OH·C₁₀H₆·N:N·C₆H₄·SO₃]₂Cu(NH₄)₂ ; with cobalt the result is uncertain. Potassium β-naphthyl-amineazobenzene-*p*-sulphonate gives no positive result with nickel or cobalt, but with copper forms an *ammino-cupri*-derivative, [NH₂·C₁₀H₆·N:N·C₆H₄·SO₃]₂Cu(NH₃)₄K₂, which when heated in aqueous solution is converted into potassium phenyl-αβ-naphthotriazole-*p*-sulphonate (cf. Witt and Schmitt, A., 1894, i, 608).

The general conclusions are that a *p*-hydroxyl group hinders co-ordination, whilst *p*-nitro- and *p*-acetyl groups have no such action; the small number of cobalt compounds is considered to be due to the nature of the metal rather than that of the organic compounds. E. W. WIGNALL.

Action of phthalic anhydride on aminoazo-derivatives. G. B. CRIPPA and P. GALIMBERTI (*Gazzetta*, 1928, **58**, 731—738).—In an attempt to protect the amino-group of benzeneazo-β-naphthyl-amine by condensation with phthalic anhydride, it was found that the latter decomposes the former substance, which loses its benzeneazo-group and gives rise to β-naphthylphthalimide, nitrogen being evolved. *p*-Acetophenoneazo- and α-naphthaleneazo-β-naph-thylamines also yield β-naphthylphthalimide. α-Naph-thylamine derivatives, on the other hand, condense to the anticipated phthalimido-derivatives, from which the corresponding phthalamic acids are obtained by alkaline hydrolysis of the phthalimide ring.

[With A. BORRONI.]—The following are described : 1-*benzeneazo-4-phthalimidonaphthalene*, m. p. 219° (*acid*; *barium salt*); 1-*o*- and 1-*m*-*tolueneazo*- and 1-*p*-*bromobenzeneazo-4-phthalimidonaphthalenes*, m. p. 194°, 198°, and 243°, respectively; 4-*p*-*acetophenone-azo-α-naphthylamine*, m. p. 197°, and its 4-*phthal-imidonaphthalene* derivative, m. p. 249°; *potassium* 4-*phthalimido-α-naphthaleneazobenzene*-*p*-*sulphonate*; and 1-*α*- and 1-*β*-*naphthaleneazo-4-phthalimidonaph-thalenes*, m. p. 211° and 257°, respectively. E. W. WIGNALL.
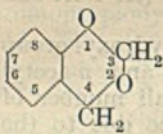
Thiocarbamido-derivatives in the azo series. G. B. CRIPPA [with G. FAINI] (*Gazzetta*, 1928, **58**, 726—731).—*p*-Aminoazobenzene and carbon disul-phide react in alcoholic solution, giving s-*di-p-benzene-azophenylthiocarbamide*, m. p. 202°, oxidised by peracetic acid to s-*di-p-benzeneazophenylcarbamide*, m. p. 270—271°, and reduced to *pp'*-diaminodiphenyl-thiocarbamide, which is converted by carbon disul-phide into di-*p*-phenylenedithiocarbamide (cf. Bolser and Hartshorn, A., 1924, i, 317). Similarly, s-*di*-4-*benzeneazonaphthylthiocarbamide*, m. p. 165°, s-*di*-4-*o*-*tolueneazonaphthylthiocarbamide*, m. p. 160°, and the

corresponding m- and p-*compounds*, m. p. 172° and 185°, respectively, are prepared. The p-compound when subjected to prolonged boiling with acetic acid furnishes a product free from sulphur, m. p. 215°. o-Aminoazobenzene reacts very slowly with carbon disulphide, yielding s-*di-o-benzeneazophenylthiocarb-amide*, m. p. 100°; similarly, benzeneazo-β-naphthyl-amine slowly gives s-*di-1-benzeneazo-β-naphthylthio-carbamide*. E. W. WIGNALL.

Mechanism of the formation of 2 : 4-dinitro-phenol from benzene and nitric acid in presence of mercury salts as catalysts. A. I. ZAKHAROV. —See this vol., 152.

Condensation of dichloroacetaldehyde with phenols. F. D. CHATTAWAY and A. A. MORRIS (J.C.S., 1928, 3241—3246).—The condensation of phenols with aldehydes to form a dioxin ring (annexed formula) is not confined to chloral (A., 1928, 632, etc.): dichloroacetaldehyde reacts even more readily. When its alcoholate is added slowly to a cooled solution of p-nitrophenol in concentrated sulphuric acid, 6-*nitro*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* (I), m. p. 113·5°, is formed. This may be converted by alcoholic potassium hydroxide into 6-*nitro*-2(or 4)-*di-chloromethyl*-4(or 2)-*chloromethylene*-1 : 3-*benzdioxin* (II), m. p. 108° (which does not, in spite of its apparent unsaturation, form an additive compound with bromine). If the temperature is not controlled, 5-nitro-2-ethoxymandelic acid is formed. The compound I is reduced by iron and hydrochloric acid to 6-*amino*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin*, m. p. 108·5—109·5° [*hydrochloride*, m. p. 210° (decomp.); *acetyl* derivative, m. p. 149—150°; *diacetyl* derivative, formed by the action of boiling acetic anhydride containing sulphuric acid, m. p. 145°]. 2 : 4-*Bisdichloromethyl*-1 : 3-*benzdioxin*-6-*diazonium chloride* was prepared, and converted into the *per-bromide*, which decomposed at 128—129° or when heated in acetic acid, giving 6-*bromo*-2 : 4-*bisdichloro-methyl*-1 : 3-*benzdioxin*, m. p. 91·5°.

When phenol is dissolved in concentrated sulphuric acid and treated with dichloroacetaldehyde alcoholate, 2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin*-6-*sulphonic acid* ($+H_2O$), m. p. 150—155° (decomp.), is obtained (*ammonium* salt prepared). The monohydrated sul-phonic acid dissolved in concentrated sulphuric acid and treated with nitric acid is nitrated to 6 : 8-*dinitro*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin*, m. p. 133·5—134·5°, also obtainable by nitration of the mononitro-compound. The action of alcoholic potassium hydr-oxide on the dinitro-compound gives rise to 6 : 8-*di-nitro*-2(or 4)-*dichloromethyl*-4(or 2)-*chloromethylene*-1 : 3-*benzdioxin*, m. p. 144°; this substance, again, does not combine with bromine. The monohydrated sulphonic acid is converted by phosphorus penta-chloride into the corresponding *sulphonyl chloride*, m. p. 105—106°, from which *methyl* and *ethyl* 2 : 4-*bis-dichloromethyl*-1 : 3-*benzdioxin*-6-*sulphonates*, m. p. 110—111·5° and 148—149·5°, respectively, and, with ammonia and with aniline, the *sulphonamide* and *sulphonanilide*, m. p. 175·5° and 166—167°, re-spectively, are obtained. E. W. WIGNALL.

Steric hindrance in the behaviour of phenyl alkyl ethers and derivatives. L. C. RAIFORD and D. M. BIROSEL (Proc. Iowa Acad. Sci., 1927, 34, 222—223).—Bromination of phenyl allyl ether in-volves both phenyl and allyl radicals; rearrangement by heat, according to Claisen's method, of the allyl ether may cause loss of bromine.
CHEMICAL ABSTRACTS.

Effect of substituents in the formation and reactions of certain ethers. L. C. RAIFORD and G. THIESSEN (Proc. Iowa Acad. Sci., 1927, 34, 220—221).—The presence of a nitro-group in diphenyl ether interferes with the entrance of bromine to a greater degree than can be ascribed to steric hindrance. Various derivatives of Cook's tetrabromodiphenyl ether have been prepared, but its structure is still doubtful. CHEMICAL ABSTRACTS.
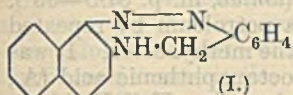
New derivatives of diphenyl. A. ANGELETTI and D. GATTI (Gazzetta, 1928, 58, 630—635).—The author confirms Bell and Kenyon's view (A., 1927, 145) that the compound, m. p. 171°, previously obtained by him is 3 : 4'-dinitro-4-hydroxydiphenyl and is identical with that described by Schmidt and Schultz (A., 1881, 909) as 4'-nitro-4-hydroxydiphenyl, whilst that with m. p. 200—201° is 4'-nitro-4-hydroxy-diphenyl (Bell and Kenyon, *loc. cit.*). 4'-*Amino*-4-*cyanodiphenyl*, m. p. 157°, may be prepared from diazotised benzidine, or tetrazotised benzidine solution may be mixed with benzidine hydrochloride. 4-*Iodo*-4'-*hydroxydiphenyl*, m. p. 194°, is obtainable either from 4-iodo-4'-aminodiphenyl or from 4-amino-4'-hydroxydiphenyl. 4-*Chloro*-4'-*hydroxydiphenyl*, m. p. 146—147°; 4-*bromo*-4'-*hydroxydiphenyl*, m. p. 155—156°; 4-*chloro*-4'-*bromodiphenyl*, m. p. 151—152°, and 4-*chloro*-4'-*iododiphenyl*, m. p. 147—148°, were also prepared. T. H. POPE.

Derivatives of cholesterol. R. L. SHRINER and L. KO (J. Biol. Chem., 1928, 80, 1—8).—Cholesteryl p-nitrobenzoate, m. p. 188·3—189·8°, $[\alpha]_D$ −6·48° in chloroform, gave, with hydrogen and platinum oxide in ethyl acetate, *cholesteryl* p-*aminobenzoate*, m. p. 237·4—238·5°, $[\alpha]_D^{25}$ +3·61° in chloroform (*hydro-chloride*, m. p. 210—211°); dihydrocholesterol yielded a *benzoate*, m. p. 135—136·8°, $[\alpha]_D^{25}$ +21·4°, p-*nitro-benzoate*, m. p. 156·5—157·7°, $[\alpha]_D^{25}$ +20·05°, and p-*aminobenzoate*, m. p. 191—192°, $[\alpha]_D^{25}$ +26·55° (*hydrochloride*, m. p. 182·5—184·5°), all rotations being taken in chloroform. The aminobenzoates and their hydrochlorides are insoluble in water and therefore fail to exhibit antihæmolytic or anæsthetic properties.
C. R. HARINGTON.

o-Aminobenzyl alcohol. A. REISSERT and K. CRÄMER (Ber., 1928, 61, [B], 2555—2566).—o-Amino-benzyl alcohol is prepared in 88% yield by the re-duction of o-nitrobenzyl alcohol with aqueous sodium hydrogen sulphide. The corresponding diazo-com-pound decomposes with unusual ease, giving saligenin. The diazotised solution couples with p-toluidine, giving p-*toluenediazo*-o-*aminobenzyl alcohol*, $C_6H_4Me\cdot N:N\cdot NH\cdot C_6H_4\cdot CH_2OH$, m. p. 108—109°, which passes normally into p-*toluidine*-o-*azo-benzyl alcohol*, m. p. 112—113°. Resorcinol and diazotised o-aminobenzyl alcohol afford resorcinol-o-azobenzyl alcohol, m. p. 180—181° (*monohydrate*,

m. p. 159—160°). β-*Naphthol-o-azobenzyl alcohol*, m. p. 185°, is converted by concentrated sulphuric acid at 70° into the *sulphoanhydro-β-naphthol-o-azobenzyl alcohol*, m. p. above 300°. β-*Naphthylamine-o-azobenzyl alcohol*, m. p. 150—151°, and its *anhydro*-compound (I), m. p. 161°, are described. *o-Hydroxymethylbenzeneazo-2-naphthol-3-carboxylic acid*, m. p. 214—216°, and the *sulphonic acid* of its *anhydride*, $C_{18}H_{12}O_6N_2S$, m. p. above 320°, were prepared. Potassium xanthate and diazotised *o*-aminobenzyl alcohol give a very explosive *diazo*-compound, which passes into *ethyl o-hydroxymethylphenylxanthate*. The last-named compound is converted by boiling alcoholic potassium hydroxide into *o*-thiolbenzyl alcohol, which is too unstable to permit purification and is characterised as the *lead* salt; the S-*benzoyl* derivative has m. p. 125—126°. The mercaptan is oxidised by ferric chloride or hydrogen peroxide to *di-o-hydroxymethylphenyl disulphide*, m. p. 144°, in poor yield. Treatment of diazotised *o*-aminobenzyl alcohol with sodium sulphide yields small amounts of *di-o-hydroxymethylphenyl sulphide*, m. p. 164°, but mainly saligenin and *o*-thiolbenzyl alcohol. Under precisely defined conditions di-*o*-hydroxymethylphenyl disulphide is prepared in fairly satisfactory yield from the diazotised aminoalcohol and sodium disulphide. Treatment of the disulphide, preferably suspended in acetic acid, with chlorine affords *6-chloro-2-hydroxymethylbenzenesulphonyl chloride*, m. p. 62°, readily hydrolysed by alkalis but volatile unchanged with steam from a suspension in 60% sulphuric acid. With ammonia, the chloride yields the *compound* $C_6H_3Cl\diagdown_{SO_2}^{CH_2}{>}NH$, m. p. 158° (*methyl* derivative, m. p. 127°), whereas with aniline a normal *anilide*, m. p. 94°, is obtained which is converted by warm, dilute sodium hydroxide into the *sulphinide*, $C_6H_3Cl\diagdown_{SO_2}^{CH_2}{>}NPh$, m. p. 151°. 7-*Chlorobenzoicsulphinimide*, m. p. 153·5°, is prepared by oxidation of the corresponding sulphinide with nitrous acid or potassium dichromate. The position of the chlorine atom in the sulphonyl chloride follows from its conversion by molten potassium hydroxide into 3-*chloro-2-hydroxybenzyl alcohol*, m. p. 116°, whilst under similar conditions 7-chlorosaccharin affords 3-*chlorosalicylic acid*, m. p. 170°. Reduction of *o*-nitrobenzyl alcohol by Bamberger's method gave an additive *product*, m. p. 83—84°, of hydroxylamino- and azoxybenzyl alcohol which readily passed into *o*-azoxybenzyl alcohol; later attempts to repeat the process yielded only *o*-hydroxylaminobenzyl alcohol, m. p. 104·5°.　　　　H. WREN.

p-Tolyl triphenylmethyl ether. P. SCHORIGIN and J. MARAKOV-SEMLJANSKI (Ber., 1928, **61**, [*B*], 2519—2521; cf. A., 1928, 59).—Attempts to prepare the ether from triphenylmethyl chloride and sodium *p*-tolyloxide or from the chloride and *p*-cresol in pyridine gave only the variety, m. p. 114°. Indications of the formation of products of lower m. p. (cf. van Alphen, A., 1927, 660) are obtained only when impure materials are used. Decomposition of *p*-tolyl triphenylmethyl ether in the presence of molten, anhydrous zinc chloride affords mainly triphenylcarbinol; triphenylmethane is produced only in minor amount.　　　H. WREN.

Condensation of benzhydrol with phenols and cresols. P. SCHORIGIN (Ber., 1928, **61**, [*B*], 2516—2519; cf. A., 1928, 59).—The action of benzhydrol on *p*-cresol in the presence of glacial acetic and sulphuric acid at 100° affords 2 : 6-dibenzhydryl-*p*-cresol, m. p. 189—190°. Under similar conditions, *o*-cresol gives *benzyhydryl-o-cresol*, m. p. 139°, whereas phenol yields 2 : 4 : 6-tribenzhydrylphenol, m. p. 166°.

H. WREN.

Colour and chemical constitution. XXIV. Complete investigation of the triphenylcarbinol or "aniline" dyes. J. MOIR (Trans. Roy. Soc. S. Africa, 1928, **17**, 51—59).—The absorption wave-lengths of 23 substances have been determined. 4 : 4'-Dihydroxybenzhydrol (I) (cf. A., 1923, ii, 108) has λ 539 (also λλ 487, 450 : wave-lengths on which comparisons are based are given first in each case); assuming the factor for replacement of ·OH by ·NH₂ to be 1·008, and by ·NMe₂ to be 1·058, the following values are calculated for benzhydrol derivatives, mostly in acid solution, and are compared with the observed values (in parentheses) : 4-amino-4'-hydroxy- (II), λ 543 (alkaline, λ 541; also λλ 552, 492); 4 : 4'-diamino- (III) λ 548 (half-neutralised, λ 548; also λλ 580, 495); 4-dimethylamino-4'-hydroxy- (IV), λ 570 (neutral, λ 571; also λ 563); 4-amino-4'-dimethylamino- (V), λ 574·5 (half-neutralised λ 574; also λλ 591, 491); and 4 : 4'-bisdimethylamino- (VI), λ 603 (half-neutralised, λ 603; also λλ 565 and 380).

In the triphenylcarbinol series (cf. A., 1921, ii, 6), using the above factors, together with the factor 1·025 for replacement of central ·H of benzhydrol by ·Ph, the values for the six products corresponding respectively with the six substances above are : benzaurin (VII), λ 552·5 (553; also 493, 455); aminofuchsone (VIII), λ 556·5 (558; also 564, 499); Doebner's violet (IX), λ 561·5 (562; also 582, 497, 380); dimethylaminofuchsone (X), λ 584·5 (neutral, λ 585; also 530, 500); dimethylaminofuchsonimonium chloride $NH_2 \cdot C_6H_4 \cdot CPh \cdot C_6H_4 \cdot NMe_2Cl$ (XI), λ 589 (590; also 410); malachite-green (XII), λ 618 (618; also 440). The absorption of 11 compounds has thus been accurately calculated from I by three factors.

In the series of aurin and its analogues, absorption bands in alkali and acid are obtained, which almost correspond with one absorption band of the substances I—VI; thus : aurin (XIII), alkaline, λ 534 (cf. I), acid, λ 485 ($λ_I$ 487), also λλ 548 and 503; parafuchsine (XIV), neutral λ 543 (cf. III), acid λ 572 ($λ_{III}$ 580), also λ 360; crystal-violet (XV), neutral, λ 596 (cf. VI), also λλ 632 and 417 (see below). From the above it is deduced that the factor for calculating λ of a 3-ring compound from λ of the corresponding 2-ring compound is 0·99.

The following are also examined : aminobenzaurin (XVI), alkaline, λ 555, acid, λ 495 (cf. II, acid, λλ 552 and 492), also λ 457; diaminofuchsone (XVII), acid, λ 556 (cf. II, λ 552), also λλ 580, 433, 492; dimethylaminobenzaurin, neutral, λ 575 (cf. IV), also λλ 548, 552, 507, and 497; bisdimethylaminofuchsone (XIX), alkaline, λ 573 (cf. IV), also λλ 605, 505, and 460;

dimethylparafuchsine (XX), neutral, λ 587 (cf. V, acid, λ 590), also λλ 455, 549, and 499; tetramethyl-parafuchsine (XXI), neutral, λ 586 (cf. V), also λλ 628, 460, and 420; and dimethyldiaminofuchsone (XXII), neutral, λ 590 (cf. V), also λλ 624, 489, 545, 453, and 420. These resemblances, with the additional λλ observed, are discussed on the basis of the author's theory (J.C.S., 1921, **119**, 1656, 1664), which is now modified by assuming that the orbits described are those of the electrons of the central carbon atom only.

The colour change on acidification of such a substance as crystal-violet (XV) (λ 596, violet —→ λ 632, green) is ascribed to the behaviour of the ·C_6H_4·$NHMe_2^+$ group merely as a loaded benzene ring, not competing for the central electron (cf. iodine-green, λ 634; XII, λ 618; p-nitro-, λ 646, p-amino-malachite-green, λ 628). The effect of addition of further acid (λ 632 —→ λ 417, yellow) can be considered as due to the behaviour of a second ·C_6H_4·NMe_2^+ group as a loaded benzene ring (cf. XII, acid, λ 440; fuchsone-dimethylimonium chloride, λ 455; tetramethyl-fuchsine, acid, λλ 420 and 460).

The behaviour of other of the above substances is discussed; the large number of absorption bands of XXII is to be attributed to the large number of theoretically possible quinonoid forms. The author suggests, in addition to his postulated "elliptical" and "trefoil" orbits, a third type, probably a distorted circular orbit, conditioned by the combinations ·ONa, :NH_2·OH and ·ONa, :NMe_2·OH.

The products of replacement of ·OH by ·NH_2 and ·NMe_2 in p-hydroxybenzyl alcohol (λ 293) have λλ 335 and 390, in p-hydroxybenzhydrol (λ 320) have λλ 350 and 400, and in fuchsone (λ 371) have λλ 425 and 455, respectively.　　　　　　　　　E. W. WIGNALL.

Naphthenic acids. VIII. Polymethylene rings of naphthenic acids in Japanese petroleum. IX. Constitution of octanaphthenic acid from Nishiyama petroleum. T. KUWATA (J. Fac. Eng. Tokyo, 1928, **17**, 305—310, 311—317).—VIII. Certain fractions of naphthenic acids derived from petroleum from Nishiyama (paraffin base oil) and Kurokawa (asphalt base oil) (cf. A., 1925, i, 1271; 1923, i, 464) were reduced to the corresponding hydrocarbons and the latter compared. A fraction containing undeca- and dodeca-naphthenic acids from Nishiyama oil, b. p. 133—170°/9 mm., d_4^{20} 0·9629, n_D^{20} 1·4649, was converted into the phenyl ester by reaction of the acid chloride with phenol. The ester was then reduced by sodium and alcohol to the naphthene alcohol, b. p. 100—133°/9 mm., d_4^{20} 0·8953, n_D^{20} 1·4592. This was converted by the action of phosphorus and iodine into the iodide, which was then reduced by zinc amalgam in alcohol to the hydrocarbon (C, 85·45; H, 15·04%), b. p. 160—192°, d_4^{20} 0·7930, n_D^{20} 1·4336. When passed over platinum-black at 300° (cf. Zelinski and Pavlov, A., 1923, i, 767) the hydrocarbon was practically unchanged, and cyclohexane compounds therefore appear to be absent. By similar methods a fraction of naphthenic acids (chiefly tridecanaphthenic acid) from Kurokawa petroleum, b. p. 168—198°/9 mm., d_4^{20} 0·9942, n_D^{20} 1·4744, yielded the alcohol, b. p. 126—155°/9 mm., d_4^{20} 0·9270, n_D^{20} 1·4756, and a hydrocarbon (C, 85·66; H, 13·67%), b. p. 203—243°, d_4^{20} 0·8425,

n_D^{20} 1·4548. When passed over platinum-black at 300° a slight change in properties occurred and some gas was formed, indicating the presence of a small proportion of cyclohexane compounds.

IX. *Octanaphthenic acid*, $C_8H_{14}O_2$, b. p. 231·5—237·5°, d_4^{20} 0·9417, n_D^{20} 1·4318 (amide, m. p. 81·5—83°), was isolated from Nishiyama petroleum by repeated fractionation of the acid and the methyl ester. It was not identical with Aschan's octanaphthenic acid (A., 1891, 1452). Bromination by the Hell–Volhard–Zelinski method yielded *methyl α-monobromo-octa-naphthenate*, b. p. 95—105°/9 mm., which when heated with dilute potassium hydroxide yielded α-*hydroxy-naphthenic acid*, d_4^{20} 1·023, n_D^{20} 1·4518. This was oxidised by lead peroxide to a *substance* (? methyl cyclopentyl ketone or dimethylcyclopentanone) (semicarbazone, m. p. 89—90°) of ketonic properties, containing some aldehyde, which was oxidised by alkaline permanganate to a neutral *substance*, m. p. 80—81°, accompanied by a (?) dibasic acid.　R. K. CALLOW.

Catalytic reduction of nitriles and oximes. W. H. HARTUNG (J. Amer. Chem. Soc., 1928, **50**, 3370—3374).—Hydrogenation of benzonitrile or benz-aldoxime in alcohol using palladised charcoal yields pure benzylamine if at least 1 mol. and 3 mols., respectively, of hydrogen chloride are present (cf. Braun and others, A., 1923, i, 1087; Rosenmund and Pfankuch, A., 1924, i, 34); otherwise secondary bases and ammonia are also formed. Mandelonitrile is similarly reduced to β-phenylethylamine (52% of the theoretical), whilst its benzoate and acetate yield 84·5% and 74·5% of theory, respectively, of the same product. Attempts to avoid reduction of the hydroxyl group were unsuccessful.　H. E. F. NOTTON.

Isomorphous replacement of a chlorine atom by the hydroxyl group in organic compounds. V. VILLIGER (Ber., 1928, **61**, [B], 2596—2599).—2 : 4-Dichlorobenzotrichloride is heated at 70—80° with 95% sulphuric acid until evolution of hydrogen chloride ceases, and the solution, after removal of dissolved hydrochloric acid, is treated with the calculated quantity of 50% nitrating acid at 10°. 2 : 4-*Dichloro-5-nitrobenzoic acid* thus produced has m. p. 161—163° after purification through the sparingly soluble *calcium* salt. The acid is transformed by an excess of sodium hydroxide into 2-*chloro-5-nitro-4-hydroxybenzoic acid*, m. p. 202—204°, from which any unchanged dichloro-acid is removed by purification through the *barium* salt. The m. p. of mixtures of the two acids lie approximately on a straight line connecting the m. p. of the individual acids, thus suggesting the formation of an isomorphous series.　H. WREN.

Esterification of aromatic and olefinic nitriles. P. PFEIFFER, I. ENGELHARDT, and W. ALFUSS (Annalen, 1928, **467**, 158—190).—A review of previous work (Pfeiffer and others, A., 1911, i, 448; 1916, i, 24, 327; 1918, i, 344; 1925, i, 547) and that now recorded leads to the generalisation that a single o-substituent inhibits practically completely the conversion of an aromatic nitrile into a carboxylic ester by heating it with methyl or ethyl alcohol and hydrogen chloride. The chemical nature of the substituent plays a minor part, for the methyl, nitro-, chloro-, phenyl, and vinyl

groups all act in the same way. The rule is similar to that which applies to the formation of imino-ethers (Pinner, "Imidoäther und ihre Derivate," 1892). Acting on the assumption that aromatic nitriles may be considered as a special class of olefinic nitriles, a number of α-substituted cinnamonitriles were examined. By starting with the cis- and trans-acids, converting these into the amides, and dehydrating, the cis- and trans-nitriles were prepared. It was then found that the trans-compounds were in all cases easily esterified, but that the cis-compounds were esterified not at all or only very slowly under the usual conditions. This accords with the similarity of the configurations of the cis-compounds and o-substituted aromatic nitriles. Ease or difficulty of esterification is, in the absence of other evidence, indicative of trans- or cis-configuration, respectively.

Whilst 4-dimethylaminostilbene, the 4'-nitro-derivative, and the 4'-nitro-2'-cyano-derivative, and the amide, acid, and esters corresponding with the last are fluorescent, transposition of the nitro- and cyano-groups yields a non-fluorescent compound (2'-nitro-4-dimethylamino-4'-cyanostilbene), and the corresponding methyl and ethyl carboxylic esters are likewise non-fluorescent.

The esterification of the nitriles was carried out by refluxing with 40 parts of anhydrous alcohol for 2 hrs. while a stream of hydrogen chloride was passed in, and the amount of ester in the washed product was determined from the percentage of nitrogen. The following data are recorded, the figures in parentheses denoting the percentage of methyl or ethyl esters, respectively, found in the product; when only one figure is given it refers to the methyl ester: Benzonitrile (65·4, 35·1) : toluonitriles : o- (0, 0); m- (92·1, 58·7); p- (83, 80); nitrobenzonitriles : o- (0, 0); m- (87, 45); p- (both high); m-nitro-o-toluonitrile (0); m-nitro-p-toluonitrile (high); chlorobenzonitriles : o- (0, 0); p- (97, 67·9); o-phenylbenzonitrile, b. p. 176—177°/16 mm. (prepared from o-phenylbenzoic acid by way of the chloride and amide), (8·4, 5·6); p-phenylbenzonitrile (82, 70·4); naphthonitriles : α- (0, 0); β- (77·1, 77); 4'-nitro-2'-cyano-4-dimethylaminostilbene (0); cinnamonitrile (96·2, 85); α-methylcinnamonitrile, b. p. 120°/14 mm. (from α-methylcinnamic acid by way of the chloride and amide) (69·8, 36·8). cis-α-Chlorocinnamonitrile, m. p. 19—21°, b. p. 128°/16 mm., and trans-α-chlorocinnamonitrile, m. p. 34°, b. p. 138—139°/17 mm., were prepared from the corresponding acids. Both were esterified readily, but inversion of the cis-compound occurred, for the trans-ester was formed in each case. cis-α-Phenylcinnamonitrile was not esterifiable. trans-α-Phenylcinnamonitrile, m. p. 49—51°, from the trans-acid, was esterified easily (39). From cis-α-phenyl-m-nitrocinnamic acid were prepared the chloride, m. p. 101°, amide, m. p. 176°, and nitrile, m. p. 133—134°, (0) (identical with the product of condensation of phenylacetonitrile and m-nitrobenzaldehyde). From the trans-acid were prepared the chloride, m. p. 93°, amide, m. p. 146°, and nitrile, m. p. 96° (51). From cis-α-phenyl-p-nitrocinnamic acid were prepared the chloride, m. p. 88—91·5°, amide, m. p. 208·5—210°, and nitrile, m. p. 121—122° (0). From the trans-acid were prepared the chloride, m. p. 95°, amide, m. p. 183—184°, and nitrile, m. p. 121—

122° (48). The cis- and trans-p-dimethylamino-p-nitrophenylcinnamamides (cf. A., 1928, 1132) yielded on dehydration the same (cis-)nitrile, m. p. 241—242°, which was not esterifiable. From dibenzylidenepropionic acid were prepared the liquid chloride, the amide, m. p. 178—179°, and (cis-)nitrile, m. p. 115—116° (0, 0). (cis-)α-Benzenesulphonyl-cinnamonitrile was not esterifiable. From α-phenylcrotonic acid were prepared the amide, m. p. 98—99°, and the (cis-)nitrile, b. p. 125°/13—14 mm. (9·6, 7·9). An attempt to prepare the nitrile by condensation of phenylacetonitrile with paraldehyde was unsuccessful. αβ-Diphenylpropionitrile was readily esterified (64, high). 4'-Nitro-4-dimethylaminostilbene-2-carboxylic acid, m. p. 206° (decomp.) (methyl ester, m. p. 158—159°; ethyl ester, m. p. 139—140°), was prepared by hydrolysis of the amide, m. p. 242—243° (decomp.), obtained by condensation of p-dimethylaminobenzaldehyde with p-nitro-o-toluamide in presence of piperidine.   R. K. CALLOW.

Pyridine as a catalyst in Perkin's synthesis of cinnamic acid. G. BACHARACH and F. BROGAN (J. Amer. Chem. Soc., 1928, 50, 3333—3334).— Addition of 8 drops of pyridine to a mixture of 20 g. of benzaldehyde, 30 g. of acetic anhydride, and 10 g. of sodium acetate, refluxed for 8 hrs., increased the yield of cinnamic acid from 60·7% of the theoretical to an optimum value of 85%.   H. E. F. NOTTON.

Reactions of nitroso-derivatives with unsaturated compounds. VII. New isomerides of o-nitrophenylpropiolates and isatogenates. L. ALESSANDRI (Gazzetta, 1928, 58, 738—742).—A preliminary note on the properties of the colourless isomerides of ethyl and methyl o-nitrophenylpropiolates and isatogenates, previously described (this vol., 64). The colourless compound of m. p. 122° can be obtained in considerable quantity by appropriate treatment of ethyl o-nitrophenylpropiolate, which it resembles in composition ($C_{11}H_9O_4N$) and mol. wt. When heated, it undergoes, at about 125°, an exothermic and irreversible change into a further yellow isomeride, m. p. 150—151°. Methyl o-nitrophenylpropiolate similarly yields a colourless isomeride, $C_{10}H_7O_4N$, which has two crystalline forms, m. p. 139° and 141°, respectively, and is converted by heating into a yellow isomeride, which also exhibits two forms, m. p. 149—150° and 161—162°, respectively. The yellow substances may perhaps belong to the same class as those described by Ruggli (A., 1919, i, 221; A., 1923, i, 833).   E. W. WIGNALL.

Diethylaminoethanol esters of diphenyl-2-carboxylic acid and derivatives. F. BELL (J.C.S., 1928, 3247—3249).—In view of the anæsthetic action of diethylaminoethyl diphenate (Roberts and Johnson, A., 1925, i, 816) some similar acids were prepared. Diphenyl-2-carboxyl chloride, b. p. 163°/10 mm. (which has a strong tendency to pass into fluorenone on distillation, and with 2-aminodiphenyl yields diphenyl-2-carboxy-2'-diphenylylamide, m. p. 194°), reacts with diethylaminoethyl alcohol to give diethylaminoethyl diphenyl-2-carboxylate, b. p. 183°/1 mm., of which the hydrochloride, m. p. 109—110°, has anæsthetic action. Similarly, diphenyl-4-carboxyl

chloride yields *diethylaminoethyl diphenyl-4-carboxylate* (*hydrochloride*, m. p. 183°).

By the action of thionyl chloride on diphenamic acid, *2'-cyanodiphenyl-2-carboxyl chloride*, m. p. 84°, is obtained, with some diphenimide; the chloride when heated distils at 222°/15 mm., giving a liquid containing only 3% of 4-cyanofluorenone, m. p. 243—244° (cf. Borsche and Sander, A., 1915, i, 299, whose process for preparing the compound from phenanthraquinone monoxime must depend on the formation of the above acid chloride). *Diethylaminoethyl 2'-cyanodiphenyl-2-carboxylate* forms a *hydrochloride*, m. p. 189°. E. W. WIGNALL.

Derivatives of 2-methylanthracene obtained by the action of oxalyl chloride. D. BUTESCU (Bull. Soc. chim., 1928, [iv], **43**, 1269—1272).— Addition of 2-methylanthracene in carbon disulphide in presence of aluminium chloride to nascent oxalyl chloride (a mixture of oxalic acid and phosphorus pentachloride) at the ordinary temperature gives no aceanthrenequinone but about 10% of *10-chloro-2-methylanthracene-9-carboxylic acid*, m. p. 158°, oxidised to 2-methylanthraquinone, and 2-methylanthracene-3-carboxylic acid, together with 9 : 10-*dichloro-2-methylanthracene*, m. p. 211°, which shows the blue fluorescence characteristic of 9 : 10-substituted anthracenes. Lower temperatures thus promote chlorination, whilst higher temperatures appear to favour the introduction of the carboxyl group (cf. Liebermann and others, A., 1912, i, 467).
R. BRIGHTMAN.

Lichen products. VI. Synthesis of divaric acid. A. SONN [with J. BURKARD] (Ber., 1928, **61**, [*B*], 2479—2481).—Ethyl acetoacetate and methyl Δ^α-hexene-α-carboxylate in presence of alcoholic sodium alkoxide afford *ethyl n-propyldihydroresorcinolcarboxylate*, m. p. 85—87°, which is converted successively into *ethyl dibromo-n-propylresorcinolcarboxylate*, m. p. 77—78°, and *dibromo-n-propylresorcinolcarboxylic acid*, m. p. 158—160° (decomp.) after softening. The dibromo-acid is transformed in alkaline solution by hydrogen in presence of palladised calcium carbonate into 2 : 4-dihydroxy-6-*n*-propylbenzoic acid, identical with divaric acid.
H. WREN.

Action of phthaloyl chloride on *p*-tolyl methyl ether and *p*-tolyl methyl sulphide. R. WEISS and W. KNAPP (Monatsh., 1928, **50**, 392—398).— Phthaloyl chloride reacts with *p*-tolyl methyl ether in presence of carbon disulphide and aluminium chloride, forming 6' : 6''-*dimethoxydi-m-tolylphthalide*, m. p. 170°, condensation occurring *ortho* to the methoxyl group. Reduction of this with sodium amalgam and alcohol yields 2' : 2''-*dimethoxy-5' : 5''-dimethyltriphenylmethane-2-carboxylic acid*, m. p. 212—214°, converted by oxidation with alkaline potassium permanganate into 2' : 2''-*dimethoxytriphenylmethane-2 : 5' : 5''-tricarboxylic acid*, m. p. 318°—320 (slight decomp.). Treatment of this phthalin with cold, concentrated sulphuric acid gives 1 : 2'-*dimethoxy-9-phenylanthrone-4 : 5'-dicarboxylic acid*, m. p. 340° (decomp.), by way of the corresponding anthranol. With *p*-tolyl methyl sulphide condensation occurs with loss of two methyl groups and a sulphur atom and 2 : 8-*di-*

methyl-5-thiofluoran (I), m. p. 228—230°, results. This is reduced by sodium amalgam and alcohol to 2 : 8-*dimethyl-5-thiohydrofluoranic acid*, m. p. 192—195°

(I.) C_6H_4 ... CO

Me ... C ... Me Me ... CH ... Me

(II.) C_6H_4—CO
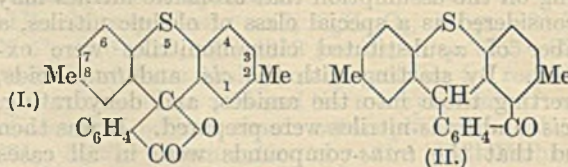
(gelatinous *sodium* salt), convertible by treatment with phosphorus pentoxide in boiling benzene into *dimethylcœrthione* (II), m. p. 188—190° (decomp.).
H. BURTON.

Condensation of phthalic anhydride with *o*-dichlorobenzene. M. TANAKA and N. TANAKA (Bull. Chem. Soc. Japan, 1928, **3**, 286—287).—Phthalic anhydride and *o*-dichlorobenzene condense in presence of anhydrous aluminium chloride at 120°, yielding o-3 : 4-*dichlorobenzoylbenzoic acid*, m. p. 190°, whilst at 150° 2 : 3-*dichloroanthraquinone*, m. p. 265—267°, is produced.

Phthalic anhydride and *o*-chlorophenol react in presence of boric and concentrated sulphuric acids at 255° for 3 hrs., giving purpurin (cf. A., 1927, 566). H. BURTON.

Naphthalic acid derivatives. K. DZIEWOŃSKI and A. KOCWA [with O. GESCHWINDOVNA] (Bull. Acad. Polonaise, 1928, *A*, 405—431; cf. Dziewoński and others, B., 1924, 901; A., 1926, 70, 279).— Compounds obtained from the sulphonation products of acenaphthene and 1 : 8-naphthalic acid and its anhydride are described. 4-Sulphonaphthalic acid is converted by alkaline fusion into 4-hydroxynaphthalic anhydride, m. p. 350—351°, which when heated with potassium hydroxide at 320° yields 5-hydroxy-α-naphthoic acid, m. p. 235° (*benzoate*, m. p. 241°), or with phosphorus pentachloride at 200° 4-chloronaphthalic anhydride, m. p. 216—217° (*imide*, m. p. 301—302°), also obtainable from the sulphonic acid by similar means. 4-Bromonaphthalic anhydride, m. p. 219—220° (imide, m. p. 286°; phenylhydrazone, m. p. 233—224°), is prepared by the action of phosphorus pentabromide on 4-sulphonaphthalic acid, whilst 4-hydroxynaphthalic anhydride yields a *bromohydroxy-anhydride*, m. p. 266—267°.

3-Sulphonaphthalic acid, m. p. 198° (*aniline* salt, m. p. 297°; *sulphonyl chloride*, m. p. 212—213°; *imide-sulphonamide*, m. p. 348°), is converted by phosphorus pentachloride into 3-*chloronaphthalic anhydride*, m. p. 223—224° (*imide*, m. p. 315°), which condenses with resorcinol to give a *fluorescein*, m. p. 170°. From 3-hydroxynaphthalic anhydride and phosphorus pentabromide is obtained a *bromohydroxy-anhydride*, m. p. 284—285° (*benzoate*, m. p. 252—253°; *imide*, m. p. 339°).

2-Sulphonaphthalic acid [*aniline* salt, m. p. 290° (decomp.)] yields on alkaline fusion 2-hydroxynaphthalic anhydride, m. p. 245—246° (*methyl ether*, m. p. 255°; *phenylhydrazone*, m. p. 238—239°; *imide*, m. p. 303—304°); the corresponding acid couples with *p*-nitrodiazobenzene, with loss of the 1-carboxyl group, to give an *azo*-compound readily converted by

warm acids or organic solvents into the peri-*naphtha-pyridazone* (annexed formula), m. p. 336—337° (decomp.). Mere benzoylation also removes the 1-carboxyl group and yields the *benzoate*, m. p. 196—197°, of 2-hydroxy-8-naphthoic acid, m. p. 257° (*acetate*, m. p. 221—222°; *anilide*, m. p. 209—210°). From 2-hydroxynaphthalic acid are prepared the 2-*chloro-anhydride*, m. p. 246—247° (*imide*, m. p. 332—333°), and the 2-*bromo-anhydride*, m. p. 253—254° (*imide*, m. p. 318°; *phenylhydrazone*, m. p. 251—252°). C. HOLLINS.

Action of magnesium *o*-tolyl bromide on the dilactone of benzophenone-2 : 2'-dicarboxylic acid. R. WEISS and S. R. KRATZ (Monatsh., 1928, **50**, 429—435).—When the dilactone of benzophenone-2 : 2'-dicarboxylic acid is treated with magnesium *o*-tolyl bromide in cold benzene solution and the mixture then heated on the water-bath, 2'-*o*-*toluoyl-benzophenone-2-carboxylic acid* (I), m. p. 188—192°, is produced. If the reaction is performed throughout in boiling benzene there is also formed some 2-*methylbenzo-phenone-2'-phthalide* (II), m. p. 170—174°, a reduction product of I. Reduction of I with red phosphorus and hydriodic acid in boiling acetic acid solution gives 2-*methyl-2'-phthalidodiphenylcarbinol*, m. p. 145—147°, whilst oxidation with alkaline potassium permanganate yields the *dilactone* (III) of 2'-(*o*-carboxybenzoyl)-benzophenone-2-carboxylic acid,

$$CO \underset{O}{\overset{C_6H_4}{<}} C \underset{C_6H_4}{\overset{O}{<}} C \underset{O}{\overset{C_6H_4}{<}} CO,$$ m. p. 280—282°, formed also by oxidation of II with chromic anhydride in boiling acetic acid solution. Treatment of III with excess of hydrazine hydrate affords *o*-*phenylene-1 : 1'-di-(4-hydroxyphthalazine)*, m. p. 350°; aluminium chloride at 200° converts III into 1-*benzoyl-anthraquinone-2'-carboxylic acid*, whilst reduction with red phosphorus and hydriodic acid in boiling acetic acid solution gives *o*-*phenylenediphthalide*, m. p. 198—200°. Reduction of this last compound with sodium and absolute alcohol yields 2'-(*o*-carboxybenzyl)di-*phenylmethane-2-carboxylic acid*, m. p. 235—237°.
H. BURTON.

Bile acids. XXII. M. SCHENCK and H. KIRCHHOF (Z. physiol. Chem., 1929, **180**, 107—123).—Bilianic acid monoxime (A., 1928, 1134) undergoes no rearrangement by treatment with sulphuric acid, but dehydrodeoxycholic (α-diketocholanic) acid dioxime (Schenck, A., 1923, i, 678) is converted into the
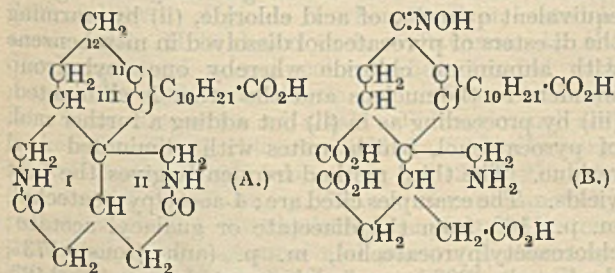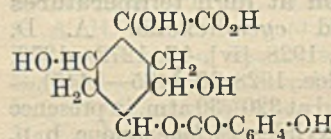
isodioxime (A), sintering at 162°, decomp. 200—202°. Dehydrocholic acid *isotrioxime* (Schenck, A., 1914, i,

487) when heated for 1 hr. with 20% hydrochloric acid slowly eliminates 1 mol. of hydroxylamine, yielding a *substance*, decomp. 205° (indefinite), and giving a yellow colour with nitric acid (see below). Hence it seems that an oximino-group attached to ring III does not undergo rearrangement, which is restricted to rings I and II. All oximes and their rearrangement products which contain an oximino-group in the 12-position give a green or bluish-green colour with nitric acid (*d* 1·4) and this reaction is applied to elucidate the structure of a large number of oximes and their rearrangement products. Thus the green colour is obtained with dehydrocholic acid trioxime and *iso*trioxime, and with the substance $C_{21}H_{38}O_9N_2$ (obtained by the action of hydrochloric acid on bilianic acid *iso*dioxime), which is assigned the structure B, fission of the lactam ring having occurred. Positive tests are also obtained with β-diketocholanic acid dioxime and its rearrangement product (Borsche and Wieckhorst, A., 1921, i, 729) and with pseudodeoxy-bilianic acid oxime, which is therefore given structure C. Negative results (yellow or brown colour only) are obtained with dehydrodeoxycholic acid dioxime, deoxybilianic and *iso*deoxybilianic acid oximes. Structural formulæ for all the above compounds are suggested.
J. W. BAKER.

Monoacyl derivatives of quinic acid. III. Synthesis of 4-*p*-hydroxybenzoylquinic acid. K. JOSEPHSON (Annalen, 1928, **467**, 287—294).—*iso*-Propylidenequinide is converted by *p*-acetoxybenzoyl chloride in presence of pyridine and chloroform into 4-*p*-acetoxybenzoyl*iso*propylidenequinide (I), m. p. 166—167° (corr.), $[\alpha]_{Hg\ yellow}^{20}$ +11·9° in chloroform (cf. Karrer and Link, A., 1928, 63), hydrolysed by hydrochloric acid in acetone solution to 4-*p*-*hydroxy-benzoylquinic acid* (annexed formula), m. p. 108—112°, $[\alpha]_{Hg\ yellow}$ −9·4° in water. Treatment of this with acetone containing 1% of hydrogen chloride affords 4-*p*-hydroxybenzoyl*iso*propylidenequinide, m. p. 191—192° (corr.; lit. 179—180°), acetylated by acetic anhydride in dry pyridine to I.
H. BURTON.

Phloridzin and quercitrin. G. ZEMPLÉN and others.—See this vol., 174.

Action of acetic anhydride on Schiff's bases. M. PASSERINI and M. P. MACENTELLI (Gazzetta, 1928, **58**, 641—646).—To the compound formed by the action of acetyl chloride on benzylideneaniline, Garzarolli-Thurnlackh (A., 1899, i, 881) ascribed the formula NPhCl·CHPh·OAc, but James and Judd (J.C.S., 1914, **105**, 1427) consider that the addition of a halogen or an acyl chloride to a Schiff's base takes place solely at the nitrogen atom, bromine and benzyl-ideneaniline thus giving NPhBr₂·CHPh. The authors find that benzylideneaniline (1 mol.) and acetic anhydride (1 mol.) react to give a *compound*, m. p.

127—129°, which yields benzaldehyde, acetanilide, and acetic acid on hydrolysis, this behaviour being best expressed by the formula OAc·NPhAc:CHPh. The *compound* OAc·NPhAc:CH·C$_6$H$_4$·OMe, m. p. 89—91°, is similarly obtained from anisylideneaniline and acetic anhydride. The action of acetic anhydride on the dianil derivative of 2-hydroxy-1-naphthyl-glyoxal (cf. Passerini, A., 1924, i, 1320) yields (1) the *acetyl* derivative of the latter, m. p. 185°, and (2) a *compound*, CHO·C(:NPh)·C$_{10}$H$_6$·OAc or NPh:CH·CO·C$_{10}$H$_6$·OAc, m. p. 155—157°, which reacts with phenylhydrazine.   T. H. POPE.

Tautomerism of *o*-nitrobenzaldehyde. III. Action of diazomethane on *o*-nitrobenzaldehyde. I. TANASESCU (Bull. Soc. chim., 1928, [iv], 43, 1264—1269).—The reactions of " nitraldin " obtained by the action of diazomethane on *o*-nitrobenzaldehyde (Arndt, A., 1927, 360; 1928, 752) are more readily explained by a dynamic structure analogous to that previously advanced for *o*-nitrobenzaldehyde (A., 1928, 178; this vol., 66) than by Arndt's *o*-nitro-phenylethylene oxide structure. The formation in acid medium of *o*-nitrosobenzoylcarbinol and not the *o*-nitroglycol; of the corresponding acetate, with acetic anhydride, and not the diacetylglycol; of the chloro-hydrin, NO$_2$·C$_6$H$_4$·CH(OH)·CH$_2$Cl, and the presence in nitraldin of a mobile hydrogen atom, determined by Zerevitinov's method, are cited in support of the dynamic structure. The formation of methylene-dibenz*iso*oxazolone when nitraldin is boiled with formic acid is attributed to the previous formation of formaldehyde and benz*iso*oxazolone which in the nascent state react too rapidly to allow of the isolation of the latter. When the transformation is effected in presence of dimethyldihydroresorcinol, the principal product is methylenebisdimethyldihydroresorcinol, only a little methylenedibenz*iso*oxazolone being formed. Excess of formaldehyde converts the latter into *N*-hydroxybenz*iso*oxazolone.   R. BRIGHTMAN.

Catalytic condensation at high temperatures of *cyclo*hexanone and *cyclo*hexene. A. D. PETROV (Bull. Soc. chim., 1928, [iv], 43, 1272—1276, and J. Russ. Phys. Chem. Soc., 1928, 60, 1435—1445).—*cyclo*Hexanone when heated at 320°/30 atm. in presence of alumina affords *cyclo*hexylidene*cyclo*hexanone, b. p. 142—145°/0·15 mm., di*cyclo*hexylidene*cyclo*hexanone, b. p. 214—219°/0·15 mm., and dodecahydrotriphenyl-ene, m. p. 224—225°, the last-named corresponding with the formation of mesitylene from acetone (cf. A., 1927, 449, 1076, 1172). In presence of zinc chloride dodecahydrotriphenylene is not obtained, and about 15% of the ketone is converted into *cyclo*hexane (cf. Kuuze, A., 1926, 1143). *cyclo*Hexene in presence of alumina at 400—440° is converted principally into aromatic hydrocarbons, b. p. 75—280°, the fraction of b. p. 75—81° containing about 15% of benzene.
                              R. BRIGHTMAN.

New rearrangement of oximes. II. P. W. NEBER and A. UBER (Annalen, 1928, 467, 52—72; cf. A., 1926, 1247).—When dibenzylketoxime is treated with the appropriate sulphonyl chloride and pyridine it is converted into its *benzenesulphonate* (I), m. p. 75°, or *p*-*toluenesulphonate*, m. p. 80°. When either salt is heated with absolute alcohol it yields benzylamine

benzene- or *p*-toluene-sulphonate, and ethyl phenyl-acetate. The action of alcoholic potassium ethoxide on I and treatment of the product with *p*-toluene-sulphonic acid gives rise to *benzyl* α-*aminobenzyl ketone* p-*toluenesulphonate*, m. p. 198°, and the corre-sponding free *base* is converted by heating with absolute alcohol into 3 : 6-*diphenyl*-2 : 5-*dibenzyl*-3 : 6-*dihydro*-p-*diazine*, m. p. 152°, the same compound being synthesised from the amino-ketone obtained by reduction of oximinodibenzylketoxime. The action of alcoholic ammonia on I yields no trace of the diazine, but the products are (1) phenylacetamidine benzene-sulphonate (II), (2) N-*benzylphenylacetamidine*, m. p. 93° (*benzenesulphonate*, m. p. 127—130°), (3) benzyl-amine benzenesulphonate, (4) phenylacetamide, (5) ammonium phenylacetate and benzenesulphonate, and, possibly, phenylacetonitrile; 1 and 3 are formed by the reactions CH$_2$Ph·C(NO·SO$_2$Ph)·CH$_2$Ph $\xrightarrow{\text{Beckmann change}}$ PhSO$_3$·C(N·CH$_2$Ph)·CH$_2$Ph $\xrightarrow{\text{NH}_2}$ NH$_2$·CH$_2$Ph + CH$_2$Ph·C(NH)·NH$_2$,PhSO$_3$H (II), the other products arising by benzylation or hydrolysis of II. Attempts to synthesise the *N*-benzyl derivative by the action of benzylamine on phenylacetiminoether yielded only *di*-(N-*benzyl*)*phenylacetamidine*, m. p. 100°. Benzyl-acetoneoxime, m. p. 85° (lit. 80°), is similarly converted into its *benzenesulphonate* (III), m. p. 80°, and p-*toluene-sulphonate* (IV), m. p. 62°, which by treatment with absolute alcohol are converted into β-phenylethyl-amine benzene- and p-toluene-sulphonates, respectively, and III is converted by the action of sunlight for 14 days into an unidentified *substance*, m. p. 86—88°, which is isomeric but not identical with acetyl-β-phenylethylamine benzenesulphonate. By treat-ment with alcoholic potassium ethoxide III is con-verted into γ-*amino*-ββ-*diethoxy*-δ-*phenylbutane* iso-lated as its p-*toluenesulphonate*, m. p. 128°, which on hydrolysis yields α-*amino*-β-*phenylethyl methyl ketone*, m. p. 175°, both compounds being readily converted into 3 : 6-*dibenzyl*-2 : 5-*dimethyl*-3 : 6-*dihydro*-p-*diazine*, m. p. 103°. The action of alcoholic ammonia on IV converts it into acetamidine p-toluenesulphonate, β-phenylethylamine, and N-(β-*phenylethyl*)*acetamidine* p-*toluenesulphonate*, m. p. 125°, which is not identical with β-*phenylpropionamidine* p-*toluenesulphonate*, m. p. 160° (*hydrochloride*, m. p. 174°), synthesised for comparison.   J. W. BAKER.

Synthesis of polyphenolic ketones. K. W. ROSENMUND and H. LOHFERT (Ber., 1928, 61, [B], 2601—2607).—Simple pyrocatechol ketones are pre-pared (i) by dissolving pyrocatechol and aluminium chloride in nitrobenzene and gradually adding the equivalent quantity of acid chloride, (ii) by warming the di-esters of pyrocatechol dissolved in nitrobenzene with aluminium chloride whereby one acyl group wanders to the nucleus and the other is eliminated, (iii) by proceeding as in (ii) but adding a further mol. of pyrocatechol, which unites with eliminated acyl residue. The third method frequently gives the best yields. The examples cited are : 4-acetylpyrocatechol, m. p. 116°, from the diacetate or guaiacyl acetate; chloroacetylpyrocatechol, m. p. (anhydrous) 173°, (hydrated) 120°; *propionylpyrocatechol*, m. p. 146°, from *pyrocatechol dipropionate*, b. p. 153—157°/14 mm., 281°/760 mm.; *butyrylpyrocatechol*, m. p. 146°, by all

three methods (*pyrocatechol dibutyrate*, b. p. 305°); *iso*valerylpyrocatechol, m. p. 108°, from pyrocatechol diisovalerate, b. p. 153—173°/vac.; *stearylpyrocatechol*, m. p. 70°, from *pyrocatechol distearate*, m. p. 83—85°; benzoylpyrocatechol, m. p. 134°, from the dibenzoate. Acetylquinol is prepared from quinol and acetyl chloride, quinol diacetate, and quinol diacetate-+-quinol. Propionylquinol, m. p. 92°, is similarly obtained. Monoketones of phloroglucinol are prepared by allowing the phenol and aluminium chloride to react in presence of nitrobenzene until a complex is formed and complete dissolution ensues and then adding the acid chloride gradually; butyrylphloroglucinol, m. p. 179—180°, hexoylphloroglucinol, m. p. (anhydrous) 120°, (hydrated) 100°, and *iso*valerylphloroglucinol, m. p. 145°, are thus obtained. Tribenzoylphloroglucinol, m. p. 185°, is obtained from the tribenzoate and aluminium chloride at 130—140°.

H. WREN.

Syntheses of polyhydroxy-chalkones [-phenyl styryl ketones], -hydrochalkones [-phenyl β-phenylethyl ketones], and -flavanones. I. J. SHINODA and S. SATO. II. Synthesis of naringenin and sakuranetin. J. SHINODA and S. SATO. III. Synthesis of hesperetin. J. SHINODA and M. KAWAGOYE (J. Pharm. Soc. Japan, 1928, 48, No. 558, 109—114, No. 560, 117—119, 119—120).— I. Polyhydroxy-derivatives of phenyl styryl and phenyl β-phenylethyl ketones may be prepared by the condensation of cinnamoyl or β-phenylpropionyl chlorides with polyhydric phenols in nitrobenzene under the influence of aluminium chloride at the ordinary temperature. Using phloroglucinol, the isomeric flavanone derivative is the chief product.

Resorcinol and cinnamoyl chloride yield 2 : 4-dihydroxyphenyl styryl ketone, m. p. 151°, identical with the product obtained by Ellison's method (cf. A., 1927, 880, where m. p. 133—134° is given). Resorcinol and β-phenylpropionyl chloride yield 2 : 4-dihydroxyphenyl β-phenylethyl ketone ($+H_2O$), m. p. 84°, also obtained by reduction of the styryl compound or by the method of Bargellini and Marantonio (cf. A., 1908, i, 801, where m. p. 88° is given). 2 : 4-*Dihydroxyphenyl β-4-methoxyphenylethyl ketone*, m. p. 82—83°, is prepared similarly, either by condensation or reduction. Phloroglucinol and cinnamoyl chloride yield 2 : 4 : 6-*trihydroxyphenyl styryl ketone* (I), m. p. 189—190°, 5 : 7-*dihydroxyflavanone* (II), m. p. 203—204° (*oxime*, m. p. 263°; *monomethyl ether*, m. p. 101°; *diacetate*, m. p. 141—142°; *triacetate*, m. p. 115—117·5°), *tricinnamoylphloroglucinol*, m. p. 147·5°, and traces of *substances*, m. p. 243° and 205°. I yields II when fused or heated in acetic acid. II is shown to be a flavanone by the development of a red colour when treated with magnesium and hydrochloric acid. It is converted into I by the action of alkali. Phloroglucinol and β-phenylpropionyl chloride yield 2 : 4 : 6-*trihydroxyphenyl β-phenylethyl ketone*, m. p. 120—121°, the *triacetate* of which, m. p. 76°, is also obtained by reduction of 2 : 4 : 6-trihydroxyphenyl styryl ketone triacetate. Phloroglucinol and *p*-methoxycinnamoyl chloride yield 2 : 4 : 6-*trihydroxyphenyl 4-methoxystyryl ketone*, m. p. 176°, and 5 : 7-*dihydroxy-4'-methoxyflavanone* (iso*sakuranetin*), m. p. 193—194°.

The latter yields a monomethyl ether and an acetate of the monomethyl ether identical with sakuranetin monomethyl ether and its acetate. 2 : 4 : 6-*Trihydroxyphenyl β-phenylethyl ketone*, m. p. 201—202°, 3' : 4'-*methylenedioxy-5 : 7-dihydroxyflavanone*, m. p. 220°, and (?) 2 : 4 : 6-*trihydroxyphenyl 3 : 4-methylenedioxystyryl ketone*, m. p. 213°, are prepared similarly.

II. *p*-*Carbethoxyoxybenzaldehyde*, b. p. 170—173°/19—20 mm., m. p. 26°, condenses with malonic acid when heated in pyridine containing a little piperidine to give p-*carbethoxyoxycinnamic acid*, m. p. 183°. Condensation of the chloride of this acid with phloroglucinol by the method described above yields a resinous product from which 5 : 7 : 4'-trihydroxyflavanone is separated by solution in alcoholic alkali, precipitation with carbon dioxide, and treatment with dilute acetic acid. Two *substances*, m. p. 177° and 267—268°, are also separated in small quantity. The synthetic 5 : 7 : 4'-trihydroxyflavanone and its derivatives [*oxime* ($+H_2O$), m. p. 231°; dimethyl ether, m. p. 118°] are identical with naringenin and its derivatives (cf. Asahina and Inubuse, A., 1928, 1020). Methylation of 5 : 7 : 4'-trihydroxyflavanone with only one molecular proportion of diazomethane yields 5 : 4'-dihydroxy-7-methoxyflavanone, identical with sakuranetin and yielding identical derivatives.

III. *iso*Vanillin, prepared by demethylation of veratraldehyde with hydrobromic acid, yields O-*carbethoxyisovanillin*, m. p. 61—62°, which condenses with malonic acid to give O-*carbethoxyhesperitic acid* (3-carbethoxyoxy-4-methoxycinnamic acid), m. p. 199°. Condensation of the chloride of this acid with phloroglucinol by the method described above yields a product from which is obtained 5 : 7 : 3'-trihydroxy-4'-methoxyflavanone, m. p. 227—228°, identical with hesperetin and yielding an identical *oxime*, m. p. 229—230°.

R. K. CALLOW.

Dynamic isomerism. XXVIII. Absorption spectra of the ketonic and enolic forms of an α-diketone. T. M. LOWRY, H. MOUREU, and C. A. H. MACCONKEY (J.C.S., 1928, 3167—3179).— The contention of Morton and Rosney (A., 1926, 454) that keto–enol tautomerides exhibit the same wavelengths of maximum absorption, disproved by Lowry, MacConkey, and Burgess (A., 1928, 766) for benzoylcamphor, is now found to be untrue for the isomerides of benzylmethylglyoxal. The ketonic form *A* (Moureu, A., 1928, 419) is obtained by distillation with sodium carbonate and has m. p. 17°, b. p. 104°/10 mm. It has absorption in the yellow, with a maximum $\log \varepsilon = 1.5$ at 4300 Å. in alcohol, or 1·8 at 4550 Å. in *cyclo*hexane.

The enolic form *B*, m. p. 70°, b. p. 134°/10 mm., formed by addition of an alkali or base to the liquid, is the stable solid phase, and is colourless, with strong absorption in the ultra-violet, having maximum $\log \varepsilon = 4.3$ at 3120 Å. in alcohol, or 4·7 at 3100 Å. in *cyclo*hexane. The inequality in λ between the isomerides is twice as great as with benzoylcamphor (*loc. cit.*), and the intensity ratio is about 600 : 1.

The absorption bands of *B* may be compared with those of benzylideneacetone and benzoylacetone. Benzylideneacetone has $\log \varepsilon = 4.36$ at 2850 Å., closely resembling benzylidenecamphor (LOWRY and French,

A., 1924, i, 1212). The absorption spectrum of benzoylacetone (Baly and Desch, J.C.S., 1905, **87**, 766; Morgan and Moss, *ibid.*, 1913, **103**, 78) is now found to have two maxima, with, in alcohol, $\log \varepsilon = 4\cdot15$ at 3100 and $3\cdot66$ at 2500 Å., in *cyclo*hexane, $4\cdot26$ at 3050 and $3\cdot80$ at 2450 Å.; by analogy with benzoyl-camphor it is assumed that these are due to two isomerides formed in equilibrium mixture when the homogeneous solid is melted or dissolved. The various bands at about 3000 Å. in the above compounds may be considered to be a general ketonic band, reinforced by conjugation of the carbonyl double linking with an olefinic double linking.

The liquid form of benzylmethylglyoxal rapidly develops enolic absorption; if, however, it is examined when freshly prepared, it no longer shows a maximum in the ultra-violet, but only a "step-out," $\log \varepsilon = 2\cdot6$—$2\cdot8$ at 3300—2700 Å. This may be compared with similar behaviour of acetylphenylethylene oxide, at wave-lengths less than 3100 Å.; this compound thus resembles benzyl acetate rather than acetophenone in absorptive properties.

Inter-transformation of the isomerides in solution was not easily effected, and when an equilibrium mixture was obtained the ratio of its components could not be determined. The additive law does not appear to apply, and it is possible that A and B may combine together. It is, however, noteworthy that the absorption curves for equilibrium mixtures show a minimum rather than a maximum at λ 2450, which is characteristic of the labile form of benzoylcamphor; benzylmethylglyoxal thus does not include a similar form among its tautomerides.   E. W. WIGNALL.

Theory of [the colour of] quinhydrones. E. WEITZ (Z. Elektrochem., 1928, **34**, 538—546).—The colour of quinhydrones is attributed to salt formation between the "functional groups" of the two components; the functional groups can function as anions or cations and are situated at the ends of a conjugated chain. Owing to the low oxidation or reduction potential of the components, the salts are incompletely heteropolar, the electrons of the cationic group being only partly given up to the anionic group, and to this is directly attributed the colour of the salts. The theory is extended to other classes of compounds, *e.g.*, triphenylmethane dyes and certain coloured inorganic salts containing colourless acid radicals.   S. K. TWEEDY.

Dehydrating action of Japanese acid earth in the anthraquinone series. M. TANAKA and S. WATANABE (Bull. Chem. Soc. Japan, 1928, **3**, 288—289).—When quinol is condensed with phthalic anhydride at 260° in presence of Japanese acid earth, quinizarin is produced. Pyrocatechol affords a mixture of hystazarin and alizarin, whilst α-naphthol at 250—260° yields α-*hydroxynaphthacenequinone*, m. p. 303°.   H. BURTON.

Indoquinonanthrene (*trans - bisang -* or **1 : 2 : 5 : 6-diphthalylanthraquinone).** R. SCHOLL and H. K. MEYER (Ber., 1928, **61**, [*B*], 2550—2555).—*iso*Violanthrone is oxidised by chromic acid in boiling glacial acetic acid to trans-bisang-*diphthalylanthraquinone* (I) for which the term "indoquinonanthrene" is proposed to express the similarity of the arrange-

ment of the rings to those of indanthrene. It is a yellow, crystalline material which sublimes at about 400° in a carbon dioxide vacuum and dissolves

(I.)   (II.)
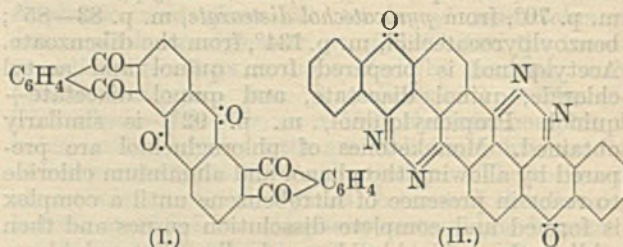
sparingly in organic media. The red vat produced by sodium hyposulphite in cold sodium carbonate solution contains *hexahydroindoquinonanthrene*, since it readily yields a *hexa-*p-*bromobenzoyl* compound. The hexahydro-derivative is converted by exposure to air or by treatment with boiling trichlorobenzene into the bluish-black *quinhydrone* ($C_{30}H_{12}O_6 + C_{30}H_{18}O_6$). Indoquinonanthrene is converted by hydrazine hydrate in hot quinoline into the dark blue *hydro*-derivative of the di-*o*-diazine (II), which is stable towards air, but is readily oxidised by sulphuric acid to the *di-o-diazine*, subliming at 460—480°/20 mm. (carbon dioxide).   H. WREN.

Oxidation of " biosterin " [biosterol] by ozone. Z. NAKAMIYA (Bull. Inst. Phys. Chem. Res., Japan, 1928, **1**, 1211—1243).—The ozonide of biosterol was separated by light petroleum into soluble (? mono-ozonide) and insoluble (? diozonide) fractions, each of which gave the same products when decomposed with boiling water. From these products were isolated acetaldehyde, formaldehyde, butaldehyde, formic acid, acetic acid, diacetyl, an acidic *substance* with properties resembling those of a sesquiterpene alcohol derivative, a neutral viscous *substance* (C 67—72%, H 9—10%), and an acidic viscous *substance* (C 63—65%, H 8—9%), these last two being the main decomposition products.   J. W. BAKER.

Rotenone and degradation products. G. M. WRIGHT (J. Amer. Chem. Soc., 1928, **50**, 3355—3360).—The revised constitutions proposed by Takei (A., 1928, 765) are independently confirmed. Rotenone oxime has m. p. 252°, rotenone hydrochloride, m. p. 255° (*oxime*, m. p. 239°), and rotenone hydrobromide, m. p. 190°. *iso*Rotenone yields a *phenylhydrazone*, m. p. 230°, but does not combine with hydrogen chloride. Rotenic acid forms a *methyl* ester, m. p. 39—40°, and a *mononitro*-derivative, m. p. 187°, and is decarboxylated at 216—225° to a *substance*, $C_{23}H_{22}O_5$, m. p. 104°, and a phenolic *substance*.   H. E. F. NOTTON.

Action of ozone on *cyclo***geraniolenes.** R. ESCOURROU (Bull. Soc. chim., 1928, [iv], **43**, 1277—1279).—A recapitulation of work already published (A., 1926, 1238).   R. BRIGHTMAN.

Camphane-2-carboxylic acid and camphanyl ketones. H. RUPE and H. HIRSCHMANN (Helv. Chim. Acta, 1928, **11**, 1180—1200).—Ethyl camphane-2-carboxylate (the acid is obtained in 70—80% yield by the action of carbon dioxide on magnesium bornyl chloride; cf. Houben, A., 1906, i, 21) is reduced by sodium and alcohol to 2-*camphanylcarbinol*, b. p.

135°/19 mm., m. p. 87—88°, $[\alpha]_D^{20}$ —27·75° in benzene (p-*nitrobenzoate*, m. p. 123°), also obtained by reducing camphane-2-carboxylamide, m. p. 98° (lit. 138°). Zinc methyl and the acid chloride afford 2-*camphanyl methyl ketone* (2-*acetylcamphane*) (I), b. p. 106°/13 mm., d_4^{20} 0·96186, $[\alpha]_D^{20}$ —54·25° (*semicarbazone*, m. p. 216°; *oxime*, m. p. 69°), which condenses with benzaldehyde in presence of hydrogen chloride, yielding 2-*camphanyl styryl ketone*, b. p. (cathode vacuum) 120—121°, m. p. 46°, $[\alpha]_D^{20}$ +25·85° in benzene. Reduction of this with hydrogen in presence of nickel gives 2-*camphanyl β-phenylethyl ketone*, b. p. 200—201°/13 mm., m. p. 36°, $[\alpha]_D^{20}$ —24·04° in benzene. 2-*Camphanyl 2-nitrostyryl ketone* has m. p. 77—78°. 2-*Camphanyl ethyl ketone* (2-*propionylcamphane*), b. p. 128—129°/13 mm., d_4^{20} 0·9549, $[\alpha]_D^{20}$ —55·69° (*semicarbazone*, m. p. 186°; *oxime*, m. p. 97—98°), is prepared using zinc ethyl, and *phenyl* 2-*camphanyl ketone* (2-*benzoylcamphane*), b. p. 178—180°/11 mm., d_4^{20} 1·0391, $[\alpha]_D^{20}$ +12·13°, by the Friedel–Crafts reaction. Treatment of I with ethyl benzoate in presence of ether and sodamide gives 2-*benzoylacetylcamphane*, m. p. 61°, whilst oxidation with sodium hypobromite yields an *acid*, m. p. 83—84°, $[\alpha]_D^{20}$ —12·99° in benzene (*methyl* ester, b. p. 102°/10 mm., d_4^{20} 1·0017, $[\alpha]_D^{20}$ —28·0°), isomeric with camphane-2-carboxylic acid, m. p. 73°, $[\alpha]_D^{20}$ —3·26° in benzene (*methyl* ester, b. p. 104—105°/11 mm., d_4^{20} 1·002, $[\alpha]_D^{20}$ —14·61°; secondary *hydrazide*, m. p. 300°). Both acids give the same p-*toluidine* salt, m. p. 185—185·5°. Magnesium bornyl chloride and benzaldehyde appear to give *phenyl-2-camphanylcarbinol*, b. p. 170—175°/14 mm.

Optical rotations of the above compounds for different wave-lengths have been measured, and the rotation-dispersions of the acids and their esters are found to be normal or nearly so.　　H. BURTON.

Camphenilane series. II. *apo*Cyclene, camphenilene, and some of their derivatives. S. NAMETKIN and Z. ALEXANDROV (Annalen, 1928, **467**, 191—200, and J. Russ. Phys. Chem. Soc., 1928, **60**, 1535—1544; cf. A., 1915, i, 699; 1924, i, 1084).—The structure of α-*iso*camphenilone (I) has now been determined by preparing it from *apo*cyclene (II) (cf. Komppa and Roschier, A., 1922, i, 1167), and examination of the products of fission of the *cyclo*propane ring in the latter by hydration has shown that fission probably takes place in all three possible ways, for fission of either the C^1—C^6 or C^2—C^6 linkings must yield the alcohols corresponding with camphenilone and α-*iso*camphenilone, and fission of the C^1—C^2 linking the alcohol corresponding with *apo*camphor; all these ketones were isolated.

(I.)　　(II.)　　(III.)
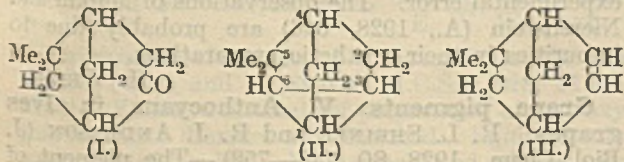
*apo*Cyclene was prepared from camphenilone-hydrazone by oxidation with mercuric oxide in alcohol. Treatment of *apo*cyclene with acetic acid and 50% sulphuric acid yielded a mixture of alcohols, m. p. 51—60°, b. p. 100·5—101°/19 mm. After oxidation of this mixture with chromic acid in acetic acid,

*apo*camphor was separated by crystallisation of its semicarbazone, and yielded *apo*camphoric acid when oxidised by alkaline permaganate. After oxidation of the mixture with concentrated nitric acid and then with alkaline permanganate, camphenilone and α-*iso*camphenilone, m. p. 65—66° (semicarbazone, m. p. 193—194°), were separated by crystallisation of the semicarbazones. *cis-apo*Fenchocamphoric acid, derived from α-*iso*camphenilone, was separated from the product of the permanganate oxidation. α-*iso*Camphenilone was separated in largest amount, and this reaction provides a convenient method of preparation. Reduction of the ketone with sodium and alcohol yielded a mixture of the stereoisomeric α-*iso*camphenilols, b. p. 196—198° (corr.). When treated with potassium and carbon disulphide and then with methyl iodide this yielded *methyl* α-*iso*camphenilylxanthate, which decomposed when heated at 150—160° to yield *camphenilene* (III), m. p. 27—28°, b. p. 131—132°. Oxidation of III with alkaline permanganate yielded *cis-apo*fenchocamphoric acid.
　　　　　　　　　　　　　　　　R. K. CALLOW.

Oxidation of dipinene. L. H. BRIGGS and W. F. SHORT (J.C.S., 1928, 3118—3121).—Application of the method of "dehydrogenating disruption" (Ruzicka), using manganese dioxide and sulphuric acid, to a dipinene, b. p. 183—184°/15 mm., d_4^{20} 0·9260, n_D^{20} 1·5174, produced by the action of hydrogen chloride and ferric chloride on pinene, led to benzoic, terephthalic, and trimellitic acids. This result supports the suggestion that certain diterpenes contain two hexagonal nuclei united through a chain of one or two carbon atoms.
　　　　　　　　　　　　　　　　R. J. W. LE FÈVRE.

New compounds from oil of turpentine. H. WIENHAUS (Förh. III nord. Kemistmötet, 1928, 211—212).—The presence of carene in German turpentine oil has been established. A *diterpene*, $C_{20}H_{32}$, m. p. 63°, b. p. 178°/8 mm., $[\alpha]_D$ +214°, has been isolated from Swedish pine resin. On hydrogenation in presence of platinum it yields a monocyclic (?) *octahydroditerpene*, $C_{20}H_{40}$, whilst when boiled with formic acid it affords a tricyclic compound, which on hydrogenation gives a saturated *tetrahydroditerpene*, $C_{20}H_{36}$. Its ozonide gives acetaldehyde when boiled with water. A sesquiterpene *alcohol*, $C_{15}H_{26}O$, regarded as tertiary, has been isolated from the same source as the previous compounds; when hydrogenated it gives a saturated *dihydro*-compound, $C_{15}H_{28}O$. The *isonitroso*-compound of verbanone has been found to give a dioxime, which yields orange precipitates with nickel salts; by fusion with alkali the first-named substance is converted into pinocamphoric acid. The unsaturated ketone o-menthen-5-one has been prepared by boiling verbanone with acids; when hydrogenated it yields o-menthan-5-one, which forms a crystalline oxime and semicarbazone. The oxime is converted by concentrated sulphuric acid into an *isooxime* (*lactam*), m. p. 119—120°. By the reduction of o-menthan-5-one a new secondary alcohol, *o-menthan-5-ol*, has been obtained. Reduction of the oxime to verbanylamine and subsequent suitable treatment yields dimethylverbanylamine and d-pinene. When oxidised with potassium permanganate the latter gives pinocamphoric acid, but it differs from α-pinene in not giving solid compounds with nitrosyl chloride

or bromine. *d*-Pinene boils at 156—157°/740·5 mm., and its d_4^{20} (0·8708) and refractive index are higher than those of α-pinene. Sylvestrene on autoxidation yields alcohols and ketones, which may be designated as sylvocarvacrols and sylvocarvones; on hydrogenation of these followed by oxidation *m*-menthanone is obtained.   H. F. HARWOOD.

Tricyclene group. G. KOMPPA (Förh. III nord. Kemistmötet, 1928, 209—210).—The constitution of tricyclenic acid has now been established by its conversion into tricyclene. Its ethyl ester was reduced with sodium and alcohol to *tricyclenol*, m. p. 110—111°, converted by phosphorus pentachloride into the corresponding *chloride*, an oil which on reduction (sodium and alcohol) gives a good yield of tricyclene. Tricyclenic acid is not identical with the teresantalic acid obtained from sandalwood oil as Semmler had suggested, since this latter acid cannot be reduced to tricyclene. The author has also prepared the *dichloro*-compound of tricyclenol, the corresponding *glycol*, and *tricyclenolphenylmethane*, m. p. 86°.
   H. F. HARWOOD.

Pinacolin rearrangement of dicyclic ditertiary glycols. J. PALMÉN (Förh. III nord. Kemistmötet, 1928, 195—208).—Contrary to the statement of Semmler and Bartels (1908) that camphenilone is not formed when santeneglycol is subjected to the pinacolin rearrangement, it has been shown that a yield of about 5% of this substance can be obtained by treating santeneglycol with concentrated sulphuric acid below 0°; the simultaneous production of resin prevented following the course of the reaction. Camphenedimethylglycol (dihydroxydimethylcamphane) readily undergoes the pinacolin rearrangement, the dicyclic ring being ruptured with production of a mixture of unsaturated monocyclic compounds. Attempts to prepare the corresponding dihydroxy--diethyl-, -dibenzyl-, and -diphenyl-camphanes from camphorquinone and the appropriate Grignard reagent failed (steric hindrance?), only one of the carbonyl groups reacting, *keto-alcohols* being formed. Those obtained by using magnesium phenyl and magnesium benzyl bromide had m. p. 78—80°, and b. p. 212°/15 mm., respectively. Treatment of santenone with sodamide and amyl nitrite affords *iso*nitrososantenone, converted by formaldehyde into a product, $C_9H_{14}O_3$, m. p. 138—140°, probably a *ketosantenone*
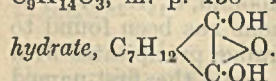
hydrate, $C_7H_{12}{<}\begin{smallmatrix}C{\cdot}OH\\|\\C{\cdot}OH\end{smallmatrix}{>}O.$ H. F. HARWOOD.

Constitution of cantharidin. Decomposition reaction of cantharidin. F. VON BRUCHHAUSEN and H. W. BERSCH (Arch. Pharm., 1928, **266**, 697—702).—Maleic anhydride and furan condense in benzene solution to form *dehydroprotocantharidin* (annexed formula), which decomposes again above its m. p., 118°, into its original components (cf. Diels and Adler, A., 1928, 1018). Subsequent treatment with hydrogen and palladised charcoal affords *protocantharidinic acid*, m. p. 117—120° with loss of water, the *anhydride* of which is very stable. The condensation of furan and dimethylsuccinic anhydride to form cantharidin could not be accomplished, but
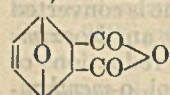
the latter was broken down into these components when passed over a dehydrogenating catalyst such as palladised asbestos at 280°. This reaction confirms the constitution of cantharidin finally accepted by Gadamer (cf. Coffey, A., 1923, i, 695, 1218).
                                                S. COFFEY.

*iso*Flavone group. III. Synthesis of genistein. W. BAKER and R. ROBINSON (J.C.S., 1928, 3115—3118).—5 : 7-Dihydroxy-4′-methoxy-2-styryl-*iso*flavone gave, on methylation with methyl sulphate and methyl-alcoholic aqueous potassium hydroxide, *5-hydroxy-7 : 4′-dimethoxy-2-styryl*isoflavone, m. p. 245—246° (*acetyl* derivative, m. p. 203—204°), which was completely methylated only by methyl sulphate and sodium hydroxide in acetone, giving 5 : 7 : 4′-*trimethoxy-2-styryl*isoflavone, m. p. 193° (similar treatment of 5-hydroxy-7 : 4′-dimethoxy-2-styrylmethyl-*iso*flavone gave 5 : 7 : 4′-*trimethoxy-2-styryl*-6(?)-*methyl*isoflavone, m. p. 211°). Oxidation of this compound by potassium permanganate in aqueous pyridine solution led to benzoic acid and 5 : 7 : 4′-*trimethoxy*isoflavone-2-carboxylic acid, m. p. 237° (decomp.), which, when heated above its m. p., gave 5 : 7 : 4′-*trimethoxy*isoflavone (genistein trimethyl ether), m. p. 162—163°, from which genistein was obtained by demethylation.
                                            R. J. W. LE FÈVRE.

Chrysanthemin and asterin. R. ROBINSON and R. WILLSTÄTTER (Ber., 1928, **61**, [*B*], 2503—2504).—Further purification of asterin has yielded a product identical in all respects with chrysanthemin; the term asterin is no longer necessary.   H. WREN.

[**Cyanidin. I.**] R. ROBINSON and R. WILLSTÄTTER (Ber., 1928, **61**, [*B*], 2504—2506).—A criticism of the reasons which have led Malkin and Nierenstein (A., 1928, 646) to assume that cyanidin chloride and 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride differ from one another.   H. WREN.

Comparison of natural and synthetic cyanidin. R. KUHN and T. WAGNER-JAUREGG (Ber., 1928, **61**, [*B*], 2506—2508).—Differences are not observable between the cyanidin chloride obtained by hydrolysis of cyanin chloride from dahlias and 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride from *O*-benzoyl-cyanidin chloride by Robinson's method. Both preparations have the same crystalline form and the same colour in solutions of equal p_H. Their colour reactions with ferric chloride, copper sulphate, and uranyl nitrate are identical with regard to shade and relative permanence. Their extinction coefficients in the ultra-violet are identical within the limits of experimental error. The observations of Malkin and Nierenstein (A., 1928, 646) are probably due to impurities in their synthetic preparations.
                                                H. WREN.

Grape pigments. V. Anthocyans in Ives grapes. R. L. SHRINER and R. J. ANDERSON (J. Biol. Chem., 1928, **80**, 743—752).—The pigment of Ives grapes (a strain of *Vitis labrusca* admixed with a little *V. æstivalis*) was isolated as the picrate, and converted into the chloride which could not be obtained crystalline; the latter was reconverted into picrate and fractionated; the pigment regenerated from the largest fraction, when hydrolysed with hydro-

chloric acid, gave monomethoxydelphinidin chloride, p-hydroxycinnamic acid, and dextrose. The methoxydelphinidin yielded an α-tetra-acetate, m. p. 102—104°, and a β-tetra-acetate, m. p. 220—230°, both of which, when oxidised with permanganate, gave syringic acid.　　　　　　　　C. R. Harington.

Interaction of piperidine with nitro- and halogenonitro-derivatives of xanthone and diphenylene oxide. R. J. W. Le Fèvre (J.C.S., 1928, 3249—3252).—Both α- and β-dinitroxanthone formed bright yellow complexes with piperidine in the cold; when boiled with an excess of reagent the former gave an indefinite product, whilst the latter yielded 5 : 5'-dinitro-2'-piperidino-2-hydroxybenzophenone, m. p. 155° (acetyl derivative, m. p. 253—255°), which, when heated at 200°, lost piperidine with regeneration of β-dinitroxanthone. 2 : 4 : 5 : 7-Tetranitroxanthone, m. p. above 300°, did not react with boiling piperidine. Unsuccessful attempts to reveal the orienting influence of oxonium oxygen are described. 2 : 7-Dibromo-4 : 6-dinitroxanthone has m. p. 265—266°.　　　　　　　R. J. W. Le Fèvre.

Dinaphthylene dioxide. I. A. Corbellini and F. Vietti (Gazzetta, 1928, 58, 766—774).—The method of preparation of dinaphthylene dioxide (cf. Pummerer and others, A., 1926, 1135; Inouye, B., 1926, 596; Thyll and Schmid, B., 1927, 470) is simplified and improved by heating crude dinaphthyl with copper oxide at 300—310°, with or without nitrobenzene; the yield is 84—87%. The substance is accurately chlorinated by the method of Zinke, Pongratz, and Funke (A., 1925, i, 384) to a dichloroderivative, m. p. 259°, is converted by bromine in carbon disulphide into a dibromo-derivative, m. p. 277°, and by excess of bromine into tetrabromodinaphthylene dioxide, m. p. 349—351°.

In order to avoid the formation of tetranitro- or hexanitro-compounds (cf. Bünzly and Decker, A., 1905, i, 884; Inouye, loc. cit.), nitration is effected in carbon tetrachloride suspension. The resulting dinitro-derivative, $C_{29}H_8O_6N_2$, can be reduced by sodium hyposulphite or by stannous chloride, provided that it is first subdivided by dissolving in sulphuric acid and precipitation by water; the reduction product is not yet described. In presence of aluminium chloride, dinaphthylene dioxide readily reacts with benzoyl chloride in carbon disulphide solution to give the dibenzoyl derivative, $C_{20}H_8O_2Bz_2$, m. p. 318·5°, and in benzene with phthalic anhydride to give the aluminium salt of the acid $C_{20}H_9O_2 \cdot CO \cdot C_6H_4 \cdot CO_2H$, decomp. 350°; with excess of phthalic anhydride the acid $C_{20}H_8O_2(CO \cdot C_6H_4 \cdot CO_2H)_2$, decomp. about 350°, is obtained.　　　　　　　E. W. Wignall.

Hydroxy-derivatives of thioxanthone dioxide. W. B. Price and S. Smiles (J.C.S., 1928, 3154—3160).—Effective methods of preparation of hydroxythioxanthone dioxides are described. Equimolecular quantities of 2-sulphinobenzoic acid and p-benzoquinone were condensed in aqueous suspension giving 2 : 5-dihydroxydiphenylsulphone-2'-carboxylic acid, m. p. 235° (diacetyl derivative, m. p. 188°; methyl 2 : 5-dimethoxydiphenylsulphone-2'-carboxylate, m. p. 195°; 2 : 5-dimethoxydiphenylsulphone-2'-carboxylic acid, m. p. 223°), which by dehydration in sulphuric

acid passed into 1 : 4-dihydroxythioxanthone dioxide, m. p. 224° (diacetyl derivative, m. p. 174°). The last compound, by oxidation with lead tetra-acetate, yielded thioxanthone dioxide 1 : 4-quinone, m. p. 185°. Similarly, 2-sulphinobenzoic acid with p-toluquinone gave methyl 2 : 5-dihydroxydiphenylsulphone-2'-carboxylic acid, m. p. 203°, and with chlorobenzoquinone gave chloro-2 : 5-dihydroxydiphenylsulphone-2'-carboxylic acid, m. p. 210°; both underwent dehydration yielding methyl-1 : 4-dihydroxythioxanthone dioxide, m. p. 175°, and chloro-1 : 4-dihydroxythioxanthone dioxide, m. p. 230°, respectively. 2-Sulphinobenzoic acid and quinizarinquinone gave 2-quinizarinphenylsulphone-2'-carboxylic acid, m. p. 263°, which would not undergo ring closure, whilst 1 : 2-naphthaquinone gave an additive product, $C_{17}H_{12}O_6S,H_2O$ (I), m. p. 156° (decomp.). Dehydration of I led to 1 : 2-naphthaquinone 2'-carboxyphenyl sulphoxide (II), m. p. 236° (phenylhydrazone, m. p. 251°; quinoxaline [from o-phenylenediamine], m. p. 292—293°); with boiling acetic anhydride II gave 3 : 4-naphthathioxanthone-1 : 2-quinone, m. p. 244—245°.

The following compounds are also described : 2 : 4-dihydroxy-2'-carboxydiphenyl sulphoxide, m. p. 204°; 1 : 4-dimethoxythioxanthone dioxide, m. p. 193°; 2-hydroxythioxanthone dioxide, m. p. 259° (methyl ether, m. p. 204°); 2 : 3-dihydroxythioxanthone dioxide, m. p. 203° (decomp.) (methyl ether, m. p. 241°).　　　　　　　R. J. W. Le Fèvre.

Carbonylbisamino-acids and their transformation products. II. F. Wessely and J. Mayer (Monatsh., 1928, 50, 439—448).—(+)Ethyl carbonylbis-α-amino-β-phenylpropionate (Ia), $CO[NH \cdot CH(CO_2Et) \cdot CH_2Ph]_2$, m. p. 142·5° (corr.) after sintering at 141°, $[\alpha]_D^{15}$ +42·28° in alcohol, prepared by the action of carbonyl chloride on (—)ethyl α-amino-β-phenylpropionate, is converted by heating with hydrochloric and acetic acids into (—)α-(5-benzyl-3-hydantoin)-β-phenylpropionic acid (IIa), m. p. 205·5°, $[\alpha]_D^{15}$ —210·7° in alcohol. Similarly, (—)ethyl carbonylbis-α-amino-β-phenylpropionate (Ib), m. p. 142·5° (corr.) after sintering at 141°, $[\alpha]_D^{15}$ —42·35° in alcohol, from (+)ethyl α-amino-β-phenylpropionate, yields (+)α-(5-benzyl-3-hydantoin)-β-phenylpropionic acid (IIb), m. p. 205·5°, $[\alpha]_D^{15}$ +211° in alcohol. Equimolecular mixtures of Ia with Ib and IIa with IIb have m. p. 144·5° (corr.) and 229·5°, respectively (cf. Wessely and John, A., 1928, 530). Whilst the i-carbonylbisphenylalanines previously described (loc. cit.) are unaffected by heating with 1 or 2 mols. of N-sodium hydroxide solution, the corresponding esters, m. p. 145° and 141·5°, respectively, both yield a mixture of the two i-acids on hydrolysis with 2 mols. of alkali. With 1 mol. of alkali the former ester gives a mixture of the two isomeric α-(5-benzyl-3-hydantoin)-β-phenylpropionic acids, m. p. 229° and 171°, respectively (loc. cit.), whilst the latter ester affords the form of m. p. 229° only. The above hydantoin derivative, m. p. 171°, is converted into its isomeride, m. p. 229°, by treatment with 1 mol. of alkali, and both these compounds are hydrolysed by 2 mols. of alkali, forming the same mixture of i-carbonylbisphenylalanines. Ethyl α-(5-benzyl-3-hydantoin)-β-phenylpropionate, m. p. 130° (corr.) after sintering at 125°, is obtained by the action of diazoethane on

the corresponding acid, m. p. (anhydrous or $+1.5H_2O$) 171—172°.

[With E. KEMM.]—When ethyl carbonylbisamino-acetate is hydrolysed wth methyl-alcoholic potassium hydroxide solution a mixture of hydantoin-3-acetic acid and carbonylbisaminoacetic acid is obtained. H. BURTON.

Electrolytic reduction of cyclic imides to hydrogenated cyclic bases. E. SPÄTH and F. BREUSCH (Monatsh., 1928, **50**, 349—356).—Although Tafel (A., 1900, i, 557; *ibid.*, ii, 588) succeeded in converting succinimide derivatives only into pyrrolidones by electrolytic reduction at a lead cathode, further reduction to pyrrolidines is now shown to take place with α- and αα′-substituted derivatives and certain other similarly constituted compounds.

The apparatus used was similar to that described by Tafel. The use of specially pure lead is essential. The following compounds were prepared from the corresponding imides in the yields stated : 3-Methyl-pyrrolidine (32%) (cf. Späth and Prokopp, A., 1924, i, 502); 3-*phenylpyrrolidine*, b. p. 120—122°/12 mm. (*hydrochloride*; *picrate*, m. p. 166°) (40·3%); 3 : 4-*di-phenylpyrrolidine*, b. p. 195—200°/14 mm. (from αα′-*diphenylsuccinimide*, m. p. 198°) (1·2%); dihydro-*iso*indole (32%); tetrahydro*iso*quinoline (15%); di-hydroindole (from isatin) (4%); *hydrobenzoisoquinol-ine*, m. p. 70° (from naphthalimide) [*picrate*, darkening at 195°, m. p. 200° (decomp.)] (15%). The imides of pyridine-2 : 3-dicarboxylic acid and diphenic acid and malonamide could not be reduced to the amines. The formation of pyrrolidone from succinimide appears to take place through γ-aminobutyric acid, ring-closure first occurring on distillation in the ordinary method of working up. R. K. CALLOW.

Piperidine derivatives. VI. 3-Methylpiper-idinoalkyl benzoates. J. R. THAYER and S. M. McELVAIN (J. Amer. Chem. Soc., 1928, **50**, 3348—3355).—3-Methylpiperidine and chloroacetone in ether yield α-3-*methylpiperidinoacetone*, b. p. 101—102°/18 mm., the *hydrochloride*, m. p. 162—163°, of which is hydrogenated (platinum) in alcohol to α-3-*methyl-piperidino-β-propyl alcohol hydrochloride*, m. p. 184—185° (free *base*, b. p. 98—100°/18 mm.). This is converted by benzoyl chloride into the *hydrochloride* (I), m. p. 165—166°, of α-3-*methylpiperidino-β-propyl benzoate*. 3-Methylpiperidine hydrochloride, para-formaldehyde, and acetone in absolute alcohol at 100° yield α-3-*methylpiperidinobutan-γ-one hydro-chloride*, m. p. 151—152°, which is hydrogenated and benzoylated to α-3-*methylpiperidino-γ-benzoyloxy-butane hydrochloride* (II), m. p. 178—180°. βγ-Di-bromobutane and silver benzoate (1 mol.) in toluene yield impure β-*bromo-γ-benzoyloxybutane* (III), b. p. 140—141°/4 mm. Acetylacetone is hydrogenated (platinum) to pentane-βδ-diol, which by successive treatment with benzoyl chloride and thionyl chloride gives β-*chloro-δ-benzoyloxypentane* (IV), b. p. 134—135°/2 mm., n_D^{20} 1·5074, d^{20} 1·1008. Unstable β-*chloro-β-methylpentan-δ-one* (V), b. p. 50—52°/14 mm., is obtained from diacetone alcohol and thionyl chloride in dry ether. The products III, IV, and V do not yield tertiary amines when treated with 3-methylpiperidine, but lose 1 mol. of hydrogen

halide. The local anæsthetic action of I and II is much greater than that of the corresponding deriv-atives with an unmethylated alcoholic residue (cf. A., 1928, 71, 72), II being closely similar in its action to cocaine. H. E. F. NOTTON.

Reduction of *cyclo*hexanone*iso*oxime (α-keto-hexamethyleneimine). A. MÜLLER and P. BLEIER (Monatsh., 1928, **50**, 399—402).—Reduction of *cyclo*hexanone*iso*oxime, m. p. 69·2° (corr.), with sodium and absolute alcohol gives 18% of hexamethylene-imine (cf. Wallach, A., 1903, i, 103; 1906, i, 175) identified as the hydrochloride, m. p. 236—237° (corr.), and the *p*-toluenesulphonyl derivative, m. p. 76·5° (cf. A., 1928, 277), together with high-boiling bases. No ammonia is evolved during the reduction (cf. Wallach, *loc. cit.*). H. BURTON.

Asymmetric nitrogen atom. LVI. Rates of transformation of stereoisomerides which simultaneously contain an asymmetric nitrogen and carbon atom ; parallel to the true auto-racemisation of " nitrogen-active " ammonium salts. E. WEDEKIND and G. L. MAISER (Ber., 1928, **61**, [*B*], 2471—2479; cf. A., 1928, 898).—The pre-paration and separation of the two forms of *l*-menthyl 2-*iso*propyltetrahydro*iso*quinolinium iodide acetate, $C_6H_4\underset{-CH_2-}{\overset{-CH_2\cdot CH_2-}{<}}NPr^\beta I\cdot CH_2\cdot CO_2C_{10}H_{19}$, is effected principally according to the method of Wedekind and Ney (A., 1909, i, 514); the more sparingly soluble iodide (β-iodide) has m. p. 161°, the more freely soluble α-iodide, m. p. 146—148°. Transformation of the α-form occurs mainly in methyl and ethyl alcohol. In acetone and chloroform the α-salt is stable; it is noteworthy that active methylallyltetrahydroquinol-inium iodide does not undergo autoracemisation in acetone (*loc. cit.*). The electrical conductivity of solutions of the α-salt in chloroform remains constant over long periods, thus indicating the absence of decomposition. Kinetic measurements of the rate of transformation of the α- into the β-iodide at 25° in methyl alcohol indicate a strictly unimolecular change, the mean velocity coefficient being 0·0050. The velocity is about one tenth of that of the autoracemisation of 1-methyl-1-allyltetrahydroquinol-inium iodide. The temperature coefficient of the transformation (2·31) for the interval 25—35° is only slightly greater than that of racemisation of the active salt.

The iodides have been transformed into the corre-sponding *nitrates* (α-*form*, m. p. 125—127°, $[\alpha]_D^{25}$ −66·0° in methyl alcohol; β-*variety*, m. p. 153—155°, $[\alpha]_D$ −20·3°), both of which are optically stable in all solvents investigated. In analogy with the behaviour of the active 1-methyl-1-allyltetrahydro-quinolinium iodide, the presence of a halogen atom as anion appears essential for transformation into the salt of higher m. p., whilst it may also be noted that precisely similar regularities are observed with com-pounds containing an asymmetric carbon atom as far as autoracemisation at the ordinary temperature is concerned.

The betaines produced by a type of autohydrolysis when menthyl 1-alkyltetrahydroquinolinium iodide acetates are treated with silver oxide suffer auto-

racemisation in acetone as well as in alcohol but at an appreciably slower rate. H. Wren.

3-Thiol-2-keto-1 : 2-dihydroquinoline-4-carboxylic acid and some quinolone derivatives. C. Gränacher and C. Kouniniotis (Helv. Chim. Acta, 1928, **11**, 1241—1252).—The compound previously described as oxindole-3-α-thiolacetic acid (A., 1923, i, 713), prepared by the action of sodium hydroxide on 3-rhodanylideneoxindole, is now shown to be 3-*thiol*-2-*keto*-1 : 2-*dihydroquinoline*-4-*carboxylic acid* (I), m. p. 165—167° [(decomp.); *S-benzyl* derivative, m. p. 230°; *S-carboxymethyl* derivative, m. p. 218—221° (decomp.)], reduced by Clemmensen's method to 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, m. p. 218—219° (cf. Aeschlimann, A., 1927, 256). Similarly, 3-rhodanylidene-*N*-methyloxindole gives 3-*thiol*-2-*keto*-1-*methyl*-1 : 2-*dihydroquinoline*-4-*carboxylic acid*, m. p. 146—150° (decomp.; S-*carboxymethyl* derivative, m. p. 210°). When I is treated with phenylhydrazine in boiling methyl alcohol, hydrogen sulphide is eliminated and the *pyrazolone* derivative (annexed formula) is obtained. Methylation of this with methyl iodide affords the 2-*methyl* derivative, m. p. 266° (2-*ethyl* derivative, m. p. 256—258°). Further ethylation of these alkyl derivatives gives the corresponding 2-*methyl*-1'-*ethyl*, m. p. 212°, and 2 : 1'-*diethyl*, m. p. 173—174°, compounds.
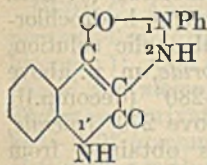
The action of aniline on I (*loc. cit.*) yields the 3-*anilino*-derivative, hydrolysed to 2 : 3-*diketo*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid*, whilst hydroxylamine gives the *anhydride* of 3-*oximino*-2-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid*. H. Burton.

Pyridinearylimines. II. Elimination and wandering of arylnitrogen complexes. W. Schneider and K. Weiss (Ber., 1928, **61**, [*B*], 2445—2451; cf. A., 1924, i, 1108).—Confirmatory evidence is adduced in favour of the authors' formulation of the dark-coloured, anhydro-bases derived from 1-phenylaminopyridinium compounds as pyridine-1-phenylimines. 2 : 4 : 6-Triphenylpyridine, m. p. 138°, is obtained by the action of carbon disulphide or phenylthiocarbimide on 2 : 4 : 6-triphenylpyridine-1-phenylimine; in a single instance the *compound* $C_{12}H_{10}NS$ was prepared by action of the carbimide. Reduction of 2 : 4 : 6-triphenylpyridine-1-phenylimine in methyl alcohol in presence of spongy platinum affords 2 : 4 : 6-triphenylpyridine and aniline. Treatment of 4 : 6-diphenyl-2-methylpyridine-1-phenylimine with boiling alcohol until the violet colour disappears yields 4 : 6-*diphenyl*-2-*o*-*aminobenzyl*pyridine, m. p. 144°, more conveniently prepared by gradual addition of sodium hydroxide to a boiling, alcoholic solution of 4 : 6-diphenyl-2-methylpyridinium iodide followed by treatment of the solution with zinc dust. The *monohydrochloride*, m. p. 256°, and *picrate*, $C_{20}H_{20}N_2,C_6H_3O_7N_3$, m. p. 202°, are described. The base can be diazotised. With methyl iodide it affords 4 : 6-*diphenyl*-2-*o*-*methylaminobenzyl*pyridine methiodide hydriodide (+CHCl₃), m. p. 158° (decomp.), in which the solvent of crystallisation is retained with remarkable tenacity. The salt yields a nitroso-derivative. 4 : 6-*Diphenyl*-2-*o*-*acetamidobenzyl*pyridine, m. p. 172°, and 4 : 6-*diphenyl*-2-*o*-*benzamidobenzyl*pyridine, m. p. 123°, are described. The last-mentioned compound is converted through its *nitroso*-derivative, decomp. 105—110°, into an *indazole* derivative, $C_{24}H_{17}N_3$, m. p. 228°, thus establishing the *ortho*-position of the amino- to the methylene group. H. Wren.

Attempt to prepare ψ-isoindole. G. W. Fenton and C. K. Ingold (J.C.S., 1928, 3295—3297).—*o*-Xylylene dibromide and *p*-toluenesulphonamide, in the presence of the alcoholic sodium ethoxide, gave 2-p-*toluenesulphonyldihydroisoindole*, m. p. 176° (corresponding *benzenesulphonyl* derivative, m. p. 140°), which by distillation with potassium hydroxide solution in an atmosphere of nitrogen yielded toluene, potassium sulphite, and dihydro*iso*indole [isolated as the *picrate*, m. p. 196—197° (decomp.)]. Similarly, 2-p-*toluenesulphonyl*-1-*methyldihydroisoindole*, m. p. 93° (obtained by toluenesulphonylation of the dihydro-base) gave toluene, sulphite, a tar, and 1-methyldihydro*iso*indole. ψ-*iso*Indole thus appears to be less stable than indole, possibly because the elements of unsaturation are more symmetrically distributed in the latter and that aromatic sextuple valency association is peripheral rather than central. R. J. W. Le Fèvre.

Indole derivatives. II. Synthesis of indolecarboxylic acids. S. Keimatsu and S. Sugasawa (J. Pharm. Soc. Japan, 1928, No. 558, 755—761; cf. A., 1928, 1030).—Ethyl β-cyanoethylsodioacetoacetate and benzenediazonium chloride react to give *ethyl* γ-*cyano*-α-*ketobutyrate phenylhydrazone*, m. p. 115°, converted by alcoholic hydrochloric or sulphuric acid into *ethyl indole*-3-*acetate*-2-*carboxylate* [*ethyl* 3-*carbethoxymethylindole*-2-*carboxylate*], m. p. 85—86°. The free *acid* decomposes at 228°, giving 3-methylindole. *Ethyl indole*-3-*propionate*-2-*carboxylate*, m. p. 95°, is similarly obtained from *ethyl* δ-*cyano*-α-*keto*-n-*valerate phenylhydrazone*, m. p. 93°. The free *acid*, m. p. 195°, loses 1 mol. of carbon dioxide at 220—230°, yielding *indole*-3-*propionic acid*, m. p. 134° (cf. Kalb and others, A., 1926, 1151). K. Ishimura.

Indole derivatives. III. Synthesis of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline. S. Keimatsu, S. Sugasawa, and G. Kasuya (J. Pharm. Soc. Japan, 1928, No. 558, 762—766).—Ethyl δ-phthalimido-α-acetylvalerate reacts with benzenediazonium chloride in alkaline alcoholic solution, yielding ethyl δ-phthalimido-α-ketovalerate phenylhydrazone, m. p. 146°, which is converted into *ethyl* 3-β-*phthalimidoethylindole*-2-*carboxylate*, m. p. 195° (cf. Manske, Perkin, and Robinson, A., 1927, 265). The latter compound, when heated with alcohol and hydrazine hydrate and then with 10% hydrochloric acid, yields 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline, m. p. 188—189° (cf. Ashley and Robinson, A., 1928, 775), which after heating with alcoholic potassium hydroxide and neutralisation with dilute sulphuric and acetic acids gives 3-β-*aminoethylindole*-2-*carboxylic acid*, m. p. 256° (decomp.). It loses carbon dioxide when heated with hydrochloric acid, yielding 3-β-*aminoethylindole*

hydrochloride, m. p. 243° (decomp.) (*acetate*, m. p. 136°; *picrate*, m. p. 245°). K. ISHIMURA.

Action of mercuric acetate on phenylcinchonic acid. B. CECCHIETTI and E. GODI (Gazzetta, 1928, **58**, 764—765).—Phenylcinchonic acid (2 mols.) reacts in alcohol with 1 mol. of mercuric acetate to give a *compound*, $C_{32}H_{20}O_4N_2Hg$, probably the mercuric salt, and with 2 mols. to give a *compound*, $C_{16}H_9O_2NHg$, regarded as having the annexed formula. E. W. WIGNALL.
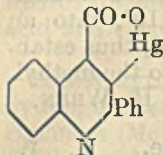
Carbazole derivatives. I. F. KEHRMANN and F. ZWEIFEL (Helv. Chim. Acta, 1928, **11**, 1213—1219).—Acetylation of 3-acetamidocarbazole, m. p. 217°, with excess of acetic anhydride in presence of anhydrous zinc chloride affords a mixture of di- and tri-acetyl derivatives, which when nitrated in acetic acid gives a mixture of α-, m. p. 226°, and β-nitro-diacetamidocarbazoles. Hydrolysis of the α-form with alcoholic sodium hydroxide solution yields 2(or 4)-*nitro*-3-*acetamidocarbazole*, m. p. 274°, hydrolysed by alcoholic sulphuric acid to 2(or 4)-*nitro*-3-*aminocarbazole*, m. p. 233°. 2(or 4) : 3-*Diamino-carbazole* (benzil condensation *product*, m. p. 273°) is readily oxidised in air. When the mixture of α- and β-nitro-derivatives is hydrolysed with cold alcoholic sodium hydroxide 4(or 2)-*nitro*-3-*acetamido-carbazole*, m. p. 198° (free *base*, m. p. 177°), goes into solution, and is precipitated by water. The *quin-oxaline* derivative from benzil and 3 : 4(or 2)-*diamino-carbazole* has m. p. 261°. H. BURTON.

Biuret reaction. I. Biuret reaction of acid imides of the barbituric acid type. M. M. RISING and C. A. JOHNSON (J. Biol. Chem., 1928, **80**, 709—722).—The theory of the biuret reaction is discussed in detail; from the sodium or potassium salt of diethylbarbituric acid there were obtained, by treatment with cupric acetate in alcohol, *compounds*, $(Na$ or $K)_2CuC_{32}H_{48}O_{14}N_8$, which are regarded as having the structure $(Na$ or $K)_2Cu(imide)_4 \cdot nH_2O$; in the above two compounds, the water, being firmly bound, is regarded as forming part of the molecular complex. A similar structure is proposed for the compounds prepared by Tschugaev (A., 1907, i, 595) and by Ley and Werner (A., 1907, i, 302), save that in these cases the water is regarded as water of crystallisation. C. R. HARINGTON.

Determination and characterisation of allantoin. R. FOSSE and (MLLE.) V. BOSSUYT (Compt. rend., 1929, **188**, 106—109).—Allantoin is hydrolysed in acid media to give glyoxylic acid (1 mol.) and carbamide (2 mols.). Allantoin may be detected by heating the sample, slightly acidified with hydrochloric acid, for 1 min. at 100° and adding 1% phenylhydrazine hydrochloride (4 drops), followed, after cooling, by 5% potassium ferricyanide (2 drops) and concentrated hydrochloric acid (1·5 c.c.). An immediate red coloration indicates allantoin. G. A. C. GOUGH.

Alkylation of diketopiperazine and peptides. C. GRÄNACHER, G. WOLF, and A. WEIDINGER (Helv. Chim. Acta, 1928, **11**, 1228—1241).—Benzylation of 2 : 5-diketopiperazine with benzyl chloride and

sodium methoxide gives 1 : 4-dibenzyl-2 : 5-diketo-piperazine, m. p. 176° (lit. 170—174°), hydrolysed by concentrated hydrochloric acid to *N*-benzylglycine hydrochloride, m. p. 226° (lit. 215°). 1 : 4-*Di-p-methoxybenzyl-2* : 5-*diketopiperazine*, m. p. 206°, is obtained similarly. *dl*-Alanine anhydride and benzyl chloride yield a mixture of two diastereoisomeric NN′-*dibenzylalanine anhydrides*, m. p. 144—145° and 89°, respectively, both hydrolysed by hydrochloric acid to *N*-benzylalanine, m. p. 269—270° (decomp.) after sintering at 265°. Similarly, *dl*-leucine anhydride affords two NN′-*dibenzyl* derivatives, m. p. 182—183° and an oil, respectively. Benzylation of hippurethylamide gives N-*benzylhippurethylamide*, m. p. 119°, hydrolysed to benzoic acid, ethylamine, and *N*-benzylglycine, together with N-*benzylhippur-benzylethylamide*, b. p. 230—240°/1—2 mm., hydrolysed to benzylethylamine, benzoic acid, and *N*-benzylglycine. N-p-*Bromobenzylhippurethylamide* has m. p. 134—136°. H. BURTON.

Substituted guanidines. F. BISCHOFF (J. Biol. Chem., 1928, **80**, 345—355).—Piperazine hydrochloride and cyanide, when boiled in alcoholic solution, yielded *diguanylpiperazine hydrochloride*, m. p. above 310° [*chloroplatinate*, m. p. 279—280° (decomp.)]; *guanylpiperidine sulphate*, m. p. above 270° [*picrate*, m. p. 242—243° (decomp.)], was obtained from piperidine and methyl*iso*thiocarbamide sulphate at the ordinary temperature. αε-Diguanidino-*n*-pentane (cf. Ripke, A., 1911, i, 620) was conveniently prepared from pentamethylenediamine hydrochloride and cyanamide in boiling alcohol; α0-*diguanidino*-n-*octane sulphate* (*chloroplatinate*, m. p. 214—216°, *picrate*, m. p. 205—206·5°, chloroaurate, m. p. 143—144°) was obtained from octamethylenediamine and methyl*iso*thiocarbamide sulphate. p-*Guanidinodi-methylaniline*, from *p*-aminodimethylaniline hydrochloride and cyanamide in boiling alcohol, had m. p. 117—122°, *nitrate*, m. p. 185°, *sulphate*, m. p. 112—112·5°; diguanylbenzidine could not be obtained pure, nor could negatively substituted aromatic amines be brought into reaction with cyanamide (cf. Kämpf, A., 1904, i, 534). C. R. HARINGTON.

Rung, Behrend, and Pinner's reaction. II. G. GASTALDI and Q. TALU (Gazzetta, 1928, **58**, 664—666).—Whereas the quaternary ammonium bases formed by glyoxaline and oxypyrazine compounds give, when treated with alkali hydroxide, two molecules of alkylamine (A., 1928, 1027), those formed by oxypyrimidine derivatives yield, under similar conditions, one molecule of alkylamine and one of ammonia. This difference in behaviour depends on the fact that, in the former case, the alkyliodides, and in the latter the hydriodides undergo scission. 6-*Keto*-1 : 2 : 4-*trimethyl*-1 : 6-*dihydropyrimidine hydriodide*, $CO\!\!<\!\!{NMe \cdot CMe \atop CH=CMe}\!\!>\!\!NHI$, m. p. 215° (decomp.), is obtained by treating a methyl-alcoholic solution of 6-keto-2 : 4-dimethylpyrimidine with potassium hydroxide (1 mol.) and methyl iodide (4 mols.). T. H. POPE.

Syntheses of heterocyclic nitrogen nuclei. II. 1 : 3 : 5-Triarylpyrazole-4-carboxylic acids and 1 : 3 : 5-triarylpyrazoles from aldehydehydraz-

ones and ethyl benzoylacetate. G. MINUNNI and S. D'URSO (Gazzetta, 1928, **58**, 691—712).—Ethyl benzoylacetate reacts with aldehydephenylhydrazones similarly to ethyl acetoacetate (A., 1925, i, 1175), yielding esters of pyrazolecarboxylic acids, from which the corresponding pyrazoles are prepared. The preparation and properties of the following compounds are described :

[With G. TROIA.]—1 : 3 : 5-Triphenylpyrazole-4-carboxylic acid (cf. Seidel, A., 1899, i, 139); *ethyl ester*, m. p. 145—146·5°; 1 : 3 : 5-triphenylpyrazole, new m. p. 140—140·5°, which was not found to crystallise with alcohol (cf. Knorr and Laubmann, A., 1888, 725; Moureu and Brachin, A., 1903, i, 581).

[With A. CARNEVALE.]—1 : 5-*Diphenyl-3-o-nitrophenylpyrazole-4-carboxylic acid*, $C_{22}H_{15}O_4N_3$,EtOH, m. p. 232·5—233·5° (decomp.); *ethyl* ester, m. p. 115·5—117·5°; 1 : 5-*diphenyl-3-o-nitrophenylpyrazole*, m. p. 116—117°. Alkaline hydrolysis of the ester yielded, besides the acid, a secondary *product*, m. p. above 255°.

[With G. AREZZI.]—1 : 5-*Diphenyl-3-m-nitrophenylpyrazole-4-carboxylic acid*, [+EtOH], m. p. 232° (decomp.); *ethyl* ester, m. p. 126·5—127·5°; 1 : 5-*diphenyl-3-m-nitrophenylpyrazole*, m. p. 137·5—139°. The *azoxy*-derivative, $C_{44}H_{30}O_5N_6$, of the acid, m. p. 240—247° (decomp.), is formed by prolonged heating of the ester with alcoholic potassium hydroxide.

[With C. VIZZINI.]—The corresponding 3-*p*-nitrophenyl compounds have m. p. : *acid*, 248—250°; *ethyl* ester, 166—167°; *pyrazole*, 153—155°; and *azoxy*-compound, 285°. In the preparation of the ester a secondary *product*, m. p. 142—145°, is obtained.   E. W. WIGNALL.

Action of diazonium salts on 6-hydroxy-2 : 5-dimethylpyrazine. III. G. GASTALDI and E. PRINCIVALLE (Gazzetta, 1928, **58**, 679—682).—The behaviour of 6-hydroxy-2 : 5-dimethylpyrazine (A., 1921, i, 602) when treated with phenyl- or *o*- or *p*-tolyl-diazonium chloride is normal, the products being the corresponding stable, yellow azo-compounds of the constitution, $N\!\!<\!\!{CMe-C(OH) \atop C(\cdot N_2R):CMe}\!\!>\!\!N$. The ease with which this occurs indicates that the pyrazine reacts in the lactimic form, but it is possible that, in its reaction with alkyl halides, the first products are *O*-ethers, which are afterwards transformed into the *N*-derivatives (A., 1928, 1027). The product of the coupling of 6-hydroxy-2 : 5-dimethylpyrazine with *p*-nitrobenzenediazonium chloride has not the characters of the azo-compounds.

3-*Benzeneazo-6-hydroxy-2 : 5-dimethylpyrazine*, m. p. 208° (decomp.), and its *sodium* salt; 3-*p-tolylazo-6-hydroxy-2 : 5-dimethylpyrazine*, m. p. 242° (decomp.), and its *sodium* salt; 3-*o-tolylazo-6-hydroxy-2 : 5-dimethylpyrazine*, m. p. 221° (decomp.), and its *sodium* salt are described.   T. H. POPE.

Fluorindenes. X. Derivatives of fluorindene and triphendioxazine. F. KEHRMANN and C. COLLAUD (Helv. Chim. Acta, 1928, **11**, 1028—1034). —When a mixture of 2 : 3-dihydroxy-6-acetamidonaphthaphenazine (A., 1925, i, 1331), *o*-aminodiphenylamine hydrochloride, and benzoic acid is boiled for about 3 min. 6-*acetamidophenylnaphtha-*

phenfluorindene is obtained. When the diamine is replaced by phenyl-1 : 2-naphthylenediamine and 4-acetamido-1 : 2-naphthylenediamine the products formed are 6-*acetamidophenyldinaphthafluorindene* and *diacetamidodinaphthafluorindene*, respectively.

Dihydroxythymoquinone and *o*-phenylenediamine react under the above conditions giving *dihydroxythymophenazine* (I), decomp. about 240° (*acetyl* derivative, m. p. 197°), whilst with *o*-aminophenol *hydroxythymophenazoxone* (II), m. p. 197° (*acetyl* derivative, m. p. 133°), is formed.
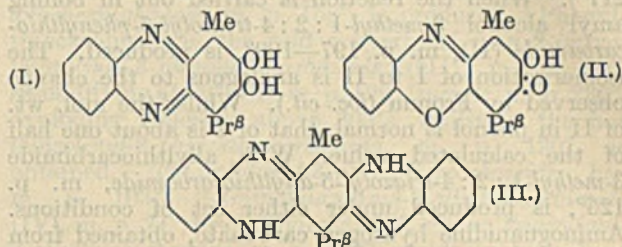
When the quinone, *o*-phenylenediamine, and anthracene are boiled together the product is *thymofluorindene* (III). With *o*-aminophenol hydrochloride in presence of benzoic acid there are formed II and *methyl*iso*propyltriphendioxazine* (in III, NH=O).

2 : 3-Dihydroxynaphthaphenazine and hydroxy*iso*rosindone react with *o*-aminophenol yielding *naphthaphenazineoxazine* and its N-*phenyl* derivative, respectively.   H. BURTON.

Carbocyanine dyes with substituents attached to the three-carbon chain. F. M. HAMER (J.C.S., 1928, 3160—3163).—The condensation of 1-methylbenzthiazole ethiodide and ethyl orthoacetate in the presence of pyridine (or, with less success, acetic anhydride) gave 8-*methyl-2 : 2′-diethylthiocarbocyanine iodide* (I), decomp. about 280° and m. p. about 290°, which, in alcoholic solution, showed an absorption
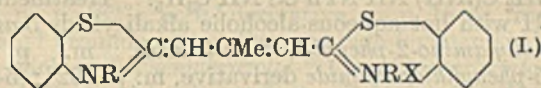
band at λ 5400 Å. with a weaker one at λ 5100 Å. In gelatinobromide emulsions the dye was a powerful sensitiser, showing maxima at λ 5900 and 5200 Å.

Similarly, 1-methylbenzthiazole methiodide gave 2 : 2′ : 8-*trimethylthiocarbocyanine iodide*, m. p. about 298° (decomp.), with maximum absorption in alcoholic solution at λ 5400 Å., and 1-methylbenzthiazole allobromide yielded 8-*methyl-2 : 2′-diallylthiocarbocyanine bromide*, m. p. 260° (decomp.), with principal absorption maximum in alcohol at λ 5450 Å.
                      R. J. W. LE FÈVRE.

Reactions between phenanthraquinone and magnesylpyrroles. Q. MINGOIA (Gazzetta, 1928, **58**, 673—679).—Phenanthraquinone reacts similarly to anthraquinone (A., 1926, 1158) with magnesylpyrrole, but the dipyrrylphenanthrol formed immediately loses $2H_2O$ from the tertiary alcoholic hydroxyl groups and the iminic hydrogen atoms, giving 9 : 10-*dipyrrolenyldihydrophenanthrene*, m. p. 190°. With magnesylmethylketole, phenanthraquinone reacts similarly to anthraquinone (cf. A., 1927, 158), giving 9 : 10-*tetra-(2′-methyl-3′-indolyl)di-*

hydrophenanthrene, m. p. 154°, which forms a *tetra-acetyl* compound, m. p. 170°.   T. H. POPE.

Reaction between triazoles and thiocarbimides. P. FANTL and H. SILBERMANN (Annalen, 1928, **467**, 274—287; cf. Fromm and others, A., 1926, 716; this vol., 199).—5-Amino-3-methyl-1 : 2 : 4-triazole reacts with phenylthiocarbimide in cold alcoholic solution forming 5-*amino-3-methyl-1 : 2 : 4-triazolyl-2-phenylthiocarbamide* (I), m. p. 137°, resolidifying with m. p. 197—199° (*picrate*, m. p. 217°). When the reaction is carried out in boiling amyl alcohol 3-*methyl-1 : 2 : 4-triazolyl-5-phenylthio-carbamide* (II), m. p. 197—199°, is produced. The isomerisation of I to II is analogous to the change observed by Fromm (*loc. cit.*). Whilst the mol. wt. of II in phenol is normal, that of I is about one half of the calculated value. With allylthiocarbimide 3-*methyl-1 : 2 : 4-triazolyl-5-allylthiocarbamide*, m. p. 125°, is produced under either set of conditions. Aminoguanidine hydrogen carbonate, obtained from disodium cyanamide and hydrazine in presence of sulphuric acid and subsequent treatment with potassium hydrogen carbonate, is converted by phenylthiocarbimide in alcoholic solution into 5-amino-3-thio-4-phenyl-1 : 2 : 4-triazole, m. p. 264° (cf. Arndt and others, A., 1922, i, 375) (*benzyl* derivative, m. p. 172°; *dibenzyl* derivative, m. p. 137°; *tribenzoyl* derivative, m. p. 138°). 5-Amino-3-methyl-thiol-4-phenyl-1 : 2 : 4-triazole and phenylthiocarb-imide yield a *compound*, $C_{23}H_{24(22)}N_8S_2$, m. p. 204°. *Anilinoguanidinophenylthiocarbamide*, m. p. 167°, is identical with the product from phenylthiuret and phenylhydrazine (Fromm and Vetter, A., 1907, i, 982). Allylthiocarbimide and anilinoguanidine give a mixture of *anilinoguanidinoallylthiocarbamide* (III), m. p. 128°, and a *compound*, $C_{11}H_{12}N_4S$, m. p. 204° (decomp.), either a triazole or a thiodiazole, formed presumably from the intermediate $NH_2 \cdot C(:NH) \cdot NH \cdot NPh \cdot CS \cdot NH \cdot C_3H_5$. Treatment of III with hot aqueous-alcoholic alkali yields 5-*amino-3-allylamino-2-phenyl-1 : 2 : 4-triazole*, m. p. 74° (5-*phenylthiocarbimide* derivative, m. p. 192°; 5-*allyl-thiocarbimide* derivative, m. p. 120°). 1-*Phenyl-1 : 2 : 4-triazolyl-5-phenylthiocarbamide*, m. p. 128°, 2-*phenyl-3-methyl-1 : 2 : 4-triazolyl-5-phenylthiocarb-amide*, m. p. 181°, and -5-*allylthiocarbamide*, m. p. 158°, are described.

Acetamidoguanidine nitrate as an extremely sensi-tive reagent for tervalent iron. A deep violet color-ation is produced with 0·01 mg. and a perceptible coloration with 0·001 mg. The coloration is obtained in presence of other cations, phosphate, or acetate, but is prevented by glycerol or tartaric acid.   H. BURTON.

Catalytic hydrogenation of hæmins and por-phyrins. R. KUHN and C. SEYFFERT (Ber., 1928, **61**, [B], 2509—2516; cf. A., 1927, 784).—Hæmin can be hydrogenated in aqueous-alkaline or pyridine solution in presence of various contacts in such a manner that addition ceases after absorption of 1 mol. of hydrogen (usually 10% less than this amount). Lower values indicate unfavourable conditions which may be due to catalyst or hæmin. Under the experi-mental conditions, particularly with platinum metals deposited on carriers, a favoured stage of hydrogen-

ation of the hæmin molecule appears to be attained with the introduction of 2 atoms of hydrogen. Spectro-scopical examination of the hydrogenated hæmin solutions does not indicate the presence of a consider-able proportion of mesohæmin, so that the production of this compound accounts for only a fraction of the hydrogen absorbed. The main amount is not absorbed by the unsaturated side-chain of hæmin. Mesoporphyrin, in which the side-chains are saturated, can be hydrogenated by the same contacts which change hæmin into dihydrohæmin. Mesoporphyrin dihydrochloride in glacial acetic acid does not become changed spectroscopically and the reaction product is identical with the original material. This is true also of mesoporphyrin dimethyl ester, so that it is concluded that the adsorbed hydrogen is only very loosely united and is removed by contact with atmo-spheric oxygen. In certain cases, dihydrohæmins appear to behave analogously. Formation of por-phyrinogens, previously achieved only with sodium amalgam or with hydriodic acid and phosphonium iodide, can be effected catalytically by use of platinum oxide in glacial acetic acid; the isolated products from mesoporphyrin dihydrochloride and mesopor-phyrin dimethyl ester are identical with the original materials. Protoporphyrin dimethyl ester is hydro-genated to a leuco-compound with about 5 mols. of hydrogen in presence of platinum oxide and the product is oxidised to mesoporphyrin dimethyl ester, addition occurring thus in the side-chain and the methine bridges.   H. WREN.

Addition of bromine to protoporphyrin di-methyl ester and to its complex zinc salt. W. KÜSTER and A. GROSSE (Z. physiol. Chem., 1928, **179**, 117—138).—The acetylene (A) and vinyl (V) side-chains of protoporphyrin dimethyl ester may exist as such or may form a conjugated ring system, $CH_2 \cdot C \cdot CH \cdot CH \cdot$. These would give the same product after addition of chlorine and hydrobromic acid only if the pyrrole nuclei attached are identical.

Bromination of protoporphyrin dimethyl ester gave a bluish-black product, *A-*(αβ-)*V-*(αβ-)*tetrabromo-protoporphyrin ester*, $C_{36}H_{36}O_4N_4Br_4$, showing three bands in the spectrum at 590, 565—545, 530—515 μμ. On treatment with methyl alcohol a bluish-black, crystalline substance, *A-α-V-β-dibromo-A-β-V-α-di-methoxyprotoporphyrin dimethyl ester*, showing bands at 620—610, 580—560, 540—525, 515—490 μμ, was obtained. When the dibromo-product was treated with zinc acetate in methyl alcohol the methyl was replaced by zinc in the group −CH:CH·OMe in the doubled molecule $(C_{37}H_{37}O_6N_4Br_2Zn)_2Zn$. Similar treatment of tetramethylhæmatoporphyrin gave the *salt* $C_{38}H_{42}O_6N_4Zn$, absorption bands, 585—570, 550—530 μμ. Hydrolysis with aqueous sodium hydr-oxide removed the two ester methyl groups. On heating the complex zinc salt of tetramethylhæmato-porphyrin with methyl-alcoholic zinc acetate one methyl ether group was hydrolysed and the methyl replaced by a zinc half atom $(C_{37}H_{39}O_6N_4Zn)_2Zn$.

Oxidation of dibromodimethoxyprotoporphyrin ester with chromic anhydride gave the imide, $NH \big\langle \begin{smallmatrix} CO \cdot CMe \\ CO \cdot C \cdot CHMe \cdot CH_2Br \end{smallmatrix}$.   Potassium cyanide with

tetrabromoprotoporphyrin dimethyl ester gave bluish-black *dibromodicyanoprotoporphyrin ester*, with bands at 610—600, 580—560, 540—530, 515—495 μμ. Hydrolysis gave *A-α-V-β-dibromo-A-β-V-α-dicarboxymethylprotoporphyrin dimethyl ester*, absorption bands, 610—600, 570—560, 540—530, 575—490 μμ. The *zinc* salt showed two absorption bands 590—570, 560—530 μμ. Reduction with hydriodic acid and red phosphorus gave *bromomethoxydicarboxymethylprotoporphyrin dimethyl ester*, absorption bands 610—600, 570—560, 535—525, 510—485 μμ. The complex zinc salt of protoporphyrin dimethyl ester was brominated. The *tetrabromo*-derivative, $C_{36}H_{36}O_4N_4Br_4Zn$, showed a 4-banded spectrum, 580, 570—540, 530, 510—490 μμ. Hydrobromic acid was removed by methyl alcohol, and the whole of the bromine by boiling with secondary sodium phosphate, giving a *product*, $C_{34}H_{26}O_4N_4Zn$; spectrum bands 570—550, 540—520 μμ. The complex copper salt of protoporphyrin ester on bromination gave a *product*, $C_{36}H_{34}O_4N_4Br_4Cu$, with bands at 580, 560—555, 530, and 510—490 μμ; the chloro-ferric salt gave a *product*, $C_{36}H_{33}O_4N_4FcClBr_4$, a metallic powder. J. H. BIRKINSHAW.

Tautomerism of some heterocyclic compounds [oxazolines, thiazolines]. E. FROMM and R. KAPELLER-ADLER [with W. FRIEDENTHAL, L. STANGLER, J. EDLITZ, E. BRAUMANN, and J. NUSSBAUM] (Annalen, 1928, 467, 240—274).—An extension of the work on the tautomerism of amino-oxazolines (A., 1926, 716). Aminothiazolines react with thiocarbimides, yielding two series of thiocarbamides according to the conditions. No tautomerism is found in either the thiazole, oxazole, or triazole series, in the first two cases presumably because of the aromatic nature of the ring systems. When 2-amino-5-chloromethyloxazoline (I) is heated with ammonium chloride (2 parts) and alcohol in a sealed tube at 100°, β-*chloro-β'-guanidino*isopropyl alcohol hydrochloride, m. p. 112° (*picrate*, m. p. 147°), is obtained. The *tribenzoyl* derivative, m. p. 178°, of the base is identical with the compound previously described (A., 1925, i, 594) as 2-amino-5-aminomethyliminazoline tetrabenzoate. When I is heated with dilute ammonia at 100° there is formed 2-amino-5-aminomethyloxazoline (*picrate*, m. p. 172°; *chloroplatinate*). Benzenesulphonylation of I yields 2-*imino-5-chloromethyloxazolinyl-3-benzenesulphonate*, m. p. 111° (*2-benzoyl* derivative, m. p. 152°), hydrolysed by cold dilute sulphuric acid to 5-*chloromethyloxazolidonyl-3-benzenesulphonate*, m. p. 106°. Benzenesulphonylation of the reaction product from disodium cyanamide and monochlorohydrin gives the *tribenzenesulphonyl* derivative, m. p. 158°, of 2-amino-5-hydroxymethyloxazoline. Sodium cyanamide and propylenechlorohydrin react, forming 2-*amino-5-methyloxazoline* (*dibenzoyl* derivative, m. p. 75°), which with phenylthiocarbimide gives 2-*imino-5-methyloxazolinyl-3-phenylthiocarbamide*, m. p. 98°. When this is heated at its m. p. or in alcoholic solution 5-*methyloxazolinyl-2-phenylthiocarbamide*, m. p. 152°, is formed, whilst dilute sulphuric acid converts it into 5-*methyloxazolidonyl-3-phenylthiocarbamide*, m. p. 114°. Similar tautomerism is exhibited by 2-*amino-5-benzylthiolmethyloxazoline*, m. p. 92° (*dibenzoyl* derivative, m. p. 112°), from I and benzylmercaptan, which gives

2-*imino-5-benzylthiolmethyloxazolinyl-3-phenyl*-, m. p. 89°, and *-3-allyl-thiocarbamides*, m. p. 87°. These last compounds are hydrolysed to 5-*benzylthiolmethyloxazolidonyl-3-phenyl*-, m. p. 107°, and *-3-allyl-thiocarbamides*, m. p. 59°, and converted as above into 5-*benzylthiolmethyloxazolinyl-2-phenyl*-, m. p. 129°, and *-2-allyl-thiocarbamides*, m. p. 100°, respectively.

p-Toluenesulphonylation of aminothiazoline (II) (Gabriel, A., 1889, 870) (*dibenzoyl* derivative, m. p. 182°) affords 2-*iminothiazolinyl 3-p-toluenesulphonate*, m. p. 143°, since on hydrolysis *thiazolidonyl* 3-p-*toluenesulphonate*, m. p. 158°, is produced. Phenylthiocarbimide in the cold converts II into 2-*iminothiazolinyl-3-phenylthiocarbamide* (III), m. p. 60°, resolidifying at 80° with m. p. 129° (*picrate*, m. p. 230°, exploding violently above 300°), whilst in the hot *thiazolinyl-2-phenylthiocarbamide*, m. p. 130°, is obtained. *Thiazolidonyl-3-phenylthiocarbamide* has m. p. 103°. 2-*Iminothiazolinyl-3-allylthiocarbimide* (IV), m. p. 71°, resolidifying at 79°, giving *thiazolinyl-2-allylthiocarbamide*, m. p. 143°, yields on hydrolysis *thiazolidonyl-3-allylthiocarbamide*, m. p. 111°. Determinations of the mol. wt. of III and IV in phenol give values which are approximately one half of the theoretical, indicating that they are additive compounds. This possibility is discounted by the formation of thiazolidones by hydrolysis, and also by the observation that diphenylmethylthiocarbamide gives a similar low value. 2-Amino-5-phenylthiazole (Hantzsch and Traumann, A., 1889, 414) (*benzoyl* derivative, m. p. 124—125°; *benzylidene* derivative, m. p. 127°; p-*toluenesulphonyl* derivative, m. p. 150°) does not react with phenylthiocarbimide in the cold, but in the hot yields 5-*phenylthiazolyl-2-phenylthiocarbamide*, m. p. 213°. 2-Amino-5-methylthiazole (*dibenzoyl* derivative, m. p. 110°) gives 5-*methylthiazolyl-2-phenyl*-, m. p. 172°, and *-2-allyl-thiocarbamides*, m. p. 178°, under all conditions.

2-*Amino-5-phenyloxazole*, m. p. 216° (*benzoyl* derivative, m. p. 182°; *acetyl* derivative, m. p. 184°), from phenacyl bromide and sodium cyanide (cyanamide?), also yields 5-*phenyloxazolyl-2-phenylthiocarbamide*, m. p. 195°, as the sole product. 3-Amino-5-anilino-1-phenyl-1 : 2 : 4-triazole (A., 1907, i, 982) (*monobenzoyl* derivative, m. p. 105°) and phenylthiocarbimide give the corresponding 3-*phenylthiocarbamide*, m. p. 194° (3-*allylthiocarbamide*, m. p. 191°). 3-Amino-5-anilino-1 : 2 : 4-triazole, m. p. 163° (cf. A., 1922, i, 378), obtained from hydrazine hydrate and phenyl-ψ-benzylcyanothiocarbamide (A., 1895, i, 461), furnishes the corresponding 3-*phenylthiocarbamide*, m. p. 203° (3-*allylthiocarbamide*, m. p. 133°). The *phenyl*- and *allyl*-*thiocarbamido*-derivatives of phenylguanazole (Pellizzarri, A., 1892, 356) have m. p. 252° and 220°, respectively. 3-Amino-5-thiol-1-phenyl-1 : 2 : 4-triazole affords the 3-*phenylthiocarbamide*, m. p. 264°. The *phenylthiocarbamides* from 3-amino-5-benzylthiol-, 3-amino-5-methylthiol-, and 5-amino-3-benzylthiol-1-phenyl-1 : 2 : 4-triazoles (*dibenzoyl* derivative, m. p. 125°) have m. p. 188°, 178°, and 154°, respectively, whilst the corresponding *allylthiocarbamides* have m. p. 129°, 138°, and 138°, respectively. Phenylhydrazine reacts with dimethyl cyanamidodithiocarbonate (Hantzsch and Wolvekamp, A., 1904, i, 718) forming 5-*amino-3-methylthiol-1-phenyl-1 : 2 : 4-triazole*, m. p.

105° (*benzoyl* derivative, m. p. 118°), whilst dibenzyl cyanamidodithiocarbonate and hydrazine hydrate give 3-*amino*-4(5?)-*benzylthiotriazole*, m. p. 109° (*hydrochloride*, m. p. 100°, ; *dibenzoyl* derivative, m. p. 148°). 5-*Benzylthioltriazolyl-3-phenyl-* and -3-*allyl-thiocarbamides* have m. p. 155° and 116°, respectively. The p-*toluenesulphonyl* derivative of 3-amino-5-methyl-thiol-1-phenyl-1 : 2 : 4-triazole (*sulphone* derivative, m. p. 304° not sharp) has m. p. 142°. Oxidation of 3-amino-5-benzylthiol-1-phenyl-1 : 2 : 4-triazole with potassium permanganate in acetic acid solution gives a *substance*, $C_{30}H_{24}N_8S_2$, m. p. 140°.

Ethylenediamine and allylthiocarbimide react yielding αβ-*di(allylthiocarbamido)ethane*, m. p. 102°, which when treated with bromine in cold chloroform solution affords αβ-*di-(5-bromomethyl-2-thiazolinyl-amino)ethane* (annexed formula, X=Br), m. p. 161°. Moist silver oxide converts this into the *glycol* (X=OH), m. p. 108°. The corresponding *dinitrile* and *dicarboxylic acid* have m. p. 118° and 147°, respectively. αβ-*Di-(5-methylene-2-thiazolinylamino)-ethane*, m. p. 153°, is obtained by the action of alcoholic potassium hydroxide on the above bromo-compound. The 1 : 4-*diphenylthiocarbimide* (*dibenzyl* derivative, m. p. 102°) and 1 : 4-*diallylthiocarbimide* (V) deriv-atives of piperazine have m. p. 263° and 153°, respec-tively. Treatment of V with bromine in chloroform solution yields 1 : 4-*di-(5-bromomethyl-2-thiazolinyl)-piperazine*, m. p. 156° [*di*-(5-p-*tolylmethyl*) derivative, m. p. 135°], which with alcoholic potassium hydroxide gives the corresponding *di*-(5-*methylene*) derivative, m. p. 166°. Hydrobromic acid (*d* 1·49) at 100° under pressure converts V into 1 : 4-*di*-(5-*methyl-2-thiazolinyl*)-*piperazine*, m. p. 280°. H. BURTON.

Aldehyde condensations with diphenyl*iso*thio-hydantoin. S. S. KINGSBURY and K. S. MARKLEY (J. Washington Acad. Sci., 1928, **18**, 558—561).— The following condensation products have been obtained from the appropriate aldehydes by the method previously described (Hann and Markley, A., 1926, 623) : 5-o-*Methoxybenzylidene-*, m. p. 296—297°; 5-p-*anisylidene-*, m. p. 199°; 5-*veratrylidene-*, m. p. 177—178°; 5-*piperonylidene-*, m. p. 232°; 5-p-*tolyl-idene-*, m. p. 197—198°; 5-p-*hydroxybenzylidene-*, m. p. above 300°; 5-o-*chlorobenzylidene-*, m. p. 234—235°; and 5-m-*nitrobenzylidene-*, m. p. 219—220°, -2 : 3-*di-phenyliso*thiohydantoin.

s-Trinitrobenzaldehyde and β-phenylpropaldehyde did not undergo the reaction, nor did *iso*butaldehyde or citronellal; citral yielded 5-*citrylidene*-2 : 3-*diphenyl-iso*thiohydantoin, m. p. 230°. E. W. WIGNALL.

[**Simplified method for the preparation of substituted μ-methylbenzthiazoles and their transformation into new, heterocyclic poly-methine dyes.**] R. SCHULOFF, R. POLLAK, and E. REISZ (Ber., 1928, **61**, [*B*], 2538—2541).—An account of work not yet completed, induced by the com-munication of König (A., 1928, 1385).

[With M. HOPMAYER.]—5-Chloro-2-methylbenz-thiazole, m. p. 68°, is prepared by reducing 4 : 4'-di-chloro-2 : 2'-dinitrodiphenyl disulphide with zinc dust and hydrochloric and acetic acids, followed by treat-ment of the zinc mercaptide with acetyl chloride. The chlorothiazole is converted by methyl sulphate into the *methosulphate*, m. p. 217°, which with p-dimethyl-aminobenzaldehyde affords the polymethine *dye*, m. p. 245°. 6-Chloro-2 : 4-dimethylbenzthiazole, m. p. 79°, is analogously prepared from the product of the action of sulphur chloride on o-toluidine hydrochloride. 6-Ethoxy-2-methylbenzthiazole, m. p. 56°, gives an *ethiodide*, m. p. 156°, and *amyliodide*, m. p. 232°. The ethiodide condenses with anisaldehyde, o-methoxy-benzaldehyde, and p-dimethylaminobenzaldehyde, giving polymethine *dyes*, m. p. 231°, 231—232°, and 257°, respectively; with cinnamaldehyde and m-nitro-benzaldehyde, *dyes*, m. p. 219—220° and 211°, respectively, are obtained. H. WREN.

Microchemical reactions of theobromine. M. WAGENAAR (Pharm. Weekblad, 1929, **66**, 1—5).—The crystal forms and optical properties of the precipitates obtained with the usual reagents are described. Iodine and bromine solutions, and potassium bismuth and potassium antimony iodides all give precipitates with solutions of 1 part of theobromine in 1000 parts, and will detect 1—2 μg. (0·001—0·002 mg.). S. I. LEVY.

Microchemical reactions of caffeine. M. WAGE-NAAR (Pharm. Weekblad, 1928, **65**, 1334—1339).— The nature of the crystalline precipitates obtained with the common alkaloid reagents is described. The most sensitive test is the salting out from aqueous solution by addition of ammonium phosphate, by which caffeine may be detected at a dilution of 1 : 5000. S. I. LEVY.

Lupinine. P. KARRER, F. CANAL, K. ZOHNER, and R. WIDMER (Helv. Chim. Acta, 1928, **11**, 1062—1084; cf. Schopf, A., 1928, 1144).—Details are given for the extraction of lupinine (283 g.) and sparteine sulphate (255 g.) from yellow lupin (100 kg.). Lupinine methiodide (Willstätter and Fourneau, A., 1902, i, 557) when converted into the meth-hydroxide and then distilled yields *methyl-lupinine*, $C_{10}H_{18}ONMe$, b. p. 140—143°/12—13 mm. (this and the compounds subsequently derived from it are probably mixtures of isomerides), reduced by hydrogen and platinum-black to *dihydromethyl-lupinine*, b. p. 136—141°/12 mm. Conversion of this into the *methiodide* gives a solid, m. p. 202—203° (30%), and oily fractions (63%), the mixture being converted as above into *dihydro-dimethyl-lupinine*, b. p. 140—145°/11—12 mm., re-duced to *tetrahydrodimethyl-lupinine* (I), b. p. 140—148°/10—11 mm. The *meth-hydroxide* from this is decomposed by distillation to a mixture of I and a mixture of unsaturated alcohols (II), b. p. 86—101°/10—11 mm., *d* 0·838, $α_D$ +0·34° (0·25 dm. tube), of the composition $C_{10}H_{19}\cdot OH$. Oxidation of this with zinc permanganate gives the corresponding glycols, further oxidised by chromic anhydride and sulphuric acid, yielding small amounts of formic acid and the *lactone*, $C_9H_{16}O_2$, b. p. 253—255°, probably β-hydroxymethyl-octoic acid lactone, thus indicating that II contains δ-hydroxymethyl-Δ^a-nonene. Reduction of II to the saturated *alcohols*, b. p. 95—103°/11 mm., $α_D$ +0·39—0·32° (in 0·25 dm. tube), and treatment of these with phosphorus pentabromide gives δ-*bromomethylnonane* (III), b. p. 100—102°/11 mm., $[α]_D^{20}$ −3·01°. Re-

duction of III by zinc dust and alcohol containing a trace of platinic chloride and finally with hydrogen and platinum affords δ-*methylnonane*, b. p. 54°/12 mm., d 0·723, $[\alpha]_D^{18}$ about −1·3°. Trimethylamine converts III into the corresponding quaternary *ammonium bromide*, m. p. 167—170°, still optically active, but δ-*methylenenonene* (IV), b. p. 53—54°/11 mm., obtained with δ-*dimethylaminomethylnonane*, b. p. 88—89°/11 mm., by distillation of the quaternary ammonium hydroxide is optically inactive. Treatment of IV with ozone gives formaldehyde and n-*propyl* n-*amyl ketone*, b. p. 76—77°/12 mm. (*semicarbazone*, m. p. 60—61°), synthesised from hexoyl chloride and zinc n-propyl iodide. The Beckmann rearrangement of n-*propyl* n-*amyl ketoxime*, b. p. 119°/15 mm., gives n-amylamine and butyric acid. n-*Amyl* iso*propyl ketone*, b. p. 82°/15 mm. (*semicarbazone*, m. p. 75°), and *methyldiethylamine picrate*, m. p. 168°, are described.
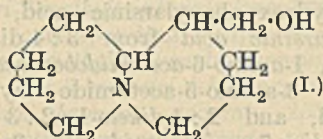
Lupinine is represented best by (I), whilst sparteine is formulated as a condensation product of 1 mol. of lupinine and 1 mol. of piperidine.   H. BURTON.

Alkaloids from *Carnegia gigantea* (Engelm.). Britt. and Rose (*Cereus giganteus*, Engelm.). G. HEYL (Arch. Pharm., 1928, **266**, 668—673).—The only isolable alkaloid from this cactus is *carnegine*, $C_{13}H_{19}O_2N$, a strongly alkaline syrup, the following derivatives of which are described; *hydrochloride* (H_2O), m. p. 207°; *hydrobromide*, m. p. 228°; double *salt* with mercuric chloride, $C_{13}H_{19}O_2N,HgCl_2,HCl$; *chloroaurate*; *chloroplatinate*. The base contains two methoxyl groups; the salts. which contain one equivalent of acid, are optically inactive. Carnegine resembles lophophorine in physiological action but is not identical with it.   S. COFFEY.

Synthesis of bases of berberine type from compounds of the type of tetrahydropapaverine. E. SPÄTH and E. KRUTA (Monatsh., 1928, **50**, 341—348).—All the known natural alkaloids of berberine type contain alkyloxy-groups in the positions 3 and 4 in the skeleton formula II (X or Y=OMe, or XX or
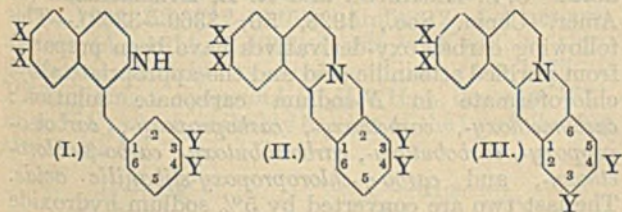
YY=O_2CH_2). The hypothesis has been put forward that such bases are formed in the plant from bases of tetrahydropapaverine type (I) by condensation with formaldehyde in the 2-position to the tetrahydro-derivative (II), which may then be oxidised to the quaternary base. Attempts to carry out syntheses of this nature have, however, always led to derivatives of type III by closure in the 6-position, viz., tetrahydro-ψ-berberine (XX=O_2CH_2, Y=OMe) (Haworth, Per-

kin, and Rankin, A., 1924, i, 1098), norcoralydine (X and Y=OMe) (Pictet and Chou, A., 1916, i, 418), and coralydine (Pictet and Malinowski, A., 1913, i, 1224). It is now shown, however, that the tetra-hydroxy-derivative, tetrahydropapaveroline (I, X and Y=OH), condenses with formaldehyde to give bases of types II and III in equal amount. It follows, therefore, that the original hypothesis still holds good if it is assumed that in the plant ring-closure occurs before alkylation.

Repetition of the synthesis of norcoralydine as described by Pictet and Chou (*loc. cit.*) gave only 46% yield of the base, m. p. 151·5—152·5° (Pictet and Chou give 80—85%, m. p. 157—158°). The yield was improved to 69% by condensing tetrahydropapaverine in hydrochloric acid with formaldehyde (2 mols.) in a sealed tube at 100°. In neither case could any trace of tetrahydropalmatine be detected. Tetrahydro-papaveroline was condensed with formaldehyde under similar conditions and the product treated with diazomethane. By careful fractionation of the product norcoralydine and tetrahydropalmatine were separated in equal amounts and in a total yield of 15%, the poorness of the yield being attributed to the unsatis-factory course of the methylation.   R. K. CALLOW.

Strychnine and brucine. VIII. R. CIUSA (Gazzetta, 1928, **58**, 774—775).—The preparation of O-acetyl*iso*strychnine by Oxford, Perkin, and Robin-son (A., 1927, 1208) confirms the presence of a hydroxyl group in *iso*strychnine, of which the author has prepared a benzoyl derivative (cf. A., 1920, i, 176).
                                E. W. WIGNALL.

Micro-crystallographic identification of yoh-imbine. G. DENIGÈS (Mikrochem., 1928, **6**, 113—115).—Yohimbine may be identified by the character-istic micro-crystalline structure of the free base and the hydrochloride. Further confirmation is obtained by addition of a drop of a solution of silver nitrate and a drop of a solution of sodium carbonate to a solution of the substance in a drop of ammonia. With yohimbine a yellowish-brown micro-crystalline mass is obtained.   J. S. CARTER.

Alkaloids of Indian aconites. II. ψ-Acon-itine. T. M. SHARP (J.C.S., 1928, 3094—3106).—Two reactions of aconitine (cf. Dunstan and Carr, J.C.S., 1894, **65**, 176, and later papers) are applied to ψ-aconitine. ψ-Aconitine, when heated in a sealed tube with methyl alcohol, gives *veratroyl-methyl-ψ-aconine*, m. p. 206—207°, $[\alpha]_D$ +29·8° [*hydro-chloride*, m. p. 249—250° (decomp.), $[\alpha]_D$ −3·41° (in water), + 0·38° (in alcohol); *hydrobromide mono-hydrate*, m. p. 237—238° (efferv.), $[\alpha]_D$ +2·15°], which, by acetylation with acetic anhydride, leads to *mono-acetylveratroylmethyl-ψ-aconine perchlorate*, m. p. 240—242°, whilst with acetyl chloride *diacetylveratroyl-methyl-ψ-aconine*, m. p. 160°, $[\alpha]_D$ +18·43°, is obtained. Similarly, tetra-acetyl-ψ-aconine with methyl or ethyl alcohol gives only *triacetylmethyl-ψ-aconine*, m. p. 280—282°, $[\alpha]_D$ −18·5°, or *triacetylethyl-ψ-aconine*, m. p. 171°, $[\alpha]_D$ −26°. The last compound, on hydrolysis, gives *ethyl-ψ-aconine*, syrup.

·ψ-Aconitine when heated above its m. p. loses acetic acid, giving crystalline *pyro-ψ-aconitine* (I),

m. p. 132—135°, [α]$_{\rm D}^{16}$ +175·2°, which is considered to contain a bridged linking, since ψ-aconitine is now shown to contain two hydroxyl groups [acetylation gives *diacetyl-ψ-aconitine*, m. p. 229° (decomp.), [α]$_{\rm D}$ +24·0°; *monoacetyl-ψ-aconitine perchlorate*, m. p. 225—228° (efferv.); benzoylation gives only *mono-benzoyl-ψ-aconitine perchlorate*, m. p. 236° (efferv.)], and I not to possess a double linking, and also since tetra-acetyl-ψ-aconine when heated loses 1 mol. of acetic acid, giving *triacetylpyro-ψ-aconine*, m. p. 155—158°, [α]$_{\rm D}$ +156·4°, which by hydrolysis furnishes *pyro-ψ-aconine*, m. p. 172°, [α]$_{\rm D}$ +227·5°, identical with the hydrolysis product from I. Moreover, acetylation of I yields *triacetyldemethylpyro-ψ-aconitine*, m. p. 228°, [α]$_{\rm D}^{19·5}$ +28·4°, giving, on hydrolysis, a *demethylpyro-ψ-aconine* different from the analogous product obtained from I or its triacetyl derivative.

The results of Schulze and Liebner (A., 1917, i, 470) are discussed.   R. J. W. Le Fèvre.

Optical activity of ψ-morphine. A. K. Balls and W. A. Wolff (J. Biol. Chem., 1928, **80**, 403—411).—The optical activity of ψ-morphine increases with increasing concentration of the base and, to a smaller extent, of potassium ions, but diminishes with increasing hydroxyl-ion concentration; curves are given showing the quantitative relationships observed, which constitute the best available means of identifying the base.   C. R. Harington.

Optically active isomerides of N-phenyl-β-methylglycineamide-p-arsinic acid and their use in the resolution of ephedrine. E. Fourneau and V. Nicolitch (Bull. Soc. chim., 1928, [iv], **43**, 1232—1264).—α-Bromopropionamide, m. p. 120—121° (yield 81·7% from α-bromopropionyl bromide), with p-aminophenylarsinic acid gives N-phenyl-β-methylglycineamide-p-arsinic acid in 74% yield (cf. Jacobs and Heidelberger, A., 1920, i, 108) (*sodium* salt), resolved by using quinine into the l-*acid*, [α]$_{\rm D}^{20}$ −15·83°, the quinine salt of which crystallises first, and the d-*acid*, [α]$_{\rm D}^{20}$ +16·1°. Attempts at resolution with cinchonine and strychnine were unsuccessful. Both d- and l-N-phenyl-β-methylglycineamide-p-arsinic acid readily effect the resolution of ephedrine, the l-acid salt of d-ephedrine and the d-acid salt of l-ephedrine separating first in the two cases.

p-α-*Bromopropionamidophenylarsinic acid* is obtained (yield, 70%) from α-bromopropionyl bromide and p-aminophenylarsinic acid. *p*-Nitrophenylacetic acid, m. p. 149·5° (yield 65% on the nitrile), was converted through the chloride into p-nitrophenyl-α-bromoacetyl chloride or bromide, and thence into p-nitrophenyl-α-bromoacetamide, m. p. 148° (crude). The latter with p-aminophenylarsinic acid gave αα-*di*-p-*nitrophenyl-succinamide*, m. p. 212°, the negative result being probably due to the proximity of two negative groups to the bromine atom, since with phenyl-α-bromoacetamide normal condensation gives (yield 56%) *phenylphenylglycineamide*-p-*arsinic acid*. Attempts to resolve this with quinine failed. Propionyl chloride on bromination at 80° affords only α-bromopropionyl bromide, b. p. 153—155°, other chlorides behaving similarly with the exception of *iso*valeryl chloride and phenylacetyl chloride. *Diethylacetyl bromide* has

b. p. 153—158°, α-*bromodiethylacetyl bromide* b. p. 98—100°/25 mm., α-bromo*iso*valeryl bromide (from *iso*valeric acid, bromine, and phosphorus), b. p. 90°/10 mm., α-*bromoheptoyl bromide*, b. p. 135°/45 mm., α-*bromolauryl bromide*, b. p. 180°/45 mm., α-*bromo-p-phenylpropionyl bromide*, b. p. 160°/22 mm., phenylacetyl chloride, b. p. 102·3°/17 mm. (86% yield, using thionyl chloride, 97% with phosphorus trichloride), and bromophenylacetyl bromide, b. p. 150°/26 mm. (yield 84%).   R. Brightman.

Heterocyclic arsenic compounds. IV. Carbamido-derivatives of arylarsinic acids. R. W. E. Stickings (J.C.S., 1928, 3131—3134).—Sodium p-arsanilate reacted with an aqueous suspension of cyanogen bromide to form p-*carbamidophenylarsinic acid*. Similarly, 5-*carbamido-2-hydroxyphenylarsinic acid* was prepared from 5-amino-3-hydroxyphenylarsinic acid, 1-*aminobenzoxazole-4-arsinic acid* from 3-amino-4-hydroxyphenylarsinic acid, 2-*aminobenziminazole-5-arsinic acid* from 3 : 4-diaminophenylarsinic acid, 1-*amino-6-acetamidobenzoxazole-4-arsinic acid* from 3-amino-5-acetamido-4-hydroxyphenylarsinic acid, and 2 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydro*-1 : 3-*quinazoline-7-arsinic acid* from 3-amino-4-carboxyphenylarsinic acid.   R. J. W. Le Fèvre.

Heterocyclic arsenic compounds. V. Benziminazolearsinic acids. M. A. Phillips (J.C.S., 1928, 3134—3140).—The following compounds are described : 2-*methylbenziminazole*-5(6)-*arsinic acid nitrate*, 2 : 2′-*dimethyl*-5 : 5′-*arsenobenziminazole*, 5 : 5′-*arsenobenziminazole*, 2-*ethylbenziminazole*-5(6)-*arsinic acid* (*calcium* and *magnesium* salts), 2-α-*hydroxyethylbenziminazole*-5(6)-*arsinic acid* (*magnesium* salt), *benziminazole*-4(7)-*arsinic acid*, m. p. 277° (decomp.) (*calcium* and *magnesium* salts), 4 : 4′-*arsenobenziminazole*, 2-*methylbenziminazole*-4(7)-*arsinic acid*, m. p. 280—282° (*magnesium* and *calcium* salts), 2 : 2′-*dimethyl*-4 : 4′-*arsenobenziminazole*, 2-α-*hydroxyethylbenziminazole*-4(7)-*arsinic acid* (*magnesium* salt), 2 : 3-*dihydroxyquinoxaline*-6(7)-*arsinic acid*, m. p. above 300° (*mono*- and *di-sodium* salts; *calcium, barium,* and *magnesium* salts), 2 : 3-*dihydroxyquinoxaline*-5(8)-*arsinic acid*, m. p. above 300° (*calcium, barium,* and *magnesium* salts).   R. J. W. Le Fèvre.

Action of alkyl chloroformates on stibanilic acid. C. S. Hamilton and R. E. Etzelmiller (J. Amer. Chem. Soc., 1928, **50**, 3360—3363).—The following carbalkoxy-derivatives have been prepared from purified stibanilic acid and the appropriate alkyl chloroformate in N-sodium carbonate solution : *carbomethoxy-, carbethoxy-, carbopropoxy-, carboiso-propoxy-, carbobutoxy-, carboisobutoxy-, carbo-β-chloro-ethoxy-,* and *carbo-γ-chloropropoxy-stibanilic acids.* The last two are converted by 5% sodium hydroxide at 70° into p-β-*hydroxyethylaminophenylstibinic acid* and d-γ-*hydroxypropylaminophenylstibinic acid,* respectively. The products were analysed by a modification of Ewins' iodometric method for arsenic (J.C.S., 1916, **109**, 1356).   H. E. F. Notton.

Interactions of selenium oxychloride and phenols. G. T. Morgan and F. H. Burstall (J.C.S., 1928, 3260—3270).—Phenol and selenium oxychloride condensed in ether or chloroform solu-

tion to give *tri-4-hydroxytriphenylselenonium chloride*, m. p. 232° (decomp.) [*sulphate*, decomp. 269—270°; *bromide*, decomp. 237°; *nitrate*, m. p. 138—139° (decomp.); *chloroplatinate*, decomp. 244°; *methyl ether* (cf. Hilditch and Smiles, J.C.S., 1908, **93**, 1384) giving *tri-4-methoxytriphenylselenonium mercurichloride*, m. p. 68—70°], which, by dissolving in aqueous sodium hydroxide and reprecipitating by carbon dioxide yielded *tri-4-hydroxytriphenylselenonium oxide*, decomp. 240°; this, by the action of bromine, gave *tri-3-bromotri-4-hydroxytriphenylselenonium bromide*, m. p. 251°, and *tri-3 : 5-dibromotri-4-hydroxytriphenylselenonium bromide*, decomp. 261°.

An *isomeric trihydroxytriphenylselenonium chloride*, $(HO \cdot C_6H_4)_3, SeCl, 2H_2O$, decomp. 125°, was also isolated in the initial condensation.

Selenium oxychloride and *o*-cresol similarly yielded *tri-4-hydroxytri-3-methyltriphenylselenonium chloride*, decomp. 231° (corresponding *nitrate*, decomp. 224°), *tri-4-hydroxytri-3-methyltriphenylselenonium oxide*, decomp. 236°, *tri-5-bromotri-4-hydroxytri-3-methyltriphenylselenonium bromide*, decomp. 253°, and *di-4-hydroxydi-3-methyldiphenyl selenide*, m. p. 98—99°. *p*-Cresol led to *tri-2-hydroxytri-5-methyltriphenylselenonium chloride*, decomp. 260—265°, *tri-2-hydroxytri-5-methyltriphenylselenonium oxide*, decomp. 160°, *tri-3-bromotri-2-hydroxytri-5-methyltriphenylselenonium bromide*, decomp. 195°, *di-2-hydroxydi-5-methyldiphenyl selenide*, m. p. 111°, and *5-chloro-4 : 4'-dihydroxy-3 : 3'-ditolyl*, m. p. 129—130°. Resorcinol and selenium oxychloride produced *tri-2 : 4-dihydroxytriphenylselenonium chloride*, m. p. 206° (with acetone of crystallisation), whilst β-naphthol and selenium oxychloride gave *di-2-hydroxydi-1-naphthyl selenide*, m. p. 186°. From salicylic acid *di-4-hydroxydiphenyl selenide di-3-carboxylic acid*, sintering at 250° and decomp. 272°, was obtained.

The results indicate that two types of reaction may take place : $3RH \cdot OH + SeOCl_2 \longrightarrow (HO \cdot R)_3 SeCl + HCl + H_2O$ (*e.g.*, phenol, resorcinol) or $3RH \cdot OH + SeOCl_2 \longrightarrow Se(R \cdot OH)_2 + Cl \cdot R \cdot OH + HCl + H_2O$ (*e.g.*, naphthol and salicylic acid); both may occur concurrently (*e.g.*, o- and p-cresols).

R. J. W. LE FÈVRE.

Formation of a heterocyclic ring closed through mercury atoms. L. VECCHIOTTI (Gazzetta, 1928, **58**, 712—715).—Aniline 2 : 4-dimercuriacetate (A., 1914, i, 1063) reacts with sodium thiosulphate similarly to *o*-chloroaniline (A., 1925, i, 1058), giving a *compound*, $[C_6H_5NHg]_x$, decomp. 162°, m. p. 184°, which probably has one of the two following structures :
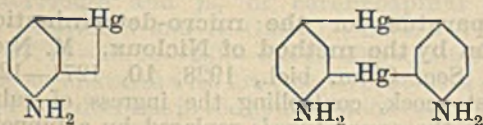
E. W. WIGNALL.

Mercuri-compounds from purine derivatives. II. [Caffeine.] L. ROSENTHALER (Arch. Pharm., 1928, **266**, 694—696; cf. A., 1924, i, 110).—When a solution of caffeine and mercuric acetate in dilute acetic acid is boiled for 2 days, *acetoxymercuricaffeine*,

sintering at 255°, slight decomp. 280°, unmelted at 300°, is formed. Potassium chloride, bromide, or thiocyanate solutions precipitate the corresponding mercuri-*compounds*, but potassium iodide converts acetoxymercuricaffeine into *mercuricaffeine*, $(C_8H_9N_4O_2)_2Hg$, m. p. above 340°. The acetoxymercuri-derivative furnishes sparingly soluble *compounds* with tartaric and salicylic acids. It is probable that the mercury atom is attached to the 8-carbon atom. S. COFFEY.

Serological differentiation of steric isomerides. K. LANDSTEINER and J. VAN DER SCHEER (J. Exp. Med., 1928, **48**, 315—320).—*l*- and *d*-Immune sera, obtained from *l*- and *d*-(*p*-aminobenzoylamino)-phenylacetic acids, diazotised and coupled with proteins, are specific. The *dl*-antigen reacts with both sera. The *d*- and *l*-immune sera also differentiate between the *d*- and *l*-acids when not combined with proteins. CHEMICAL ABSTRACTS.

Physico-chemical behaviour, as dissolved sodium salts, of electro-dialytically purified protein groups from pathological human blood- and exudate-plasma. I. and II. K. HARTL and W. STARLINGER (Z. ges. exp. Med., 1928, **60**, 289—314, 315—335; Chem. Zentr., 1928, ii, 459—460).—I. The isoelectric point of albumin is p_H 4·75, varying between 4·95 and 4·38; for globulin, 5·14 (5·35—4·95); for fibrinogen 4·81. The specific viscosities are 0·109, 0·160, 0·250, respectively, with marked deviations in both directions; specific refractions 0·00151, 0·00173, 0·00209. Similar protein fractions show marked differences in homogeneity. Nephelometry is not suitable for the volumetric investigation of plasma-protein.

II. The base-combination diminished irregularly within the protein concentration 1·4—12·3 g.-% with increasing concentration. The base-combining power diminished with increasing concentration of hydroxide, but considerable individual differences were observed in similar protein fractions. Differences were also observed in conductivity; hence the differences exhibited by the proteins in pathological conditions are very great. A. A. ELDRIDGE.

Spectrophotometric method of studying hæmoglobin and other coloured substances in solution. G. E. DAVIS (Proc. Iowa Acad. Sci., 1927, **34**, 279—280).—The spectrophotometric method for determining hæmoglobin in blood is fairly accurate. Irregularities in the shape of the spectral transmission curve for one of the absorption bands of oxyhæmoglobin were observed. CHEMICAL ABSTRACTS.

Hydrolysis of ovalbumin by trypsin in relation to the formation of diketopiperazines. A. BLANCHETIÈRE (Compt. rend., 1928, **188**, 112—113; cf. A., 1927, 269).—Hydrolysis of crude and denatured ovalbumin with trypsin at 38° and p_H 8·5 leads to the formation of about 38% of diketopiperazines in about 70 days. The reaction is more irregular in the case of the denatured protein, owing possibly to flocculation. G. A. C. GOUGH.

Mol. wt. of serum-albumin and of serum-globulin. T. SVEDBERG and B. SJÖGREN (J. Amer. Chem. Soc., 1928, **50**, 3318—3332).—The partial

specific volumes (0·748 and 0·745) and ultra-violet absorption spectra of serum-albumin and serum-globulin, isolated by a rapid and simple procedure from horse blood, have been determined. Measurements by the sedimentation velocity and sedimentation equilibrium methods (cf. A., 1927, 716; 1928, 783), using isoelectric solutions in an acetate or phosphate buffer medium, show that both proteins are homogeneous with regard to mol. wt. over a wide range of concentration. The mol. wt. of the former, 67,500±2000, and that of the latter, 103,800±3000, are both simple multiples of that of egg-albumin (cf. A., 1928, 533), and are nearly identical with those of hæmoglobin and phycocyan, respectively. At concentrations below 0·5%, serum-albumin undergoes, without change in absorption spectrum, a reversible partial decomposition into non-centrifugable products. Prolonged fractionation of either protein causes a complicated degradation and aggregation of the molecules, with formation of increasing amounts of non-centrifugable matter. These changes account for the apparent heterogeneity of both proteins observed by previous workers. Fractionation products such as the eu- and pseudo-globulins probably differ only in their content of impurity.
H. E. F. NOTTON.

Determination of tryptophan in proteins. Rate of liberation of tryptophan by enzymes. I. K. RAGINS (J. Biol. Chem., 1928, 80, 543—550, 551—556).—The accuracy of the vanillin–hydrochloric acid reaction for the determination of tryptophan in protein hydrolysates (A., 1925, ii, 448) is confirmed; whilst native proteins fail to give the reaction satisfactorily, the presence of some of the tryptophan in peptide combination in the material precipitated by mercuric sulphate does not interfere with the determination. For the quantitative precipitation of tryptophan by mercuric sulphate the chloride concentration must not exceed 0·3%. Pepsin does not liberate tryptophan from proteins, nor does erepsin liberate an additional amount of this amino-acid after the action of trypsin; tryptophan is liberated by trypsin very rapidly from caseinogen, less so from edestin and squash-seed globulin.
C. R. HARINGTON.

Hydrolysis of proteins by hydrofluoric acid. E. CHERBULIEZ and R. WAHL (Helv. Chim. Acta, 1928, 11, 1252—1255).—Protein substances are hydrolysed with hot 25—50% hydrofluoric acid (cf. Hugounenq and Morel, A., 1909, i, 195, 685) in a lead vessel, and after removal of fluoride ions as calcium fluoride, the hydrolysis products are analysed for total nitrogen. When a comparison is made of the results with those for hydrochloric acid hydrolysis it is found that the percentage of ammonia-nitrogen is higher, the result of partial deamination of the amino-acids formed. The amount of humins formed is relatively large, and it is shown that under the conditions of hydrolysis about 37% of the sugar is destroyed in a mixture of amino-acids and dextrose. The method appears to have no advantage over the usual one.
H. BURTON.

Loosely-bound sulphur in egg-albumin. W. D. TREADWELL and W. EPPENBERGER (Helv. Chim.

Acta, 1928, 11, 1035—1042).—Hydrolysis of a 1·5% solution of egg-albumin with an equal volume of 0·1N-sodium hydroxide solution at 78° in rigid absence of air follows the course of a bimolecular reaction. Subsequent determination of the sulphide ions formed, by electrometric titration with lead ions, gives a limiting value of 0·266%, which is about one half the value found by Osborne (A., 1902, i, 250) and one sixth of the total sulphur present. The mol. wt. of ovalbumin is of the order of 12,000.
H. BURTON.

Composition and characteristics of the proteins. S. P. L. SØRENSEN (Förh. III. nord. Kemistmötet, 1928, 72—91).—A review of recent work, mainly 1920—1926, on the determination of the composition and structure of the proteins. H. F. HARWOOD.

Volumetric determination of protein solutions. W. D. TREADWELL and W. EPPENBERGER (Helv. Chim. Acta, 1928, 11, 1053—1062).—When protein solutions are treated with excess of tannin the resulting precipitate adsorbs colloidal ferric ferrocyanide, causing decolorisation of the solution, and the end-point is reached when a permanent blue colour remains in the solution. During the titration the mixture is stirred, but not violently enough to cause either disintegration of the precipitate or coagulation of the Prussian-blue. Addition of acid or alkali causes marked diminution in the adsorption (when marked deviations from the isoelectric point are obtained), and the addition of varying amounts of neutral salts gives widely differing results. Protein solutions containing salts should be dialysed before titration. The method needs very careful manipulation. Gelatin–tannin precipitates adsorb more Prussian-blue than egg-albumin precipitates.
H. BURTON.

Determination of peptide and basic forms of nitrogen. C. O. APPLEMAN, W. E. LOOMIS, T. G. PHILLIPS, W. E. TOTTINGHAM, and J. J. WILLAMAN (Plant Physiol., 1927, 2, 497—501).—A report of a Committee of the American Society of Plant Physiologists. CHEMICAL ABSTRACTS.

Sources of error in organic micro-elementary analysis. II. Determination of carbon and hydrogen. F. BÖCK and K. BEAUCOURT (Mikrochem., 1928, 6, 133—143; cf. Friedrich, A., 1923, ii, 788).—A critical discussion. Errors due to the presence of carbon and hydrogen compounds in the oxygen etc. used and impurities given off by rubber connexions may be avoided by the insertion of a platinised asbestos catalyst followed by a bubbler and absorption vessel in front of the combustion tube.
J. S. CARTER.

Apparatus for the micro-determination of carbon by the method of Nicloux. M. NICLOUX (Bull. Soc. Chim. biol., 1928, 10, 1271—1272).—The stopcock, controlling the ingress of sulphuric acid to the apparatus, is replaced by a funnel on a capillary stem fitted with a ground-in plunger (cf. A., 1927, 436, 996). G. A. C. GOUGH.

Sulpho-chromic oxidation of carbonaceous substances. General wet method of micro-determination of carbon. A. BOIVIN (Compt. rend., 1928, 187, 1076—1078).—The carbonaceous

substance is oxidised in solution by heating on a water-bath for 30 min. with sulphuric acid, potassium dichromate, and silver chromate. The apparatus used is that of Nicloux (A., 1927, 436) with the modification that any carbon monoxide present is burnt to the dioxide by an electrically heated platinum filament, the necessary oxygen being supplied by decomposition of the chromic acid.

B. W. ANDERSON.

Determination of nitrogen. M. R. R. SIVAN and M. S. RAJU (Madras Agric. Dept. Yearbook, 1926 (1927), 6—10).—The substance is heated with concentrated sulphuric acid and a platinum spiral as in Kjeldahl's method; the cooled liquid is neutralised with sodium hydroxide, calcium is precipitated as oxalate, the diluted solution is filtered through dry paper, and the ammonia determined by Nessler's method. CHEMICAL ABSTRACTS.

Determination of maltose and dextrose. W. BRAUN and B. BLEYER [with W. ELHARDT] (Z. anal. Chem., 1929, **76**, 1—38).—The various existing methods for the determination of dextrose and maltose have been carefully investigated with special reference to their limitations and to inherent and systematic errors. Methods are given for the determination of dextrose and maltose by the reduction of Fehling's solution, the determination of mixtures of dextrose and maltose by reduction of Fehling's and Barfoed's solutions, the determination of mixtures of dextrose, maltose, and dextrin by reduction of Fehling's and Barfoed's solutions, inversion and reduction of Fehling's solution, the micro-determination of maltose by reduction of Fehling's solution, and the determination of dextrose, maltose, and their mixtures by reduction of an alkaline solution of iodine. The necessary tables and full details are given, together with actual examples illustrative of the calculations involved. J. S. CARTER.

Determination of anthraquinone in mixtures with benzanthrone. P. I. SOKOLOV and L. GUREVICH (J. Chem. Ind. Moscow, 1928, **5**, 308—309).—Sielisch's method is untrustworthy. The mixture (1 g.) is boiled under reflux with glacial acetic acid (45 c.c.); a mixture of chromium trioxide (5 g.), glacial acetic acid (5 c.c.), and water (5 c.c.) is added during 2 hrs., the liquid boiled for a further 2 hrs., then diluted with cold water (400 c.c.). The benzanthrone is thus oxidised to anthraquinone-1-carboxylic acid, whilst the anthraquinone is unaffected. After 1 hr. the precipitate is collected, washed with water and then with 150 c.c. of 1% sodium hydroxide solution, and treated at 70° with 15 c.c. of a 10% solution of sodium hyposulphite in 10% sodium hydroxide. The red solution of anthraquinone is filtered through a Gooch crucible, the residue washed with a 1% sodium hyposulphite solution, and the filtrate treated at 70° with 5 c.c. of 30% hydrogen peroxide solution to precipitate the anthraquinone, which is collected, washed with water, dried, and weighed. If the sample contains more than 50—60% of anthraquinone, treatment with hyposulphite may be omitted. CHEMICAL ABSTRACTS.

Biochemistry.

Regulation of respiration. XX. Quinhydrone electrode for determination of hydrogen-ion concentration. R. GESELL (Amer. J. Physiol., 1928, **87**, 1—7).—An electrode for use with small quantities of blood or cerebrospinal fluid is described.

B. A. EAGLES.

Regulation of respiration. XXI. Sodium cyanide and p_H of cerebrospinal fluid. R. GESELL and A. B. HERTZMAN (Amer. J. Physiol., 1928, **87**, 8—14).—Intravenous injection of sodium cyanide in the dog produces an initial alkalinity of the cerebrospinal fluid followed during recovery by an increasing acidity. B. A. EAGLES.

Regulation of respiration. XXII. Alveolar oxygen and p_H of cerebrospinal fluid. XXIII. Hæmorrhage and p_H of cerebrospinal fluid. A. B. HERTZMAN and R. GESELL (Amer. J. Physiol., 1928, **87**, 15—19, 20—23).—XXII. The administration of gaseous mixtures with low oxygen content is accompanied by a decrease in the hydrogen-ion concentration of the cerebrospinal fluid. Re-administration of air is followed by an increased hydrogen-ion concentration exceeding the original level.

XXIII. Hæmorrhage produces no change in the hydrogen-ion concentration of the cerebrospinal fluid. Re-injection of the blood always increases it.

B. A. EAGLES.

Regulation of respiration. XXIV. Mechanical asphyxia and p_H of cerebrospinal fluid. R. GESELL and A. B. HERTZMAN (Amer. J. Physiol., 1928, **87**, 24—28).—Mechanical asphyxia increases the hydrogen-ion concentration of the cerebrospinal fluid. B. A. EAGLES.

Method of oxygenating blood. L. E. BAYLISS, A. R. FEE, and E. OGDEN (J. Physiol., 1928, **66**, 443—448).—An artificial "lung" consisting of alternate revolving and stationary plates is described. The oxygenator consisting of five pairs of plates has an air volume of 600 c.c. and when revolving at a speed of 200 r.p.m. contains 54 c.c. of blood at any moment. When running in an atmosphere of oxygen it will introduce 19 c.c. of oxygen per minute into the blood flowing through it.

B. A. EAGLES.

Seasonal variation of the carbon dioxide content of the blood of the snail. M. DUVAL (Compt. rend., 1929, **188**, 104—107).—The carbon dioxide and sodium hydrogen carbonate contents of the blood of the snail are slightly lower during the periods of hibernation and inactivity. This is in contrast to the sodium chloride content, which increases as the density of the blood increases. The mechanism which tends to oppose these variations is unknown. G. A. C. GOUGH.

Manganese–copper–iron complex in hæmoglobin formation. R. W. TITUS, H. W. CAVE, and J. S. HUGHES [with H. L. KEIL] (J. Biol. Chem., 1928, 80, 565—570).—The hæmoglobin formation of young rats on a diet of milk supplemented with iron was accelerated about equally by addition of copper and of manganese, and still more by a combination of the two.   C. R. HARINGTON.

Effect of proteins and vitamins on hæmoglobin production in the rat. G. F. CARTLAND and F. C. KOCH (Amer. J. Physiol., 1928, 87, 249—261).—Rats fed on diets containing 10% of gluten or 18% of caseinogen can regenerate their blood satisfactorily after severe hæmorrhage. Vitamins-A and -E and probably -B are not specifically essential for hæmoglobin formation in the rat.   B. A. EAGLES.

Sulphur content of the hæmoglobin in the blood of pure-bred dogs and of some other animals. E. TIMÁR (Biochem. Z., 1928, 202, 365—379).—The sulphur contents of the hæmoglobin of the blood of cats and of cattle (as well as of some horses) are respectively 0·97% and 0·58%, and hence the proportions of iron and sulphur in the blood are expressed by the ratios Fe : S$_5$ and Fe : S$_3$. The value 0·58% is only rarely found in the case of the blood of dogs of ordinary breed, the values usually found being 0·70%, 0·61%, and 0·50%. These three values give no simple relationship between iron and sulphur, but, as in the case of the figures for cats, cattle, and horses, they confirm the findings of Valer (cf. A., 1928, 191). The hæmoglobin of the blood of pure-bred dogs contains 0·57% S (corresponding with the ratio Fe : S$_3$), and this value is also found in the cases of the ass and the fox. There is 0·71% S in hæmoglobin from the goose. In hæmoglobin which contains 0·58 or 0·97% S all the sulphur must be present as cysteine or cystine.   W. McCARTNEY.

New organic phosphorus constituent of erythrocytes. S. POSTERNAK (Compt. rend., 1928, 187, 1165—1167).—From the so-called acid-soluble fraction of the phosphorus compounds from horse's erythrocytes, a substance, probably α-ketotrihydroxyadipic acid βδ-diphosphate, [α] +8·8° (after neutralisation with ammonia, +15·04°), has been isolated. When hydrolysed in an autoclave at 125—130° for 6—7 hrs. it gives a product which reduces Fehling's solution more strongly than the original substance.   G. A. C. GOUGH.

Phosphoaminolipins and sterols of bloodserum and plasma. M. A. MACHEBŒUF (Compt. rend., 1929, 188, 109—111).—Adjustment of the p_H of blood-serum or -plasma to 3·8 with 0·02N-sulphuric acid after removal of the globulins by the addition of half-saturated ammonium sulphate gives a precipitate which dissolves in a small volume of water on the addition of ammonia (p_H 7·3). Repeated dissolution and precipitation of this product gives a substance consisting of phosphoaminolipins (22·7%), cholesteryl esters (17·7%), and proteins (59·1%). Extraction of a neutral solution of the mixture with ether gives no lipins, whilst addition of alcohol gives a precipitate which dissolves in excess and slowly reappears after boiling.   G. A. C. GOUGH.

Cholesterol and lipoid phosphorus of the blood in infancy and childhood. M. B. GORDON and D. J. COHN (Amer. J. Dis. Children, 1928, 35, 193—200).—Blood-serum from the umbilical cord at birth contains 89 mg. per 100 c.c. of cholesterol and 4·1 mg. per 100 c.c. of lipoid phosphorus; blood-serum in the first week affords similar values. The cholesterol content, which is 136 mg. per 100 c.c. at the end of the first year, increases to 169 mg. in the sixth year. At the end of the first year the lipoid phosphorus content is 5·8—6·1 mg. per 100 c.c., remaining constant during the next four years, and reaching 7·8 mg. in the sixth year.   CHEMICAL ABSTRACTS.

Cholesterol and cholesteryl ester in the bloodserum of cattle late in pregnancy and during the early lactation period. R. E. SHOPE and J. W. GOWEN (J. Exp. Med., 1928, 48, 25—30).—The total cholesterol and cholesteryl ester of bovine serum during the " dry " period of late pregnancy is low. Following parturition the total cholesterol and cholesteryl ester of bovine serum show a still greater, very transient decrease followed by a gradual rise to reach a fairly constant level 40—50 days *post partum*. This lactation level is very much higher than the " dry " level.   CHEMICAL ABSTRACTS.

Biometry of calcium, inorganic phosphorus, cholesterol, and lipin-phosphorus in the blood of rabbits. I. Normal rabbits. A. R. HARNES (J. Exp. Med., 1928, 48, 549—565).—Determinations were made throughout the year on eighty rabbits. The serum contained 14·5±0·10 to 18·5±0·39 mg. of calcium and 4·96±0·20 to 6·82±0·20 mg. of inorganic phosphorus per 100 c.c.; the whole blood contained 51·1±1·18 to 83·3±1·34 mg. of cholesterol and 94·8±1·40 to 168·3±10·18 mg. of lecithin per 100 c.c. Correlation coefficients are as follows : inorganic phosphorus and lecithin, —0·794±0·088; calcium and cholesterol, —0·887±0·051; cholesterol and lecithin 0·560±0·164.   CHEMICAL ABSTRACTS.

Blood-urobilin. Determination in normal human blood. M. A. BLANKENHORN (J. Biol. Chem., 1928, 80, 477—485).—Blood-serum is treated with zinc acetate and alcohol and kept for 24 hrs. at 0°; the solution is then cleared on the centrifuge and the fluorescence determined by comparison with standard solutions of acriflavine. The average concentration of urobilin in normal human blood-serum is 0·28 mg. per 100 c.c.   C. R. HARINGTON.

Physiology of ergothioneine. B. A. EAGLES and H. M. VARS (J. Biol. Chem., 1928, 80, 615—622).—Out of many samples of pig's blood one was encountered which yielded no ergothioneine; transference of these pigs, which had been fed on garbage, to diets rich in maize led to formation of ergothioneine in the blood. In accordance with this observation, solutions prepared by hydrolysis with sulphuric acid of egg-albumin, various cereal proteins, and, in particular, zein gave a positive reaction for the thiolglyoxaline ring, indicating the probable presence of thiolhistidine, whilst caseinogen and gelatin failed to give this reaction.   C. R. HARINGTON.

Blood-chemistry of the albino-rat. A. K. ANDERSON and H. E. HONEYWELL (Penn. Agric.

Exp. Sta. Bull., 1927, No. 213, 7).—Non-protein nitrogen and urea values are slightly higher than for human blood. Creatinine, creatine, uric acid, chlorides, and dextrose were also determined.
CHEMICAL ABSTRACTS.

Yeast feeding and blood-constituents of hens. A. A. HERVATH (Amer. J. Physiol., 1928, **87**, 208—220).—Hens fed with active yeast show an increase in the inorganic phosphorus and uric acid of the plasma. Inactive (heated) yeast causes a fall in the inorganic phosphorus and but a small rise in the uric acid of the plasma. The addition of taka-diastase to an inactive yeast ration makes it similar to active yeast in so far as its effect on the phosphorus and uric acid of the plasma is concerned. B. A. EAGLES.

Serum-proteins and complex ions. S. G. T. BENDIEN and L. W. JANSSEN (Rec. trav. chim., 1928, **47**, 1042—1057).—A study of the factors involved in the precipitation of proteins by acidified vanadium salts. B. A. EAGLES.

Micro-determination of serum-protein. E. FRIED (Z. ges. exp. Med., 1928, **60**, 515—520; Chem. Zentr., 1928, ii, 700).—Total protein is precipitated by half-saturation of 0·1 c.c. of serum with ammonium sulphate and addition of 1—2 c.c. of 0·02N-acetic acid, and globulin by half-saturation with ammonium sulphate after five-fold dilution with water, centrifuging, and filtering with suction through asbestos.
A. A. ELDRIDGE.

Catalase number and index of blood of newly-born kittens. F. VON KRÜGER (Biochem. Z., 1928, **202**, 18—20).—The number of blood-corpuscles and the catalase number are considerably smaller in cats 6 days to 8 weeks old than in fully-grown cats, whilst the catalase index is the same.
P. W. CLUTTERBUCK.

Influence of simultaneous hunger and thirst on the catalase number and index of blood. F. VON KRÜGER (Biochem. Z., 1928, **202**, 21—28).—During simultaneous thirsting and starving, the blood-corpuscle number per unit volume of blood and the catalase number are considerably increased, but the catalase index is unaltered.
P. W. CLUTTERBUCK.

Relationship of lactic acid to optical activity of blood. S. L. WRIGHT, jun., E. F. HERR, and J. R. PAUL (J. Biol. Chem., 1928, **80**, 571—587).—The optical rotation of the ultra-filtrate from blood-serum, both in normal blood and in blood from diabetic subjects, was observed immediately after shedding, and after the blood had been incubated until glycolysis was complete. The initial dextro-rotation was converted during glycolysis into a lævorotation of a somewhat lower degree; the phenomenon has been shown to be due principally to the accumulation of the lævorotatory salts of d-lactic acid. Some such phenomenon may account for the results of Lundsgaard and Holbøll (A., 1925, i, 1494) and others. C. R. HARINGTON.

Absorption of lævulose by red blood-corpuscles. G. EISNER and F. LEWY (Biochem. Z., 1928, **202**, 91—98).—Dextrose is readily but lævulose is little or not at all absorbed by erythrocytes, and the latter sugar must therefore play a different rôle in metabolism from that of the former. Increased absorption under insulin could not be definitely established.
P. W. CLUTTERBUCK.

Determination of blood-sugar. T. L. BYRD (J. Lab. Clin. Med., 1927, **12**, 609—613).—The author's micro-modification of Folin and Wu's method is trustworthy; further comparisons have been made. CHEMICAL ABSTRACTS.

Blood-sugar determination and separation of sugar with live yeast. A. L. RAYMOND and J. G. BLANCO (J. Biol. Chem., 1928, **80**, 631).—In view of the work of Benedict (A., 1928, 438) the term "disappearance" is substituted for "adsorption" in the authors' recent paper (A., 1928, 1392).
C. R. HARINGTON.

Blood-sugar. M. SOMOGYI and H. V. KRAMER (J. Biol. Chem., 1928, **80**, 733—742).—Determinations of true sugar in blood (i.e., the difference of the total and non-fermentable reducing substances; cf. A., 1927, 1214) by three independent methods gave practically identical results, so that no evidence is afforded of the existence in blood of a fermentable sugar other than dextrose. C. R. HARINGTON.

Blood-sugar. E. R. ORENT (J. Lab. Clin. Med., 1927, **12**, 433—438).—Kramer and Gittleman's micro-method accords well with Folin and Wu's method. Results obtained with dextrose solutions, normal and diabetic human blood, and the blood of dogs in convulsions following ligation of the hepatic artery were compared. CHEMICAL ABSTRACTS.

Colorimetric resorcinol–hydrochloric acid micro-method of blood-sugar determination. B. GLASSMANN and A. ZWILLING (Z. physiol. Chem., 1929, **180**, 124—126).—A modification of the method for the determination of blood-sugar (A., 1926, 192, 1169) involving the use of a colorimeter at the ordinary temperature is described. The values so obtained agree, within the experimental error, with those obtained by the Hagedorn–Jensen method.
J. W. BAKER.

Blood micro-analysis. I. TEPLOV (Biochem. Z., 1928, **202**, 14—17).—The micro-burette usually used in micro-titrations is replaced by a graduated pipette, the fluid being drawn into and expelled from this by movement of a screw working on a rubber balloon.
P. W. CLUTTERBUCK.

Muscle-hæmoglobin in the fowl. R. P. KENNEDY and G. H. WHIPPLE (Amer. J. Physiol., 1928, **87**, 192—195).—Spectrophotometric analysis of chicken-blood hæmoglobin is identical with that of dog-blood hæmoglobin. The muscle-hæmoglobins of the two animals are also identical. B. A. EAGLES.

Red colouring matter of cardiac and skeletal muscle. R. SCHÖNHEIMER (Z. physiol. Chem., 1929, **180**, 144—148).—Specimens of hæmin isolated respectively from the heart-muscle of an ox and from the skeletal muscle of a dog were each converted into the corresponding mesoporphyrin (by the action of hydrogen iodide in acetic acid), which by comparison of the methyl and ethyl esters are shown to be identical with each other and with that obtained from blood. J. W. BAKER.

Occurrence and decomposition of pyrophosphate in cells. I. K. LOHMANN (Biochem. Z., 1928, **202**, 466—493).—Pyrophosphate is present in fresh muscle to the extent of about 20% of the total acid-soluble phosphate. It can be isolated from frog, rabbit, and crab muscle as well as from baker's yeast by neutralising the trichloroacetic acid extract of the cells with barium hydroxide, precipitating barium pyrophosphate in acetic acid solution, and converting the barium salt by way of the lead or copper salt into the sodium salt. By analysis of the latter, by preparation of roseocobaltic pyrophosphate, and by comparison of the curves of velocity of hydrolysis by acids and of electro-titration with the corresponding curves of authentic pyrophosphate, the identity of the biological material is established. Quantitatively the biological pyrophosphate is determined as the difference between "true" inorganic phosphate plus phosphagen-phosphate and the value obtained after 7 minutes' further hydrolysis by means of N-hydrochloric acid at 100°. The electrometric titration curve of pyrophosphoric acid in the region p_H 1·73—12·25 has been determined. In the hydrolysis of pyro- to ortho-phosphoric acid displacement of the reaction towards the alkaline side occurs below p_H 6·8 and to the acid side above this value.　　　　　W. McCARTNEY.

Non-specific pressor principle of tissues. J. B. COLLIP (J. Physiol., 1928, **66**, 416—430).—Fresh tissue is thoroughly minced and added to five volumes of boiling water, the mixture is boiled for 5 min., and the filtrate is concentrated in a vacuum to one third of its volume. After removing fatty substances mechanically and by ether extraction, the concentration is continued in a vacuum until the extract is syrupy and the concentrate is extracted with three volumes of acetone. The acetone layer contains much of the pressor fraction. The residue is re-extracted several times. The combined acetone extracts are concentrated in a vacuum to a syrup which is again extracted with acetone. An aqueous or saline solution of the final acetone extract after all traces of acetone have been removed is used for studying its effects after intravenous injection. The pressor effect is enhanced by small doses of ergotamine, antagonised by cocaine, and unaffected by atropine. The height and duration of the response are directly related to the size of dose. Small amounts of the extract have little or no effect on isolated intestine, uterus, or heart.　　　B. A. EAGLES.

Methionine. G. BARGER and F. P. COYNE.—See this vol., 175.

Normal lipin content of organs. II. B. REWALD (Biochem. Z., 1928, **202**, 99—105).—The lipin contents of the acetone–ether and alcohol extracts of the fresh and dried corpus luteum, ovary, testis, thyroid, suprarenal, and pancreas are tabulated. The genital glands are richest and the thyroid and pancreas least rich in lipins (cf. A., 1928, 1154).
　　　　　P. W. CLUTTERBUCK.

Distribution of unsaturated fatty acids in tissues. III. **Vital organs of the ox.** W. R. BLOOR (J. Biol. Chem., 1928, **80**, 443—454).—Figures are given for the lipin distribution of the liver, kidney, pancreas, lung, and brain of the ox. Much variability was observed, not only between different organs, but also between the same organ in different animals; the least variable constituent was the phospholipin fraction, which is therefore regarded as fairly characteristic of a given organ. Lecithin and kephalin were found in equimolecular amounts. The iodine values of the lecithin and kephalin fractions of the various organs were closely similar, and a general resemblance was observed in the iodine values of all phospholipin fractions; the unsaturated acids contained large amounts of arachidonic acid, but no trebly unsaturated acid.　C. R. HARINGTON.

Highly unsaturated fatty acid of liver-lipins. Preparation of arachidonic acid. J. B. BROWN (J. Biol. Chem., 1928, **80**, 455—460).—Crude liver-fat was hydrolysed, the mixed acids were converted into the methyl esters, and the latter distilled. Bromination of all fractions yielded almost exclusively *methyl octabromoarachidonate*, m. p. 228—231°, which, when reduced with zinc dust in alcohol, gave *methyl arachidonate*, b. p. 200—210°/7 mm.; hydrolysis of the latter gave arachidonic acid with the correct iodine value. The work of Hartley (A., 1909, ii, 597) is thus confirmed.　　　C. R. HARINGTON.

Protoplasm and glutathione. A. GIROUD (Compt. rend. Soc. Biol., 1928, **98**, 376—377; Chem. Zentr., 1928, i, 2946).—Glutathione is always combined with protoplasm and appears to be specially associated with the chondriosomes.　　A. A. ELDRIDGE.

Composition of protoplasm. V. W. LEPESCHKIN (Science, 1928, **68**, 45—48).—Protoplasm consists chiefly of proteins and lipins probably in unstable chemical combination; salts, and possibly carbohydrates and the decomposition products of proteins, are also present. Living protoplasm is a hydrophilic colloid, the protein–lipin compounds forming the dispersion medium.
　　　　　CHEMICAL ABSTRACTS.

Electrical conductivity of protoplasm. S. GELFAU (Protoplasma, 1928, **4**, 192—200).—The average conductivity of the various specimens was equivalent to that of 0·05N-potassium chloride solution; an exception was that of starfish eggs, equivalent to 0·25N.　　　CHEMICAL ABSTRACTS.

Structure of living matter in the light of colloid research. J. SPEK (Kolloid-Z., 1928, **46**, 314—320).—A lecture on the application of the concepts of colloid chemistry to biological problems.
　　　　　E. S. HEDGES.

Imitation of organic forms by means of albumin and mineral acids. L. A. HERRERA (Atti R. Accad. Lincei, 1928, [vi], **8**, 460—464).—Further experiments are described (see this vol., 90).

Normal cerebrospinal fluid in children. D. STEWART (Arch. Dis. Childhood, 1928, **3**, 96—108).—Normal cerebrospinal fluid of children contains 15—55 mg. (lumbar), 12—50 mg. (cisterna magna), 5—18 mg. (lateral ventricles) of protein per 1000 c.c.; the protein content does not vary with increasing age. The chloride content is 630—760 mg. per 100 c.c.; the sugar content is 45—66% of the blood-sugar.
　　　　　CHEMICAL ABSTRACTS.

Tryptophan reactions in the cerebrospinal fluid. B. S. WALKER and F. H. SLEEPER (J. Lab. Clin. Med., 1927, 12, 1048—1052).—The amount of tryptophan in cerebrospinal fluid and egg-albumin varies, although not quantitatively, with the protein content. CHEMICAL ABSTRACTS.

Cholesterol and cholesteryl ester content of bovine colostrum. R. E. SHOPE and J. W. GOWEN (J. Exp. Med., 1928, 48, 21—24).—The total amount of cholesterol found in colostrum and milk is comparatively low. The amount in colostrum declines at a decreasing rate as milk secretion develops, until at 48 hrs. the cholesterol is nearly the same as that found in milk 3 or 7 months after parturition. The morning milk differs from the evening milk in that the cholesterol present as ester is greater in amount. CHEMICAL ABSTRACTS.

Lipin content of butter. B. REWALD (Biochem. Z., 1928, 202, 391—393).—The lipin (lecithin) content of butter, deduced from the phosphorus content, is 1·17—1·73%. Differences in different butters may be due to such factors as the nature of the fodder supplied to the cattle, the period of lactation, and the season of the year. Skim milk contains only traces of lipins. W. McCARTNEY.

Action of heat on lipins. B. REWALD (Biochem. Z., 1928, 202, 394—398).—Although isolated lipins are very readily decomposed by heat and by atmospheric oxygen, in a natural condition and accompanied by fats they may be boiled or roasted without undergoing any considerable decomposition. W. McCARTNEY.

Dextrose content of the vitreous humour. F. ASK (Särt. acta ophthalm., 1928, 5, 23—28; Chem. Zentr., 1928, i, 3084).—In pathological conditions, especially glaucoma, the vitreous humour contains less dextrose than the aqueous humour. A. A. ELDRIDGE.

Pancreatic secretion. R. CARUSI (Folia Clinica, 1928, 3, 209—255).—An internal and an external pancreatic secretion exist, but changes in the secretions are not always accompanied by corresponding histological changes. The external secretion is composed of trypsin, lipase, and amylase. The internal secretion is produced by the islets of Langerhans and is able to act on carbohydrates. The various methods suggested for determining the enzymes are discussed and a modified method for determining amylase is given. T. H. POPE.

Does a gastric lipase exist ? G. MELLI and M. RADICI (Folia Clinica, 1928, 3, 169—190).—The authors conclude that the lipase, the existence of which in the gastric juice is affirmed by some and denied by others, is actually the lipase which occurs normally in the gastric mucosa and leaves this accidentally as a result of trauma following probing. The functions of this lipase are probably limited to the interior of the individual cells. The stomach plays no part in the digestion of fats. T. H. POPE.

Elimination of thiocyanate, a source of error in the ferric chloride test for lactic acid. L. A. CRANDALL (J. Lab. Clin. Med., 1928, 13, 1046—1047).—The presence of potassium thiocyanate in gastric contents, particularly of patients who smoke, affects the ferric chloride test for lactic acid; it is removed by the addition of saturated mercuric chloride solution. CHEMICAL ABSTRACTS.

Colorimetric determination of inorganic sulphate in urine. B. S. KAHN and S. L. LEIBOFF (J. Biol. Chem., 1928, 80, 623—629).—The urine is treated with benzidine hydrochloride and the precipitate of benzidine sulphate separated on the centrifuge and diazotised; a standard solution of ammonium sulphate is treated similarly. The two solutions are then treated with phenol and excess of sodium hydroxide and the resulting colours compared. C. R. HARINGTON.

Effects of sera from normal and anæmic persons on growth of seedlings. L. B. UPJOHN, R. ISAACS, and F. G. GUSTAFSON (Arch. Int. Med., 1928, 42, 909—915).—Seedlings of *Lupinus albus* grown in Shive's nutrient saline solution and containing serum from normal persons show an average rate of growth of 76% of the rate of growth in Shive's solution alone. The growth of seedlings in solutions containing serum from patients with pernicious anæmia did not vary significantly from that in serum taken from normal persons. B. A. EAGLES.

Utilisation and rate of excretion of ingested creatine by normal and arthritic subjects. F. A. CAJORI, L. M. WRIGHT, and E. STILZ (Arch. Int. Med., 1928, 42, 901—908).—Arthritic patients are as efficient as normal subjects in their ability to retain creatine administered orally. The rate of excretion, however, is slower in the arthritic patients, and this may be due to a disturbance of peripheral blood-flow. B. A. EAGLES.

Atopy : blood-calcium and gastric analysis. L. H. CRIEP and W. S. McELROY (Arch. Int. Med., 1928, 42, 865—871).—Patients in atopic conditions have a normal blood-calcium value, but frequently show achlorhydria and hypoacidity. B. A. EAGLES.

Blood-sugar of corpuscles and plasma in diabetic and alimentary hyperglycæmia. M. SOMOGYI (Arch. Int. Med., 1928, 42, 931—938).—The distribution of blood-sugar between corpuscles and plasma can be determined only from true sugar values. The relative sugar content of corpuscles is the same in the blood of diabetics and normal individuals. The distribution of sugar is unaffected by changes in blood-sugar level caused by ingestion of dextrose. B. A. EAGLES.

Rational insulin therapy based on daily blood-sugar curves. A. GOTTSCHALK and A. SPRINGBORN (Klin. Woch., 1928, 7, 1129—1133; Chem. Zentr., 1928, ii, 458).—The metabolic picture is best obtained clinically by means of blood-sugar curves extending over 24 hrs. A. A. ELDRIDGE.

Salabrose (tetraglucosan) in diabetes. E. KAUFMANN (Z. ges. exp. Med., 1928, 60, 116—132; Chem. Zentr., 1928, ii, 367).—Oral administration of tetraglucosan is usually followed in diabetic and in normal subjects by a rise in the blood-sugar, which also follows intravenous injection. With rabbits, tetraglucosan has no effect on insulin hypoglycæmia. The use of tetraglucosan in diabetes is discussed.

After removal of dextrose by fermentation, the substance may be determined polarimetrically or colorimetrically by reduction of picric acid to picramic acid. The latter method is unsuitable for its determination in urine.   A. A. ELDRIDGE.

Clinical calorimetry. XLIII. Thresholds of ketosis in diabetes, epilepsy, and obesity. W. S. McCLELLAN, H. J. SPENCER, E. A. FALK, and E. F. DU BOIS (J. Biol. Chem., 1928, **80**, 639—652).— The threshold of ketosis (i.e., excretion of 0·1 g. of acetone in 24 hrs.) was reached in normal, diabetic, and epileptic subjects when the fatty acid : dextrose ratio of the food metabolised, calculated by the formula of Woodyatt (Arch. Int. Med., 1921, **28**, 125), exceeded 1·5; in a case of obesity the ratio could be raised to 2·4 without producing ketosis.
                                     C. R. HARINGTON.

Urinary C : N and O : N ratios in phloridzin diabetes. A. R. PESKIN (Biochem. Z., 1928, **202**, 5—13).—In phloridzinised dogs and rats, other dysoxidisable substances than sugar are excreted in increased amounts in the urine; the substances are rich in hydrogen and not identifiable with acetone compounds (cf. A., 1926, 639, 642).
                                     P. W. CLUTTERBUCK.

Bile acids in jaundice. I. KATAYAMA (Arch. Int. Med., 1928, **42**, 916—930).—Calculated as sodium glycocholate, the bile acids of normal blood-serum vary from 5 to 12 mg. per 100 c.c. Bile acids are absent from normal urine. There is a marked increase in the bile acids of the serum, accompanied by urinary excretion of bile acids in patients with cholecystitis, disease of the liver, catarrhal jaundice, obstructive jaundice, cardiac decompensation, and duodenitis. Changes in concentration of bile acids in the blood bear no relation to variation of bilirubin in the blood. Bile acids appear in the urine when the blood-serum value exceeds 20 mg. per 100 c.c.
                                     B. A. EAGLES.

Determination of bilirubin in blood. H. F. SHATTUCK, J. A. KILLIAN, and M. PRESTON (J. Lab. Clin. Med., 1927, **12**, 802—810).—The icterus index was more trustworthy than van der Bergh's method, the latter being unsatisfactory in 50% of the cases of latent jaundice.   CHEMICAL ABSTRACTS.

Urea tolerance test. S. E. KING (Arch. Int. Med., 1928, **42**, 877—892).—Following the ingestion of 1 g. of urea per 10 lb. body-weight the blood-urea of normal individuals returns to its control level in 14 hrs. In the cases of impaired renal function investigated, there remained after 14 hrs. an average elevation above the control level of 10·3 mg. of urea-nitrogen per 100 c.c. of blood.   B. A. EAGLES.

Chemical changes in dog's blood in experimental peritonitis. T. G. ORR and R. L. HADEN (J. Exp. Med., 1928, **48**, 339—342).—The changes in chloride, urea, and non-protein nitrogen resemble those in pyloric and high intestinal obstructions, but there is no alkalosis.   CHEMICAL ABSTRACTS.

Intestinal p_H in experimental rickets. B. L. OSER (J. Biol. Chem., 1928, **80**, 487—497).—In agreement with Shohl and Bing (A., 1928, 1288) the fæcal p_H in experimental rickets in rats is variable,

and its measurement is not a sound measure of the vitamin-D content of the diet (cf. Jephcott and Bacharach, A., 1928, 332); the relative alkalinity of the intestinal tract of rachitic rats is most marked in the colon, and is thought to be associated with the decreased reabsorption of phosphorus in these animals, this reabsorption taking place in the normal animal from the colon.   C. R. HARINGTON.

Trypsin secretion of infants. T. LUKACS (Amer. J. Dis. Children, 1926, **31**, 235—240).—In infectious diseases of children the trypsin content of the fæces is decreased, but in rickets it is increased.
                                     CHEMICAL ABSTRACTS.

Coagulation of the blood in parathyroid tetany. J. C. BROUGHER (Amer. J. Physiol., 1928, **87**, 221— 224).—Blood-coagulation is delayed in parathyroid tetany. One ounce of cod-liver oil given by stomach tube restores the coagulation time to normal after a period of 2—4 hrs.   B. A. EAGLES.

Cholesterol in malignant tumours. A. H. ROFFO (Prensa med. Argentina, 1924, 20 pp.; Chem. Zentr., 1928, ii, 791—792).—The dried substance contains 3% (or up to 10%) of cholesterol. The non-tumour portion of rats contains more cholesterol than normal rats. On a sterol-free diet the cholesterol content of the animals increased with growth of the tumour, which was, however, markedly arrested.
                                     A. A. ELDRIDGE.

Existence of substances resembling insulin in benign and malignant human tumours. A. H. ROFFO and L. M. CORREA (Rev. Soc. Argentina Biol., 1927, **3**, 68—71; Chem. Zentr., 1928, ii, 369).— Experiments on rat sarcomata have been extended to human tumours with analogous results, but smaller quantities of substances resembling insulin have been obtained.   A. A. ELDRIDGE.

Chemical changes in the body occurring as the result of vomiting. A. F. HARTMANN and F. S. SMYTH (Amer. J. Dis. Children, 1926, **32**, 1—28).— Chloride is lost and hydrogen carbonate retained in compensation; non-protein nitrogen is increased if necessary to maintain the normal osmotic pressure. Excess of non-protein nitrogen and sodium hydrogen carbonate is excreted on administration of sodium chloride, but the excretion of all three substances depends on the total crystalloid concentration of the blood.   CHEMICAL ABSTRACTS.

Chemical changes occurring in the body as the result of certain diseases. I. Effects of diarrhœa, vomiting, dehydration, and oliguria on the acid–base balance of the plasma of infants with mastoiditis. A. F. HARTMANN (Amer. J. Dis. Children, 1928, **35**, 557—575).—Vomiting produces a reduction in the hydrogen chloride and base chloride reserve; dehydration an increase in the blood plasma-lactic acid and -protein; oliguria an increase in phosphoric acid and non-protein nitrogen.
                                     CHEMICAL ABSTRACTS.

Metabolism of Eskimos. P. HEINBECKER (J. Biol. Chem., 1928, **80**, 461—475).—As compared with inhabitants of temperate zones, Eskimos have a higher basal metabolic rate; they have increased power of oxidising fats which enables them to fast

without developing ketosis; during fasting, the normally high sugar tolerance is reduced, and the respiratory quotient falls to low levels which indicate conversion of fat into carbohydrate.

C. R. HARINGTON.

Basal metabolism of Australian aborigines. H. S. H. WARDLAW and C. H. HORSLEY (Austral. J. Exp. Biol., 1928, 5, 263—272).

Influence of food on longevity. H. C. SHERMAN and H. L. CAMPBELL (Proc. Nat. Acad. Sci., 1928, 14, 852—855).—Two sets of about 200 rats were fed on separate diets; diet A consisted of $\frac{1}{8}$ dried whole milk, $\frac{5}{6}$ ground whole wheat, 2% of the weight of wheat of table salt, and distilled water *ad lib.* Diet B consisted of $\frac{1}{3}$ dried whole milk, $\frac{2}{3}$ ground whole wheat, and salt and water as in A. The rats were fed on these diets until natural death occurred, and the length of life was noted in each case. It was found that whilst diet A was adequate, diet B was better, the rats fed on B living approximately 10% longer than those fed on A. A. J. MEE.

Influence of age on the composition of the lipin fraction in the animal organism. V. S. SADIKOV and E. S. GOLOVTSCHINSKAYA (Biochem. Z., 1928, 202, 421—438).—The amount of lipin fraction obtainable from cats when treated according to the process described by Sadikov and Shchegl'ska (A., 1928, 194) varies considerably according to the age of the animals and to other circumstances. Variations according to age are also found in the composition of the fraction. The possible nature and causes of these variations are discussed.

W. McCARTNEY.

Influence of diet on muscle-hæmoglobin. G. H. WHIPPLE, A. H. GROTH, and F. S. ROBSCHEIT-ROBBINS (Amer. J. Physiol., 1928, 87, 185—191).—Pups of the same litter were divided into two groups and after weaning were fed on an adequate synthetic bread ration or on a bread ration plus large amounts of cooked liver. After 15—20 weeks on these diets the liver-fed pups had concentrations of blood- and muscle-hæmoglobin distinctly greater than those of the bread-fed controls. B. A. EAGLES.

Respiratory metabolism in infancy and childhood. III. Glycogen storage in children. S. Z. LEVINE, J. R. WILSON, and H. RIVKIN (Amer. J. Dis. Children, 1926, 31, 496—503).—Glycogenesis occurred during high carbohydrate feeding, and glycogenolysis during starvation in all cases (except diabetic) studied. CHEMICAL ABSTRACTS.

Respiratory quotient of the excess metabolism of exercise. C. H. BEST, K. FURUSAWA, and J. H. RIDOUT (Proc. Roy. Soc., 1929, B, 104, 119—151).—The respiratory quotient of the excess metabolism of very mild exercise is below unity, that of moderate exercise approximates to unity, whilst that of very severe exercise may exceed unity and reach values up to 1·70. The respiratory quotient of the total metabolism for the period of exercise and recovery is below unity for mild or moderate exercise but slightly exceeds unity in the case of very severe exercise. W. O. KERMACK.

Action of exercise and work on alkali reserve of blood. B. KRAVTSCHINSKI (Russ. J. Physiol., 1928, 11, 415—432).—The alkali reserve of 54 normal individuals varied from 47 to 75 vols.-% of carbon dioxide. Walking, running, or strenuous exercise lowered the alkali reserve. The extent of lowering depends more on the intensity than on the amount of work done. Exercise produces no acidosis in trained subjects but does so in beginners.

B. A. EAGLES.

Free energy of glycogen–lactic acid breakdown in muscle. D. BURK (Proc. Roy. Soc., 1929, B, 104, 153—170).—It is calculated that the free energy of the anaërobic reaction, glycogen—→lactic acid, is $1\frac{1}{2}$—2 times the heat of reaction. This conclusion holds whether or not the lactic acid is neutralised by buffer mixtures such as that present in muscle. In the case of aërobic oxidation of glycogen to carbon dioxide the difference between free energy and heat of reaction is negligible because of the large magnitude of the latter. W. O. KERMACK.

Fate of acetoacetic acid in normal and diabetic dogs before and after evisceration. I. L. CHAIKOFF and S. SOSKIN (Amer. J. Physiol., 1928, 87, 58—72).—Following its intravenous administration sodium acetoacetate disappears rapidly from the blood of normal and eviscerated-normal animals. It disappears at a slower rate from the blood of fasted depancreatised animals, but in eviscerated-diabetic animals the disappearance is as rapid as in normal animals. Since the muscles of fasted depancreatised animals can utilise acetoacetic acid as rapidly as normal muscle, it is argued that ketosis cannot be attributed to an impediment in the normal path of the catabolism of ketonic compounds. It is concluded that the appearance of excess of ketonic compounds in the tissue fluids of the diabetic animal is due to an increased rate of production by the liver.

B. A. EAGLES.

Clinical calorimetry. XLIV. Changes in rate of excretion of acetone substances during the day. W. S. McCLELLAN and V. TOSCANI (J. Biol. Chem., 1928, 80, 653—658).—Ketosis was induced in normal individuals by exclusive administration of meat; the rate of excretion of acetone substances was highest in the late afternoon and night and lowest in the morning, and thus bears a relationship to the total metabolic rate. C. R. HARINGTON.

Behaviour of α-ketovalerolactone-γ-carboxylic acid in the animal body. R. ENGER and H. SIEDENTOPF (Ber. Sächs. Ges. Wiss., Math-Phys. Kl., 1928, 80, 122—126; Chem. Zentr., 1928, ii, 585).—After intravenous injection of α-ketovalerolactone-γ-carboxylic acid into dogs, the urine and blood did not contain increased amounts of acetone, neither was the blood-sugar increased. In perfused surviving liver there was a temporary increase of β-hydroxybutyric acid, and (after 30 min.) an increase in acetone formation. The nature of the decomposition is discussed. A. A. ELDRIDGE.

β-Oxidation. II. Metabolism of phenyl-substituted acids and of acetophenone in dogs. A. J. QUICK. **III. Fate of γ-phenylbutyric acid in depancreatised dogs.** J. E. SWEET and A. J.

Quick. **IV. Metabolism of conjugated glycuronic acids.** A. J. QUICK (J. Biol. Chem., 1928, **80**, 515—525, 527—534, 535—541).—II. δ-Phenylvaleric acid was conveniently prepared by boiling cinnamylidenemalonic acid with hydriodic acid and phosphorus. This acid, as also Δ^α- and Δ^β-δ-phenylpentenoic acids, were oxidised in the dog exclusively to benzoic acid, which was excreted in conjugation with glycuronic acid and glycine in the ratio of 2 : 1. Mandelic acid was excreted unchanged, β-phenyl-β-hydroxypropionic acid was excreted for the most part unchanged, the remainder being oxidised to benzoic acid, whilst acetophenone gave benzoic acid and phenylmethylcarbinol, the latter being conjugated with glycuronic acid. Neither acetophenone nor β-hydroxy-β-phenylpropionic acid is therefore a probable intermediate in the physiological oxidation of β-phenylpropionic acid.

III. The depancreatised dog is able to oxidise γ-phenylbutyric acid to phenylacetic acid; it is unlikely, therefore, that the diabetic organism has lost the power to oxidise butyric acid.

IV. Glycuronic acid does not relieve insulin hypoglycæmia in mice. Menthyl glycuronate, bornyl glycuronate, and monobenzoylglycuronic acid are all partly oxidised in the dog; in the last case benzoic acid appears in the urine; in man the conversion of benzoylglycuronic acid into hippuric acid is complete. It is thought that, in the dog, all benzoic acid is first conjugated with glycuronic acid, and that a part of the latter is then converted into hippuric acid. C. R. HARINGTON.

Significance of plant sterols for animal organisms. R. SCHÖNHEIMER (Z. physiol. Chem., 1929, **180**, 1—37). **Action of sitosterol** [with D. YUASA.]—Comparative experiments of the effect of cholesterol and sitosterol and other plant sterols on various animals have been carried out. Morphological examination of rabbits to the food of which have been added similar quantities of cholesterol and sitosterol respectively shows that the usual fatty condition of the liver and other organs is produced in the first case but, contrary to von Gierke, no effect is produced by sitosterol. These results are confirmed by a chemical analysis of the brains and skins, a large increase in sterol content over that in the normal animals being found in the former case but not in the latter. Similar results accrue from an examination of the blood-serum. Examination of various types of animals, herbivorous, omnivorous, and carnivorous (rats, mice, and cats), all give similar results, the increase in sterol content and pathological effect on the organs occurring only when cholesterol is added to the food.

Deposition of unchanged plant sterols in animal organisms ?—In various experiments with rabbits fed on sitosterol the total sterol in the animal was isolated and converted into its acetate, and plant sterols were sought for by Bohmer's method (Abderhalden, "Handb. biol. Arbeitsmeth.," 6, (1), 539). In no case was the m. p. (113—114°) raised to 116° (which is caused by the presence of only 1% of sitosterol in cholesterol), and hence no appreciable deposition of plant sterol occurs.

Presence of plant-sterol esterases in animals ? [with D. YUASA.]—Cholesterol (0·2—0·3 g.) was introduced under the skin of a dog under aseptic conditions and, after 11 days, examination showed that 9·5—11% had been esterified. In similar experiments with plant sterols (sito-, stigma-, ergo-, and copro-sterols) no trace of esterification could be detected, the plant sterol behaving purely as a foreign substance.

Sterol equilibrium in rabbits fed on sitosterol.—Similar quantities of cholesterol and sitosterol were added to the food of rabbits over the same periods (with careful control experiments), the fæces collected and examined every 3 days, and the sterol content was determined. When cholesterol is added to the food, only about 50% of the excess appears in the fæces, whilst, within the experimental error, the whole of the sitosterol is excreted. By isolation of the sterol present in the fodder and the fæces as its digitonide and determination of its optical rotation, liberation of the free sterol, and comparison of the m. p. of its acetate and benzoate it is shown that the sterols present in the fodder and in the fæces are identical (cf. Dorée and Gardner, A., 1908, ii, 514). It is concluded that cholesterol and plant sterols undergo different metabolic processes, the latter passing through the animal unaltered and totally unabsorbed. J. W. BAKER.

Relationships between cholesterol metabolism and the production of the bile acids. Y. HORIYE (Biochem. Z., 1928, **202**, 409—420).—No experimental support could be found for the view that endogenous cholesterol is involved in the production of bile acids. When a cholagogue was administered orally to rats, the cholesterol content of their livers increased. It is concluded that the liver stores up part of the cholesterol set free in the organism by the action of the cholagogue. W. McCARTNEY.

Bile salt metabolism. I. Control diets, methods, and fasting output. H. P. SMITH, A. H. GROTH, and G. H. WHIPPLE. **II. Influence of foodstuffs.** H. P. SMITH and G. H. WHIPPLE. **III. Influence of tryptophan, tyrosine, and related substances. IV. How much bile salt circulates in the body ?** G. H. WHIPPLE and H. P. SMITH (J. Biol. Chem., 1928, **80**, 659—669, 671—684, 685—695, 697—707).—I. In dogs on a standard diet the daily output of bile salt is, on the average, 100 mg. per kg., this being secreted at a practically uniform rate; by fasting the output may be reduced to 30—40 mg. per kg. per diem, this residual amount being regarded as endogenous in origin. The bile salts were determined by the method of Foster and Hooper (A., 1919, ii, 376).

II. Variations in the diet of dogs with biliary fistula show that increase of protein in the diet causes increased output of bile salts, whilst alcoholic extracts of meat, yeast, and lipins are without any such effect.

III. Substitution of gelatin for the standard salmonbread diet of the dogs caused a fall in the secretion of bile salts; supplementation of the gelatin with tyrosine or p-hydroxyphenylglycine was without effect, but addition of tryptophan, and to a smaller extent of isatin and indigo, gave increased output;

the indole derivatives produce also increased outflow of bile, and, in combination with a sugar diet, may exercise a cholagogue effect with no simultaneous increase in the output of bile salts.

IV. Re-feeding of the bile salt secreted by a dog with a biliary fistula raises the secretion of bile salts to a steady level of 700—800 mg. per kg. per diem; administration of still more bile salt produces only a temporary increase in secretion. This indicates that the above amount represents the bile salt normally kept in circulation in the dog, additional amounts disappearing from the body in a manner as yet unexplained. C. R. HARINGTON.

Metabolism of the bile. III. Enterohepatic circulation of bile acids. C. H. GREEN, M. ALDRICH, and L. G. ROWNTREE (J. Biol. Chem., 1928, 80, 753—760).—After oral administration of bile salts to a dog with a biliary fistula there is a delay in the excretion due to the time taken for absorption from the intestine. Whilst in the normal fasting animal no difference is observed in the bile-salt concentration in different parts of the circulation, injection of bile salts into the duodenum is followed by an increase in their concentration in the portal blood.
C. R. HARINGTON.

Compounds of lecithin with amino-acids. L. GUERCI (Annali Chim. Appl., 1928, 18, 495—503).—Treatment of lecithin with pancreas extract, the amino-acids of vitellin or egg-protein, or glycine shows that lecithin forms with amino-acids colloidal compounds which are difficult to isolate and represent the first stage in the union of lecithin with albumins. It is thought that lecithin acts as an intermediate substance in the formation of amino-acids from fatty acids. T. H. POPE.

Effect of protein hydrolysis products on metabolism. III. Specific dynamic effects of protein hydrolysates and amino-acids. D. RAPPORT and H. H. BEARD (J. Biol. Chem., 1928, 80, 413—430).—Glutamic and aspartic acids, arginine, and cystine had definite specific dynamic effects, whilst histidine had no such action. Up to the present this work (cf. also A., 1927, 694) indicates that the specific dynamic effect of a protein is a simple summation of the effects of its constituent amino-acids.
C. R. HARINGTON.

Behaviour of various protein degradation products in the intermediate region. N. KOTSCHNEV (Pflüger's Archiv, 1928, 218, 635—641; Chem. Zentr., 1928, i, 3087).—Analyses of the portal blood of dogs showed that amino-acids and polypeptides were resorbed from the intestine. The amino-acids were partly resynthesised to polypeptides in the liver and passed into the blood. The kidneys retain amino-nitrogen during the resorption. The spleen, muscle, and intestine participate in the synthesis of polypeptides. In hunger, only the spleen delivers polypeptides to the blood. A. A. ELDRIDGE.

Biological value of yeast-protein for the rat. E. U. STILL and F. C. KOCH (Amer. J. Physiol., 1928, 87, 225—248).—Young rats will grow on diets containing yeast as the sole source of protein. More satisfactory growth is obtained with caseinogen.

Compared with caseinogen the biological value of dried raw yeast-proteins is 45%. B. A. EAGLES.

Storage of protein by sucking pigs. W. WÖHLBIER (Biochem. Z., 1928, 202, 29—69).—Sucking pigs excrete, with increasing age, increasing amounts of nitrogen, and a smaller proportion of the protein absorbed is therefore stored. The nitrogen stored as protein in the first 4 weeks was 89·1, 84·8, 74·7, 67·7% of that absorbed. For an increase in weight of 100 g., 0·957 g. of nitrogen was excreted. Calorific measurements show that for storage of 1 kg., the utilisation in calories increases from 3776 in the first week to 5628 in the fourth week. The daily mean yield of milk for the single test of the sow varies greatly, e.g., from 393 to 721 g. during the first 14 days, the total yield for milk per sow varying daily from 4·5 to 4·9 kg.
P. W. CLUTTERBUCK.

Conditions for the formation of carbamide in the isolated liver. III. P. P. ASTANIN and W. M. RUBEL (Biochem. Z., 1928, 202, 70—74; cf. A., 1928, 669).—Formation of carbamide from ammonium carbonate in the isolated liver occurs only in presence of the perfusing fluid and simultaneously of erythrocytes and serum. P. W. CLUTTERBUCK.

Origin and fate of uric acid and resorption of nucleic acid in the dog. S. RABINOVICH (Pflüger's Archiv, 1928, 219, 402—406; Chem. Zentr., 1928, ii, 463).

Origin and fate of creatine and creatinine. W. MOCHNATSCH (Pflüger's Archiv, 1928, 218, 655—660; Chem. Zentr., 1928, i, 3087).—In hunger creatine originates from the liver and kidneys; during digestion only from the liver. A large part of the creatine passed into the circulation is retained in the intestinal wall. A. A. ELDRIDGE.

Effect of fasting and of creatine feeding on creatine content of rat tissues. A. CHANUTIN and H. SILVETTE [with B. W. RAWLES, jun.] (J. Biol. Chem., 1928, 80, 589—608).—The creatine content of the muscles and kidneys of white rats is increased by fasting, other tissues not being affected. Feeding of large amounts of creatine, particularly after prolonged fasting, causes an increase in the creatine content of the muscles, and, to a smaller extent, in that of the liver and heart. The creatine content of the blood is little affected by fasting, but is much increased by feeding creatine. The results indicate that the greater the rate of endogenous catabolism the greater is the rate of both formation and storage of creatine. C. R. HARINGTON.

Effect of dextrose on the metabolism of growing rats. W. ARNOLDI and S. UENO (Z. ges. exp. Med., 1928, 61, 424—437; Chem. Zentr., 1928, ii, 464).—Protein and fat were gradually replaced in the diet by sugar. There was at first increase in weight, positive nitrogen-balance, and diminished urinary elimination of carbon; then (9% protein, 35% fat-cal.) the weight became stationary and afterwards (6%, 2%) fell. A. A. ELDRIDGE.

Diets and dextrose tolerance. J. S. SWEENEY (Arch. Int. Med., 1928, 42, 872—876).—The antecedent diet has no significant influence on the dextrose tolerance curve in normal men. B. A. EAGLES.

Action of intravenous injection of lactic acid on alkali reserve of blood. B. KRAVTSCHINSKI (Russ. J. Physiol., 1928, **11**, 433—444).—Intravenous injection of lactic acid causes a lowering of the alkali reserve from 10 to 40% of its original value. The degree of lowering depends, not only on the amount injected, but also on the rate of injection. The alkali reserve returns to normal in the course of 2—4 hrs. B. A. EAGLES.

Secretions of digestive glands and blood chemistry. I. Alkali reserve and chlorides in blood. S. I. PRIKLADOVITZKI and M. P. BRESTKIN (Russ. J. Physiol., 1928, **11**, 445—469).—Normal digestive activity causes a fluctuation in the alkali reserve depending on the kind of food taken. Feeding with lean meat raises the alkali reserve in the course of the first two hours. It gradually returns to its initial value. It is also raised by feeding white bread. Feeding with fat causes a fall followed by a rise. Fluctuations of alkali reserve in the course of digestion are generally accompanied by inverse fluctuations of the chloride content of the blood. B. A. EAGLES.

Behaviour of the diastase in the blood, urine, and fæces of the dog before and after ligation of the pancreatic ducts. F. GALLI (Folia Clinica, 1928, **3**, 120—133).—In dogs with the pancreas intact, the amount of diastase in the blood is always greater than that in the urine, but the maximum and minimum values in the two cases never correspond. Ligation and resection of the pancreatic ducts always cause very great increases of the amounts of the enzyme in the blood and urine, but here again no fixed relationships are observed; with the blood this increase persists a week after the ligation, but the diastase content of the urine gradually diminishes. The lack of pancreatic secretion in the intestine causes the disappearance from the fæces of the amylolytic enzyme, which is not found in the fæces a week after the ligation. T. H. POPE.

Relation between potassium and dialysable and undialysable calcium in the intermediate region. S. NEDSVEDSKY (Pflüger's Archiv, 1928, **218**, 647—654; Chem. Zentr., 1928, i, 3087).—Experiments with angiostomised dogs showed that potassium is resorbed in the intestine more quickly than calcium. By passage through the intestinal wall a considerable proportion of the calcium becomes undialysable, but dialysable again after passage through the liver. Calcium is but slightly excreted through the kidneys, whilst 85% of the potassium is eliminated in the urine. A. A. ELDRIDGE.

Mineral food of agricultural animals. II. Influence of calcium carbonate on the development of calves. J. ZAYKOVSKY and A. KRASNOKUTSKA (Biochem. Z., 1928, **202**, 239—245).—Feeding of calcium carbonate to calves produces no appreciable effect on their development. W. McCARTNEY.

Effect of X-radiation on nitrogen and sodium chloride metabolism. A. JUGENBURG (Strahlenther., 1927, **25**, 288—303; Chem. Zentr., 1928, ii, 463).—The nitrogen content of the blood is reduced, and that of the organs is increased or decreased, according to the dose. The milk-nitrogen is particularly increased. A. A. ELDRIDGE.

Mitogenetic radiation of stimulated muscle and of other tissues. W. W. SIEBERT (Biochem. Z., 1928, **202**, 115—122).—The rate of subdivision of yeast-cells is increased by the action at a distance of the pulp of muscle which has recently been electrically stimulated, but is unaffected by pulp of resting muscle under the same conditions. This effect is due to mitogenetic radiation from the stimulated muscle. The rays may be deflected by a polished metal surface and so directed on to suitable cultures, which then show increased subdivision. Similar experiments with spleen, testes, ovary, skin, and liver pulps showed these to be devoid of radiating power, but bone marrow of both rat and guinea-pig, minced Jensen rat sarcoma, and carcinomatous tissue always showed activity. P. W. CLUTTERBUCK.

Cause of mitogenetic radiation. W. W. SIEBERT (Biochem. Z., 1928, **202**, 123—130).—Addition of suitable amounts of lactic acid to resting muscle does not cause it to radiate, but if the muscle is then kept in pure oxygen it becomes active, the radiation being therefore probably associated with the oxidation of lactic acid. Pulp of electrically stimulated muscle becomes active in atmospheric air, pure oxygen being unnecessary. Unstimulated muscle treated with lactic acid and kept in ordinary air can be caused to radiate by addition of copper salts, but not by addition of peroxidase. A similar radiation can be detected with Warburg's charcoal model in which oxalic acid is oxidised on the carbon surface, and in the spontaneous oxidation of lævulose in phosphate buffer (p_H 8) in presence of oxygen and also in the oxidation of pyrogallol to purpurogallin by peroxidase and hydrogen peroxide. The activity of both the charcoal model and the tumour tissue was completely lost by addition of $0.00002N$-cyanide. P. W. CLUTTERBUCK.

Effect of hydroxyquinoline [on dogs]. C. GRABBE (Arch. exp. Pharm., 1928, **137**, 96—115).—Hydroxyquinoline administered *per os* is excreted by the dog principally through the kidneys as the sulphuric acid ester. It increases the nitrogen metabolism of starving animals. E. A. LUNT.

Action of synthalin. H. STAUB (Z. klin. Med., 1928, **107**, 607—658; Chem. Zentr., 1928, ii, 458—459).—Intravenous administration of synthalin causes in fasting rabbits a primary hyperglycæmia and a slight secondary hypoglycæmia. Continued peroral administration also results in no marked reduction of blood-sugar. The incidence of the toxic effect of synthalin is discussed. The liver- and muscle-glycogen is diminished, and the formation of lactic acid is increased. The action of synthalin in no way resembles that of insulin. A. A. ELDRIDGE.

Synthesis of 4(or 5)-glyoxalinylethylmethylcarbinol and its behaviour towards polyneuritis of pigeons. Y. SAHASHI (Bull. Inst. Phys. Chem. Res., Tokyo, 1928, **7**, 1191—1195).—Administration of β-4(-or 5-)*glyoxalinylethylmethylcarbinol* [δ-4(or 5)-*glyoxalinylbutan-β-ol*] temporarily cured the severe spastic form of polyneuritis in pigeons, but the

birds died 7—10 days after the first appearance of spasms. J. W. BAKER.

Has alcoholic extract of polished rice any noxious effect on pigeons? Y. SAHASHI, T. NOGUCHI, and N. HASHIMOTO (Bull. Inst. Phys. Chem. Res., Tokyo, 1928, 7, 1196—1201).—Since a group of pigeons fed on well-washed polished rice and McCollum's salts with the addition of a large quantity of the alcoholic extract of polished rice lived longer than another group fed on the same diet without the alcoholic extract, it is concluded that the latter has no noxious effect on pigeons. Moreover, signs of polyneuritis appeared even earlier in pigeons fed on polished rice powder which had been previously extracted with alcohol than in those fed on the unextracted rice powder. J. W. BAKER.

Variations in the cholesterol content of organs in naphthalene intoxication. D. MICHAÏL and P. VANCEA (Compt. rend. Soc. Biol., 1927, 97, 1097—1100; Chem. Zentr., 1928, ii, 791).—During the first ten days the cholesterol content of most of the organs is increased; it is unchanged in the lungs, heart, muscles, and vitreous humour, and falls in the lens and retina. In 30 days it is normal, but subnormal in the suprarenals, spleen, brain, lungs, and heart. In the lens it diminishes until cataract appears, with the growth of which it then increases.

A. A. ELDRIDGE.

Toad poisons. VI. Poisonous constituents of *Bufo bufo japonicus*. M. KOTAKE (Bull. Inst. Phys. Chem. Res., Tokyo, 1928, 7, 1244—1248; cf. A., 1928, 1138).—The species of toad used by the author is now known to be *Bufo vulgaris formosus* and not *Bufo bufo japonicus* as previously stated. Crystals of *bufotalin* have also been separated from the alcoholic extract and converted into the *acetyl* derivative, *bufotaliene*, and *bufotalone*. J. W. BAKER.

Influence of calcium salts on snake-venom hæmolysis. S. KANISAWA (Acta Dermatol., 1927, 479—490; Chem. Zentr., 1928, ii, 460).—In the cases studied, hæmolysis was arrested by calcium chloride or lactate in concentrations >0·025% and accelerated in concentrations <0·01%. A. A. ELDRIDGE.

Catalase system in animal tissues under different physiological and pathological conditions. II. Determination of catalase and anticatalase in the tissues of normal guinea-pigs and white rats. III. Effect of chronic intoxication with morphine, arsenic, and alcohol. E. D. GAGARINA and V. D. YANKOVSKI (Zhur. exp. biol. Med., 1928, 9, 50—57, 59—67).—II. Aqueous extracts of various organs partly lose their catalase activity, especially at 37°, owing to inactivation by an anticatalase; the inactivation can be prevented by alcohol (1 in 10⁴).

III. Morphine intoxication increases the catalase content of tissues, particularly liver and muscle, and decreases that of the blood. The anticatalase diminishes except in the liver and muscles. Chronic arsenic poisoning causes increase of both catalase and anticatalase, except in the blood, where it is decreased. Chronic alcohol poisoning of rats causes a fall in the catalase and anticatalase content of

the liver and kidneys, and a rise in that of the blood and muscles. CHEMICAL ABSTRACTS.

Determination of morphine in biological material. A. K. BALLS and W. A. WOLFF (J. Biol. Chem., 1928, 80, 379—402).—Finely-divided muscle is extracted with alcohol containing hydrochloric acid, and the extract is evaporated, the alcohol being replaced with water; after removal of fat, the aqueous solution is treated with phosphoric acid, and then adjusted to p_H 9·0 by addition of potassium hydroxide; the morphine is then removed by continuous extraction with chloroform containing 20% of alcohol and a little hydrochloric acid; the residue after evaporation of the chloroform is again dissolved in phosphate solution at p_H 9·0 and re-extracted; finally, the chloroform is evaporated, the residue dissolved in dilute hydrochloric acid, and the morphine determined by precipitation as the silicotungstate. Urine is adjusted to p_H 9·0 and extracted continuously with chloroform; the chloroform is evaporated and the residue dissolved in phosphate solution at p_H 3·0; extraction with chloroform at this stage removes coloured impurities; the morphine is obtained by adjusting the reaction to p_H 9·0 and repeating the extraction, and is then determined as above. Modifications of the method applicable to blood and fæces are also described. The method cannot be used with material containing less than 20 mg.-% of morphine; it avoids the two main disadvantages of existing methods, viz., loss of morphine by adsorption on precipitates or by oxidation. C. R. HARINGTON.

Physical and pharmacological influences on the action of curare. III. Effect of calcium, barium, and magnesium. IV. Physostigmine and nicotine. S. HORI (Folia pharmacol. japon., 1928, 4, 259—268, 279—280; Chem. Zentr., 1928, ii, 586). A. A. ELDRIDGE.

Action of calcium ions on the frog's heart. A. J. CLARK, G. H. PERCIVAL, and C. P. STEWART (J. Physiol., 1928, 66, 346—355).—The effects produced on the frog's heart by variations in the total calcium content of the perfusion fluid are explained as due to variations in the concentration of calcium ions. The mechanical response of the frog's heart varies directly as the concentration of calcium ions, when the latter falls below a value of 0·43 millimolar. B. A. EAGLES.

Effect of sulphur on carbohydrate metabolism. E. FÖLDES (Z. ges. exp. Med., 1928, 60, 571—582; Chem. Zentr., 1928, ii, 464).—Absorption of sulphur (ointment) through the skin usually causes a diminution of the blood-sugar. With rabbits, the suprarenals became enlarged and contained an increased quantity of sulphur. A. A. ELDRIDGE.

Action of hydrocyanic acid in frogs. V. KARASSIK (Russ. J. Physiol., 1928, 11, 339—350).—The arterial colour of venous blood of frogs poisoned with hydrocyanic acid becomes darker when the frogs are warmed and reappears on cooling them. There is an increase in the absorption of oxygen by the tissues during the period of warming. B. A. EAGLES.

Reducing substances of the blood in lead poisoning. A. MITTLESTEDT (Moskovski med. zhur.,

1927, **7**, 1—4).—No abnormality was observed, but in the chronic stage the increase caused by bread feeding was greater than usual.

CHEMICAL ABSTRACTS.

Photochemical dissociation in intermittent irradiation and the absolute absorption spectrum of the respiratory enzyme. O. WARBURG and E. NEGELEIN (Biochem. Z., 1928, **202**, 202—228).—A method has been described (cf. A., 1927, 1221; 1928, 537, 549, 851, 1390) for the calculation of the relative absorption spectrum of the respiratory enzyme from the photochemical dissociation of its carbonyl compound using the stationary condition attained during irradiation of cells in mixtures of carbon monoxide and oxygen. The velocity of attaining this condition is now determined and it is shown that the absolute absorption spectrum may be calculated therefrom. The spectrum of the carbonyl compound of the respiratory enzyme is that of an iron–carbonyl group attached to an organic molecule which is the same as that carrying the iron–carbonyl group in carbon monoxide-hæmin (tetrapyrrole nucleus). P. W. CLUTTERBUCK.

Enzyme action. I. Amylase from Cholam (*Sorghum vulgare*). V. N. PATWARDHAN and R. V. NORRIS (J. Indian Inst. Sci., 1928, **11**, A, 121—133).—Cholam amylase prepared by making under definite conditions an extract of malted cholam is less active in the production of sugar from starch than is malted barley enzyme, but for the same amount of sugar produced in the same solution much more starch is liquefied by the cholam amylase than by the barley amylase. Sugar production and liquefaction reach a maximum at 50—55°. Dialysis of cholam malt amylase results in a decrease of its activity, but the effect is not so marked as in the case of amylases of animal origin. Sodium chloride activates cholam malt amylase most effectively at a concentration of $N/500$, whilst other chlorides in equivalent proportions have an approximately equal action and affect sugar production and liquefaction to the same extent. Hippuric acid accelerates, whilst asparagine, alanine, glycine, and *l*-leucine inhibit the action of cholam malt amylase. Maltose also has a retarding influence. Precipitated cholam malt amylase shows a peculiar irregular variation in its activity at p_R between 4·5 and 5·5, which is exhibited in respect of both its sugar-producing and in its liquefying power. When the enzyme is purified by dialysis no such abnormality is found, both the crude enzyme and the enzyme purified by dialysis showing a maximum activity between p_H 4·86 and 4·66. With excess of substrate the rate of hydrolysis is approximately proportional to the amount of enzyme present. Although it appears probable that the sugar-producing and liquefying properties are due to different enzymes all efforts to separate them have failed.

W. O. KERMACK.

Enzyme action. II. The nature of amylase. D. NARAYANAMURTI and R. V. NORRIS (J. Indian Inst. Sci., 1928, **11**, A, 134—139).—Electrodialysis has been applied to purify solutions of cholam malt amylase. The purified enzyme solution shows enhanced activity and gives no protein tests, but a marked Molisch reaction. By means of electro-osmosis the enzyme has been separated into a fraction relatively more active in liquefying, and a second relatively more active in sugar-producing, the former tending to migrate towards the cathode.

W. O. KERMACK.

Influence of amino-acids on the action of ptyalin. J. T. GROLL (Pharm. Weekblad, 1928, **65**, 1315—1922).—The activation of various amylases by amino-acids observed by Sherman (A., 1920, i, 101; 1922, i, 283) has not been confirmed in the case of amylase in saliva. S. I. LEVY.

Effect of polarised light on starch hydrolysis. A. E. NAVEZ and B. B. RUBENSTEIN (J. Biol. Chem., 1928, **80**, 503—513).—The hydrolysis of starch by diastase proceeds more rapidly in the light than in the dark, but no difference could be observed in the effect of ordinary light and of polarised light of similar intensity and wave-length (cf. Baly and Semmens, A., 1925, i, 12). C. R. HARINGTON.

Inhibitory action of pancreatic extract on glycolysis. I. Effect of inhibitor on glycolysis of muscle-tissue and extract. E. RONZONI, J. GLASER, and D. P. BARR. **II. Effect of inhibitor on glycolysis of malignant tumours.** D. P. BARR, E. RONZONI, and J. GLASER (J. Biol. Chem., 1928, **80**, 309—330, 331—344).—I. Fresh pancreas is minced and twice extracted with water at 0°, the extracts are treated with 2 vols. of 95% alcohol and filtered, the filtrate is freed from alcohol by evaporation at 30°, cleared on the centrifuge, and extracted with ether. The aqueous solution contains the anti-glycolytic factor described by Winfield and Hopkins and others (A., 1916, i, 189); the active substance is partly precipitated by the above treatment with alcohol, but this first fraction is largely contaminated with trypsin. The partly purified material is completely precipitated by increasing the concentration of alcohol to 90%. In agreement with Foster and Woodrow (A., 1924, i, 897) such an extract was found to inhibit the lactic acid formation of excised rabbit's muscle to the extent of 60%; the incompleteness of the inhibition was not due to failure to penetrate the muscle-cells, and, moreover, the inhibition of the loss of carbohydrate was practically complete, indicating the existence of a non-carbohydrate source of lactic acid. Addition of the pancreatic inhibitor to muscle extract entirely inhibits loss of carbohydrate and phosphate and formation of lactic acid, whether sodium fluoride be present or not; formation of lactic acid by muscle extract must therefore proceed through a hexosephosphate, and it is the formation of this ester which is prevented by the pancreatic extract.

II. The glycolytic activity of malignant tumours is reduced by mincing the tissue, and abolished by freezing, grinding, or extraction; glycogen cannot be utilised in the process; the glycolysis is not affected by the pancreatic inhibitor, the reason being that in this case intermediate formation of hexosephosphate does not occur. C. R. HARINGTON.

Formation of lactic acid from glycogen with dried muscle and activators. H. VON EULER, E. BRUNIUS, and S. PROFFE (Svensk Kem. Tidskr.,

1928, **40**, 100—102; Chem. Zentr., 1928, ii, 72).—The formation of lactic acid from glycogen by dried muscle is greatly stimulated by yeast juice, whilst a co-zymase preparation effected only a slight production of lactic acid. A. A. ELDRIDGE.

Vegetable oxidoreductase. D. MICHLIN (Biochem. Z., 1928, **202**, 329—336).—A method of preparing highly purified preparations of potato oxidoreductase is described. These preparations reduce nitrates 250 times as quickly as they reduce methylene-blue. In the presence of potassium cyanide methylene-blue solutions remain coloured even after 8 hrs., although the enzyme is also present. The presence of alkali does not affect the reducing actions on nitrates. The differences between the actions of animal and vegetable oxidoreductases are discussed. W. McCARTNEY.

Enzymic proteolysis. III. P. RONA and E. MISLOWITZER (Biochem. Z., 1928, **202**, 453—465; cf. A., 1928, 923).—Trypsin does not reduce the size of the particles in an albumin solution, but in peptic hydrolysis of albumin the particle size is reduced approximately to the same extent as in peptic hydrolysis of caseinogen. The increase of amino-groups during hydrolysis is related to the hydrolysis of the products containing the residual nitrogen. In the colloidal fraction of albumin solution scarcely any increase in the number of amino-groups occurs, but there is an increase in the number of carboxyl groups. W. McCARTNEY.

Behaviour of pepsin. F. GALLI (Folia Clinica, 1928, **3**, 191—208).—Gross' caseinogen method for determining the peptic activity of gastric juice is found unsatisfactory and a new method, which depends on the liquefaction of gelatin and gives more certain and exact results, is described. Examination of a number of patients suffering from gastric troubles shows that, although as a rule variation of the pepsin content of the gastric juice is accompanied by variation of the content of hydrochloric acid, there is no fixed relationship between the two. When the free acid is lacking, pepsin also is usually absent but is occasionally present in small proportion. T. H. POPE.

Hydrolytic action of *Ricinus* lipase. II. **Hydrolysis of lecithin.** III. **Hydrolysis of phytin.** A. PIUTTI and E. DE' CONNO (Annali Chim. Appl., 1928, **18**, 512—519, 520—528; cf. this vol., 99).—II. By a stable emulsion of *Ricinus* lipase, containing about 38% of ricinoleic acid, 4% of proteins, and 58% of water, lecithin is hydrolysed, either in aqueous emulsion or in toluene solution containing 35—40% of water, into fatty acids and glycerophosphoric acid. The latter undergoes no scission, and the realisation of such decomposition by Plimmer and Bayliss (A., 1906, i, 325) is regarded as due to the presence of small proportions of other enzymes (glycerophosphatases) in *Ricinus* seeds (cf. Grosser and Husler, A., 1912, ii, 367). The fact that only about 30% of the lecithin undergoes hydrolysis is ascribed to inhibition of the enzymic action by the glycerophosphoric acid formed.

III. *Ricinus* seeds rich in lipase contain also enzymes able to hydrolyse proteins and glycero-phosphates, together with a small proportion of a phytase. The last is also present in the industrial lipase preparation used in the previous experiments, but the very high lipolytic activity of this preparation exerts an inhibiting influence on the phytase. T. H. POPE.

Uricolysis. I. K. FELIX, F. SCHEEL, and W. SCHULER (Z. physiol. Chem., 1929, **180**, 90—106).—The conversion of uric acid into allantoin and carbon dioxide by the action of uricase (in the form of powdered pig's liver) at 37—38° (greatly retarded action below 23°) has been studied quantitatively. The optimum condition for fission of carbon dioxide occurs sharply at p_H 9·9, whilst for the decomposition of the uric acid two maxima appear on the curve at p_H 8·9 and 9·9—10·0, respectively. At the former only a very small quantity of carbon dioxide is evolved (about 20% of the quantity equivalent to the uric acid when the latter has been completely destroyed, the actual volume depending on the duration of the investigation), but at the second point, which is common to both curves, it is always equivalent to the uric acid destroyed. Throughout the whole course of the reaction (p_H 8·6) 1 atom of oxygen is absorbed for each mol. of uric acid decomposed. If the whole of the uric acid is destroyed at the first optimum point (p_H 8·9), that is, with evolution of only 20—30% of the equivalent quantity of carbon dioxide, the enzyme then removed, and the effect of hydrogen-ion concentration on the evolution of carbon dioxide by introduction of a fresh sample of liver investigated, the maximum is again found at p_H 9·9 and the evolution of carbon dioxide now proceeds in the complete absence of oxygen. Hence the decomposition occurs in two stages, the first being the oxidation of the uric acid to an unknown intermediate, which, in the second stage, eliminates carbon dioxide. Since uroxanic acid (Biltz and Robl, A., 1920, i, 883) readily decomposes into allantoin and carbon dioxide, the action of the liver powder on the potassium salt of this acid was studied under similar conditions, but no appreciable quantity of carbon dioxide was evolved. By extracting the liver powder at p_H 8·9 a specimen relatively rich in the oxidase and relatively poor in the decarboxylase was isolated. J. W. BAKER.

Rate of multiplication of yeast at different temperatures. O. W. RICHARDS (J. Physical Chem., 1928, **32**, 1865—1871).—The rate of multiplication of *Saccharomyces cerevisiæ* increases regularly with a rise in temperature between 4° and 30°, except for a change in the rate which occurs at 9°. A critical temperature for this particular strain of yeast exists at 30°, above which the rate of growth decreases with a rise in temperature. At 30°, abnormal, elongated cells are formed indicating that the process of bud formation is critically affected at this temperature. These abnormal cells are maintained in number only if the temperature is kept constant within limits narrower than those achieved by the usual type of laboratory incubator. The need for precise temperature control of yeast cultures is emphasised. L. S. THEOBALD.

Production of acids by *Aspergillus fumaricus.* R. SCHREYER (Biochem. Z., 1928, **202**, 131—156).—

In the course of time the mould loses the power of forming fumaric acid and gives rise to citric and gluconic acids. Citric acid is obtained from sugars having three, five, six, or twelve carbon atoms, from lactose, glycerol, and mannitol. The mould accumulates gluconic acid in young calcium carbonate cultures, and the formation of this acid is favoured by increased oxygen tension, accelerated diffusion, and removal of carbon dioxide. The acid is obtained only in small amount in barium carbonate cultures. The temperature for optimum growth is between 21° and 23°, the minimum about 6° and the maximum 31—32°. Ammonium nitrate is the best source of nitrogen.   P. W. CLUTTERBUCK.

Citric acid formation by moulds. III. Theories of citric acid formation and the appearance of acetaldehyde in the mould cultures. K. BERNHAUER and K. SCHÖN (Biochem. Z., 1928, 202, 164—179).—The greatest amount of acetaldehyde obtained in presence of sodium sulphite is about 0·6% of the sugar used. The amount differs with the different sources of carbon, lævulose and sucrose giving most, dextrose much less, and glycerol least. In these experiments, owing to the alkaline reaction, the amount of citric acid formed is small, whilst using "dimedon" in place of sulphite, the formation of citric acid is almost completely inhibited. "Dimedon" is attacked by *Aspergillus niger* and is therefore unsuitable as a means of removing aldehyde during its growth. It is concluded that no relationship exists between the processes resulting in the formation respectively of aldehyde and citric acid.
                                P. W. CLUTTERBUCK.

***Penicillium glaucum.* Production of methyl ketones from triglycerides or fatty acids in the metabolism of the mould.** C. ACKLIN and W. SCHNEIDER (Biochem. Z., 1928, 202, 246—283).—The conditions of growth and of nutrition of *P. glaucum* have been studied. The effects considered were those of different nutrient media, of different sources of carbon and nitrogen, of different hydrogen-ion concentrations in buffered and unbuffered solutions, of change of p_H during the growth of the organism, of maintenance of constant p_H, and of the presence of iron (ionic and in complex form) as a catalyst.
                                W. MCCARTNEY.

Nutrition of *Polytoma uvella*, Ehrenberg (*Flagella Chlamydomonadinæ*), and the synthetical power of heterotropic protozoa. Mesotropic protozoa. A. LVOV (Compt. rend., 1929, 188, 114—116).—The synthetic medium of Pringsheim (which contains sodium acetate, glycine, potassium carbonate, magnesium sulphate, and dipotassium hydrogen phosphate; cf. Beitr. z. allgem. Bot., 1921, 2, 88) for the culture of *Polytoma uvella* may be modified by replacing the glycine by any of a large number of amino-acids or amines (glucosamine or histamine). Cystine gives the best results. Whilst this organism is capable of obtaining its carbon and nitrogen from ammonium acetate (heterotropic), *Glaucoma pyriformis* requires complex substances such as peptones (mesotropic).   G. A. C. GOUGH.

Fermentation of dextrose by organisms of the genus *Serratia*. C. S. PEDERSON and R. S. BREED (J. Bact., 1928, 16, 163—185).—*Serratia marescens* produced acetic, formic, succinic, and *l*-lactic acids, ethyl alcohol, acetylmethylcarbinol, βγ-butylene glycol, carbon dioxide, and a little hydrogen. Similar, but not identical, products were obtained from other strains.   CHEMICAL ABSTRACTS.

Respiration and glycolysis of trypanosomes. II. B. VON FENYVESSY and L. REINER (Biochem. Z., 1928, 202, 75—80).—Trypanosomes decompose sugar partly by oxidation and partly by glycolysis, aërobic and anaërobic glycolysis taking place about equally. Hydrocyanic acid and "germanin" do not affect the course of glycolysis. Between p_H 7 and 8 oxidation predominates in the more alkaline and glycolysis in the more acid solutions.
                                P. W. CLUTTERBUCK.

Determination of caseinogen hydrolysis by *Clostridium botulinum*. G. M. DACK and W. L. WOOD (J. Infect. Dis., 1928, 42, 172—175).—In a medium containing peptone and caseinogen the toxin titre is related to the caseinogen hydrolysis.
                                CHEMICAL ABSTRACTS.

The *Coccaceæ*. XII. Action of streptococci on caseinogen. XIII. Production of carbon dioxide by streptococci. XVI. Biochemical reactions produced by streptococci. G. J. HUCKER (New York Agric. Exp. Sta. Bull., 1928, Nos. 141—143).—XII. Pure caseinogen is not available to the streptococci provided that these are washed free from extracellular enzymes and other impurities, but certain strains of the organisms, particularly those from dairy products, utilise pure caseinogen if large amounts of unwashed cells are present. Pyogenic streptococci do not produce growth under any conditions when pure caseinogen is the only source of nitrogen furnished. Many of the organisms which will not grow in pure caseinogen solutions increase the amount of free amino-nitrogen when grown in milk.

XIII. Of the representative strains of streptococci studied, most produced small amounts of carbon dioxide from peptone and these amounts increased with increased amounts of peptone in the medium. *S. kefir* and *S. citrovorus* produced no carbon dioxide from peptone but formed relatively large amounts from dextrose.
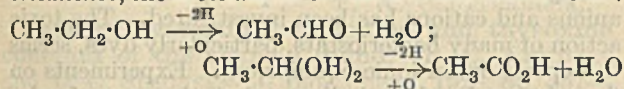
XIV. From the study of 358 authentic strains of streptococci an attempt has been made to classify the organisms on the basis of biochemical behaviour. Two groups can be distinguished according to the type of lactic acid which they produce. One group consists of those strains which generally prefer lævulose to dextrose, attack the pentoses, hydrolyse lactose faster than acid is produced, form relatively large amounts of volatile acid, often produce carbon dioxide, and produce always *l*-lactic acid. The strains of the other group (which includes all the commonly encountered types) produce *d*-lactic acid, do not hydrolyse lactose more rapidly than acid is produced, and sometimes produce large amounts of acid from certain sources of carbon. The acids produced by the first group are acetic acid and an acid which is possibly formic acid; those produced by the second group are acetic acid and an acid which is higher in the series and may be propionic

acid. Constant results were obtained in quantitative acid production from sugars if conditions of growth were controlled. W. McCartney.

Proteolytic bacteria of milk. III. Action on caseinogen and gelatin. W. C. Frazier and P. Rupp (J. Bact., 1928, **16**, 187—196).—Some of the organisms decomposed the calcium more easily than the sodium compound of caseinogen; in one case the reverse held. Increasing amounts of fermentable sugar up to 0·1% did not in general affect the degradation of caseinogen.

Chemical Abstracts.

Mechanism of oxidative processes. XV. Nature of the acetic acid fermentation. H. Wieland and A. Bertho (Annalen, 1928, **467**, 95—157).—A series of investigations has been carried out on the acetic acid fermentation by *Bacterium orleanense*, the mechanism of which is considered to be:

$$CH_3 \cdot CH_2 \cdot OH \xrightarrow[+O]{-2H} CH_3 \cdot CHO + H_2O ;$$
$$CH_3 \cdot CH(OH)_2 \xrightarrow[+O]{-2H} CH_3 \cdot CO_2H + H_2O$$

(cf. A., 1913, i, 1304). It was not found possible to separate the enzymes from the bacteria, and all experiments were carried out with suspensions of the bacteria of known concentrations, buffered to p_H 5·6.

With alcohol as substrate the consumption of free oxygen was strictly proportional to time. In presence of 0·0002M-hydrogen cyanide the velocity fell to 16% of normal. Titration of the acetic acid formed indicated a greater dehydrogenation of acetaldehyde than would be expected from its concentration relative to alcohol, an effect which is attributed to the preferential adsorption and reaction of aldehyde formed on the surface of the same enzyme which catalyses the first stage of the reaction. When benzoquinone was used as hydrogen-acceptor in absence of free oxygen, the dehydrogenation was more rapid, but the same linear relation with time was found. The bacteria were shown to be unaffected by quinone or quinol in the concentrations used. The reaction was much less sensitive to hydrogen cyanide than the reaction with free oxygen; a concentration of 0·01M first produced a noticeable retardation. The rate of hydrogenation of the quinone was only slightly lowered by the presence of free oxygen. On the other hand, the free oxygen began to be consumed only when the quinone was practically used up, and thereafter was taken up at the normal rate. It is concluded that the same enzyme catalyses the reaction with both quinone and free oxygen. The linear relation between reaction and time shows that adsorption on the enzyme surface is more rapid than the chemical reaction. Since quinone displaces free oxygen as hydrogen-acceptor when both are present, quinone must be strongly adsorbed and occupy the surface of the enzyme to the exclusion of oxygen, *i.e.*, it inhibits the oxygen reaction for the same reason as hydrogen cyanide, and the reaction with quinone is less retarded by hydrogen cyanide on account of this strong adsorption of quinone. The hypothesis of activation of both the hydrogen of the substrate and of free oxygen is rejected. Activation of the former alone is considered sufficient. There is no reason why quinone should be able to dispense

with an activation inhibited by hydrogen cyanide if molecular oxygen needs it. Using methylene-blue as hydrogen-acceptor the reaction was very slow and its course was not linear. There was evidence of retardation of the reaction by excess of methylene-blue. The non-linear course of the reaction made observation of times of complete decolorisation quantitatively valueless. Retardation by hydrogen cyanide was first marked at a concentration of 0·01M. With methylene-blue in presence of free oxygen the latter was consumed at the normal rate, whilst when sufficient hydrogen cyanide was added normally to inhibit reaction with free oxygen, free oxygen was taken up at about 6% of the normal rate. This rate was increased somewhat by increasing the amount of methylene-blue, and was presumably determined by the rate of reaction of free oxygen with leuco-methylene-blue, which was found in separate experiments to be low and little affected by hydrogen cyanide. It is concluded that the interior of the cell, as well as its external walls, are active in the dehydrogenation process. The methylene-blue is unable to penetrate the wall, and reacts only on its outer surface, whilst molecular oxygen, quinone, and hydrogen cyanide can all diffuse into the interior of the cell, where 90% of the action takes place.

A parallel series of experiments was carried out with acetaldehyde as substrate. The reaction was little retarded by hydrogen cyanide, and addition of acetaldehyde restored the activity of a mixture, containing alcohol as substrate, poisoned by hydrogen cyanide. These effects appeared to be due to formation of cyanohydrin, which was shown to occur rapidly. The cyanohydrin itself, however, had a minor retarding effect. The course of the reaction of acetaldehyde with free oxygen, quinone, or methylene-blue was similar to the reaction of alcohol, although slower. Mixtures of acetaldehyde and alcohol consumed alcohol at a rate which was the mean of the rate of consumption by each separately. The two reactions are, therefore, brought about probably by the same enzyme. Contrary to Neuberg and Windisch (A., 1926, 324), the Cannizzaro reaction plays little part in the formation of acetic acid from acetaldehyde (cf. also Myrbäck, Euler, and Sandberg, A., 1928, 924). Carefully controlled experiments showed that the rate of consumption of oxygen was actually about forty times that calculated on the basis of dismutation alone, the rate of which was also measured. Similar experiments with *B. pasteurianum* (cf. Neuberg and Molinari, Naturwiss., 1926, **14**, 756) showed that these bacteria brought about dehydrogenation of acetaldehyde at 100 times the rate of dismutation.

Salicylaldehyde and *o*-hydroxybenzyl alcohol were not dehydrogenated by *B. orleanense*. Dithioglycollic acid or cystine did not act as hydrogen-acceptors in presence of alcohol. The dehydrogenation of succinic acid by dithioglycollic acid in presence of minced liver previously reported (A., 1924, i, 1172) is erroneous.

The catalase activity of *B. orleanense* was also measured. Hydrogen peroxide was rapidly decomposed in a reaction apparently of high order, retarded

by hydrogen cyanide. This retardation was parallel to that of the dehydrogenation of alcohol. No free hydrogen peroxide could be recognised in any of the reaction mixtures, whether containing hydrogen cyanide or not, so that the inhibitory effect of hydrogen cyanide on the dehydrogenase activity must be of the same order.   R. K. Callow.

Precipitation of magnesium ammonium phosphate crystals during the growth of bacteria in media containing nitrogenous substances. S. A. Scudder (J. Bact., 1928, **16**, 157—161).— Crystals having the composition $MgNH_4PO_4,6H_2O$, $MgNH_4OP_2O_5$, and $K_2Mg_2(SO_4)_3$ were isolated from agar cultures of *B. alkaligenes*, *M. catarrhalis*, and *C. diphtheriæ*; favourable factors are the presence of meat infusion, peptone, and inorganic phosphate, and a decrease in the amount of sodium chloride and water.   Chemical Abstracts.

Influence of radium on the metabolism of bacteria participating in the nitrogen cycle. J. Stoklasa and J. Kricka (Zentr., Bakt. Par., 1928, II, **74**, 161—183; Chem. Zentr., 1928, ii, 161).— α-Rays in the form of air containing emanation stimulate the nitrogen assimilation of *Azotobacter* although amounts greater than a certain limit retard the assimilation. Hydrolysis of proteins by proteolytic enzymes is not promoted by radium emanation. Denitrification by *B. Hartlebii* or *B. fluorescens liquefaciens* is promoted, by growth stimulation, by weak doses of radium emanation, and inhibited by strong doses. The destruction of dextrose by *Azotobacter* is also increased by radioactive air, unusually large quantities of carbon dioxide, acetic acid, and formic acid being produced. In protein degradation by *B. Hartlebii* the monoamino-nitrogen is specially increased by α-rays. Nitrogen assimilation is retarded in liquid medium by β- and γ-, or by γ-rays, although these rays stimulate the activity of proteolytic enzymes. Denitrification is also increased. In the decomposition of dextrose by *Azotobacter* β- and γ-rays cause greatest formation of alcohol, lactic acid, and acetaldehyde; protein degradation proceeds with special increase of amide-nitrogen.   A. A. Eldridge.

Influence of carbohydrates on the bacterial decomposition of urea. M. Ishikawa (J. Infect. Dis., 1928, **43**, 67—80).—The decomposition of urea by *Bacillus ammoniogenes*, *B. aërogenes*, *B. Morgani*, *B. proteus vulgaris*, and *Staphylococcus aureus* is accelerated by the presence of a utilisable carbohydrate. Symbiosis of such organisms with one which does not decompose urea, in a medium containing a carbohydrate fermentable only by the latter, increases the amount of ammonia produced.   Chemical Abstracts.

Biochemical production of fats. V. Kulikov (Oil Fat Ind. Russia, 1928, No. 4, 21—23; Chem. Zentr., 1928, ii, 822).—The bacterial production of fats (36%) consisting of palmitin and stearin, and of waxes, is described.   A. A. Eldridge.

Growth of hæmophilic bacilli with certain iron salts. J. M. Bourn (J. Infect. Dis., 1927, **41**, 294—303).—Successive cultures in veal infusion broth required the presence of sodium aquopentacyano-ferroate.   Chemical Abstracts.

Oxidation processes with the iron-containing component of hæmoglobin. K. Bingold (Klin. Woch., 1928, **7**, 928—951; Chem. Zentr., 1928, ii, 160—161).—Pneumococci, strepto-bacilli, and certain streptococci, when grown on a hæmatin nutrient medium, decompose the hæmatin. In hydrogen peroxide, but not under reductive conditions, decolorisation occurred. In the decomposition of hæmoglobin hæmatin is not necessarily produced, but all oxidases produce a fermentative degradation to hæmatic acid.   A. A. Eldridge.

Physico-chemical behaviour of bacteria. A. E. Stearn and E. W. Stearn (Univ. Missouri Stud., 1928, **3**, 1—84).—Bacteria possess individual characteristic isoelectric points and ranges. The relation between the p_H of reaction, isoelectric point, and retention of anions and cations has been investigated. The toxic action of many bacteriostats, particularly dyes, seems to depend on an ionic equilibrium. Experiments on flocculation by dyes indicate that the same fundamental mechanism is effective as in staining and growth inhibition.   Chemical Abstracts.

Microbiological death rates. C. H. Werkman (Proc. Iowa Acad. Sci., 1927, **34**, 85—86).—A study of the survivor-curves obtained by subjection of *Staphylococcus aureus* to the action of various bactericidal substances. The toxicity of monohydric alcohols increases with mol. wt.; introduction of hydroxyl groups (*e.g.*, propyl alcohol, propylene glycol, glycerol) causes a diminution of toxicity. Phenyl groups substituted in the alcohol molecule greatly increase the toxicity, but partial oxidation diminishes it. Introduction of an amino-group prolongs the induction period, but does not markedly reduce toxicity. Diminution of surface tension leads to increased toxicity.   Chemical Abstracts.

Effect of metallic salts on the development of bacteria. II. Silver. P. H. Andresen (Zentr. Bakt. Par., 1928, I, **107**, 392—397; Chem. Zentr., 1928, ii, 777).—A suitable medium is described, and the effect of silver salts on *Bacillus coli*, *B. proteus*, and staphylococci recorded.   A. A. Eldridge.

Distribution and stability of the antigenic properties of diphtheria toxin. Rôle of non-specific colloids. P. Sédallian, A. Leulier, and (Mme.) Clavel (Compt. rend., 1928, **187**, 1297—1299).— The powers of immunisation of the supernatant liquid and of the precipitate produced at p_H 4·7 have been determined. The former fixes no antitoxin when placed in contact with it, and the latter fixes only a small amount. The precipitate, however, when dissolved in fresh Martin broth, fixes almost as much as the original toxin, and it is suggested that the broth contains non-specific substances of the protective colloid type, capable of conferring powers of adsorption, and analogous to Ehrlich's toxones.   J. Grant.

Bilirubin as a potential hæmopoetic hormone. F. Verzár and A. Zih (Klin. Woch., 1928, **7**, 1031—1032; Chem. Zentr., 1928, ii, 457).

Interrenin. M. GOLDZIEHER (Klin. Woch., 1928, 7, 1124—1125; Chem. Zentr., 1928, ii, 457).—A physiologically active substance, *interrenin*, which, when injected intravenously, reduces arterial blood-pressure and causes a decrease of blood-lipins, has been prepared from the suprarenals.

A. A. ELDRIDGE.

Physiology of glands. L. ASHER. CXVI. Respiratory metabolism during work under normal conditions and after adrenaline. W. H. SCHEUCHZER (Biochem. Z., 1928, 201, 148—164).—Further experiments with Asher's respiration chamber for rats confirmed the results of Curtis (*ibid.*, 1925, 164, 97). Subcutaneous injection of adrenaline causes only a trifling increase of metabolism during work, the body temperature being decreased. The work appears therefore to be performed more economically under the influence of adrenaline.

P. W. CLUTTERBUCK.

Seasonal variations in iodine and thyroxine contents of the thyroid gland. E. C. KENDALL and D. G. SIMONSEN (J. Biol. Chem., 1928, 80, 357—377).—A new method of isolating thyroxine from the thyroid gland is described which consists of a combination of the authors' original sodium hydroxide hydrolysis (A., 1915, i, 600) with subsequent treatment with barium hydroxide (cf. Harington, A., 1926, 644). A seasonal variation of 300% was observed in the iodine content of the glands employed. The thyroxine isolated represented, on the average, 5% of the total iodine. Partly on the basis of this figure, and partly on comparison of physiological activity, it is concluded that the acid-insoluble fraction of the iodine obtained after preliminary alkaline hydrolysis of the thyroid contains iodine compounds other than thyroxine; further, since the whole of the activity of desiccated thyroid cannot be accounted for by the thyroxine which can be isolated from it, it is thought that thyroxine must first be converted into an "active" form, before it can exercise its specific physiological effect.

C. R. HARINGTON.

Action of thyroxine on the glycogen content of skeletal muscle and of the liver of guinea-pigs. O. BÖSL (Biochem. Z., 1928, 202, 299—319).—In young and adult guinea-pigs receiving sufficient food for maintenance of normal body-weight subcutaneous injections of thyroxine cause loss of weight. The glycogen content of the skeletal muscle undergoes no decrease under these conditions, but that of the liver diminishes to an extent which varies according to the individual, so that, in these respects, thyroxine behaves like thyroid gland. The effect of small doses of thyroxine on the glycogen of the liver can be compensated by supplying more food to the animals. The glycogen content of the skeletal muscle of animals treated with thyroxine while receiving only half of the normal amount of food is reduced, on the average, more strongly than that of controls, and under these conditions the livers of the animals receiving thyroxine are free from glycogen. In guinea-pigs receiving normal amounts of food and stimulated to increased activity the glycogen content of the skeletal muscle, and still more that of the liver, is increased as compared with that of resting animals. Control animals

stimulated to activity also show these increases and, on the average, to a greater extent.

W. MCCARTNEY.

Action of thyroxine on the protein, water, and mineral metabolism. A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1928, 61, 239—277; Chem. Zentr., 1928, ii, 459).—In dogs, thyroxine causes increased excretion of nitrogen and water; secretion of urea is increased, that of ammonia being at first reduced. In man the effect on the protein metabolism is small; ammonia excretion is increased. In myxœdema the disturbances are counteracted by thyroxine.

A. A. ELDRIDGE.

Carbohydrate metabolism of the white mouse with and without administration of insulin. IV. E. J. LESSER and R. AMMON (Biochem. Z., 1928, 202, 294—298).—When the mouse receives injections of dextrose alone part of this is converted into glycogen and part is burnt in the organism, but when insulin is injected immediately after the injection of dextrose some glycogen (originally present) disappears, and almost all of the injected sugar disappears also. The carbohydrate metabolism is thus greatly accelerated by insulin as a result of the increased oxidation which takes place. The disappearance of glycogen may occur only in the later stages of the action of insulin.

W. MCCARTNEY.

Blood-sugar and respiratory metabolism following simultaneous administration of dextrose and insulin. I. M. RABINOWITCH and E. V. BAZIN (J. Biol. Chem., 1928, 80, 723—731).—Observation of the curves of blood-sugar and respiratory metabolism, following simultaneous administration of dextrose and insulin, indicates that the latter, in normal individuals, inhibits rather than increases the rate of oxidation of sugar.

C. R. HARINGTON.

Examination of insulin for vitamin-*B*. C. J. STUCKY (Arch. Int. Med., 1928, 42, 780).—Commercial preparations of insulin contain neither the antineuritic nor the heat-labile growth-promoting factors of vitamin-*B*.

E. BOYLAND.

Effect of ethylene on the vitamin-*B* content of celery. M. F. BABB (Science, 1928, 68, 231).—No diminution of the vitamin-*B* content was observed in ethylene-blanched celery.

A. A. ELDRIDGE.

Vitamin-*B* content of wheaten bread baked with varying amounts of yeast. A. SCHEUNERT and M. SCHIEBLICH (Biochem. Z., 1928, 202, 380—386).—The vitamin-*B* content of wheaten bread can be raised by increasing the amount of yeast used in the baking. If the increase amounts to 3—6 times the usual quantity, the bread produced satisfies the vitamin-*B* requirements of pigeons and of young growing rats.

W. MCCARTNEY.

Relationship between the ability to darken photographic plates and the vitamin-*A* content of cod-liver oil and pig's fat. L. S. FRIDERICIA and S. V. GUDJÓNSSON (Bibl. for Laeger, 1927, 12 pp.; Chem. Zentr., 1928, ii, 782).—No parallelism was detected.

A. A. ELDRIDGE.

Effect of scurvy-producing diets and tyramine on the blood of guinea-pigs. M. T. HANKE and

K. K. Koessler (J. Biol. Chem., 1928, **80**, 499—502).—No anæmia was produced in guinea-pigs by subcutaneous administration of tyramine, whether in combination with a normal diet or with one deficient in vitamins-*A* and -*C* (cf. Iwao, A., 1914, i, 360).
                                        C. R. Harington.

Irradiation of sterols ; relation between irradiated sterols and antirachitic vitamin. R. Fabre and H. Simonnet (J. Pharm. Chim., 1928, **8**, [viii], 489—506).—A summary of the present state of knowledge regarding vitamin-*D*. Some experiments on the variation in absorption spectrum of alcoholic solutions of ergosterol after irradiation for varying periods are described.   E. H. Sharples.

Photochemistry of vitamin-*D*. S. K. Kon (Rocz. Chem., 1928, **8**, 502—518).—Ergosterol was completely removed from cholesterol by repeated boiling in acetone solution with potassium permanganate. Cholesterol so purified remains biologically inactive after irradiation. The amount of radiant energy necessary to produce a demonstrable amount of vitamin-*D* from ergosterol is 700—1000 ergs between 256 and 293 μμ, independently of the wave-length of ultra-violet light used. The efficiency of this process is the same when solid ergosterol is used, or dilute or concentrated alcoholic solution, and is the same for ergosteryl acetate as for the free sterol, indicating that the hydroxyl group does not play any part in the formation of vitamin-*D*. Activation does not take place in acetone solution, as the solvent has itself a strong absorption band in the same region as ergosterol. The formation of vitamin-*D* from ergosterol is probably a complicated process with low quantum efficiency.   R. Truszkowski.

Antirachitic substances. IX. Activation of ergosterol. C. E. Bills, E. M. Honeywell, and W. M. Cox, jun. (J. Biol. Chem., 1928, **80**, 557—563).—Samples of carefully purified ergosterol were subjected to ultra-violet irradiation for various periods in alcoholic solution and then examined both spectrophotometrically and by biological test. The maximum physiological activity was attained before the absorption curve showed any significant alteration ; with increasing length of exposure the activity decreased and the band at 248 μμ (cf. Heilbron and others, A., 1927, 381, 1123) appeared ; the latter band reached its maximum intensity coincidently with the disappearance of physiological activity, and is associated therefore with the destruction rather than with the formation of vitamin-*D*. The freer the access of oxygen the more rapid is the development and subsequent fading of the band at 248 μμ ; such a band, showing similar behaviour on irradiation, is observed in the spectrum of *iso*ergosterol (Reindel and others, A., 1927, 241).   C. R. Harington.

Destruction of vitamin-*E* in a diet of natural foodstuffs. J. Waddell and H. Steenbock [with E. van Donk] (J. Biol. Chem., 1928, **80**, 431—442). —Incorporation of 1% of ferric chloride with an adequate natural diet leads to destruction of vitamin-*E*, whilst vitamin-*A* is not affected.
                                        C. R. Harington.

Amino-acid synthesis in plants. W. F. Loehwing (Proc. Iowa Acad. Sci., 1927, **34**, 115—118).— Fruit formation robs the vegetative structures of tomato plants of nitrates, ammonia, and amino-acids. Nitrates, when absorbed by defruited plants, accumulate at and are reduced to nitrites, ammonia, and amino-acids in the vicinity of the meristem. Alkalinity and the presence of sugars appear indispensable for the reduction, which is not attributed to enzymes.   Chemical Abstracts.

Effect of ethylene on the respiration of bananas during ripening. L. O. Regeimbal, G. A. Vacha, and R. B. Harvey (Plant Physiol., 1927, **2**, 357—359).—Ethylene (1 in 10³ of air) was allowed to act for 15—20 min. at 25°, aspiration of air free from carbon dioxide then being resumed. Electrometric determination of the rate of production of carbon dioxide showed that the rate of respiration quickly trebled, and then became subnormal, owing either to increase of oxidation or to increase in the permeability of the membranes. Treatment increases the activity of the diastatic and respiratory enzymes. Treated bananas contain 20—25% more sugar (and correspondingly less starch) than untreated.
                                        Chemical Abstracts.

Ripening of rice seed and chemical properties of rice of the early-ripening sub-varieties. T. Tadokoro (J. Coll. Agric. Hokkaido, 1927, **20**, 333—354).—In ripening, the non-protein nitrogen decreases and the diamino-nitrogen, sodium chloride-soluble and ethyl alcohol-soluble proteins of rice seed increase. The oryzanin increases in specific rotation, in free amino-nitrogen, and lysine, but decreases in arginine and ash until a point is reached when the changes are reversed. In the middle part of the ripening period the ash and phosphorus decrease, the acetyl value of the starch increases, and its specific rotation decreases. Early-ripening varieties are richer in fat, non-protein nitrogen, and water-soluble protein nitrogen, and poorer in ash and protein nitrogen than later-ripening varieties. The oryzanin of the early varieties is lower in free amino-nitrogen than that of the later varieties.
                                        Chemical Abstracts.

Action of glycerophosphatase of plant seeds and enzymic synthesis. A. Němec (Biochem. Z., 1928, **202**, 229—235).—During the after-ripening of seeds, glycerophosphatase action is considerably decreased, and the greater this decrease the greater is the subsequent germinating power. During the germination of maize and barley a slight decrease of glycerophosphatase action is obtained in the first two days followed by a considerable increase, whereas with soya beans and peas there is a continuous increase of glycerophosphatase action. When the seed meal is autolysed with added glycerol and phosphate, the amount of free phosphate decreases, suggesting enzymic union of glycerol and phosphate.
                                        P. W. Clutterbuck.