BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1927.

General, Physical, and Inorganic Chemistry.

pp'-Groups in atomic spectra. R. A. Sawyer (Physical Rev., 1926, [ii], 27, 106).—It is suggested that the pp' frequency is associated with the difference in frequency between the two lowest singlet levels in the spectrum concerned and with the difference in level between the two lowest doublet levels in the next spectrum (once more ionised atom).
A. A. Eldridge.

Discharge tubes for producing intense continuous hydrogen spectrum. Z. Bay and W. Steiner (Z. Physik, 1927, 45, 337—342).—Two forms of discharge tube are described, designed for continuous operation at 0·5 amp., 3000 volts *A.C.*, adapted to give an intense source of the continuous spectrum of hydrogen between 3300 and 1950 Å. In one form the light is emitted axially through a suitable window from a column of hydrogen contained in a tube of length 60 cm. and of diameter 5 mm., silvered internally, and immersed in a stream of cooling water. The second form dispenses with the cooling medium by using a glass tube of length 60 cm. and of diameter 5 cm. in which is mounted co-axially a porcelain tube of diameter 8 mm. silvered on its inner surface; the space between the porcelain tube and the containing wall is packed with glass wool. Current–emission data are cited. R. W. Lunt.

Variation of intensity ratios of optically excited spectrum lines with the intensity of the exciting light. R. W. Wood (Nature, 1927, 120, 725).—It is shown that lines resulting from a two-stage absorption process are reduced to 0·25 and from a three-stage process to 0·125 of their initial intensity values; this explains why it is unsatisfactory to form an image of the lamp on the resonance tube by means of quartz lenses. A. A. Eldridge.

Infra-red radiation of hydrogen. A. H. Poetker (Physical Rev., 1927, [ii], 30, 418—428).—Six higher members of the Paschen series (γ to 0 inclusive) were observed at wave-lengths: —, 10049·8, 9546·2, 9229·7, 9015·3, 8863·4 Å., in agreement with values calculated from Bohr's theory. The secondary spectrum of hydrogen was observed from 10654·5 to 7504·51 Å., about 425 lines, mostly new, being tabulated. A. A. Eldridge.

Spectrum of beryllium. R. F. Paton and W. H. Sanders (Physical Rev., 1926, [ii], 27, 106).—The spectrum of beryllium from 5200 to 2000 Å. has been examined. A. A. Eldridge.

Instantaneous spectrograms of carbon, silicon, tin, lead, and cerium; antimony, bismuth, and manganese; chromium, molybdenum, and tellurium; iron, cobalt, and nickel; palladium, iridium, and platinum. H. Nagaoka, D. Nukiyama, and T. Futagami (Proc. Imp. Acad. Tokyo, 1927, 3, 392—397, 398—402, 403—408, 409—414, 415—418).—The method previously described (cf. this vol., 809, 911) has been applied to the above elements and the results obtained are tabulated.
W. E. Downey.

Abnormal multiplets and inter-combinations in the spectrum of O II. F. Croze and C. Mihul (Compt. rend., 1927, 185, 702—704).—A study of the Zeeman effect has enabled a classification to be obtained of the groups of combinations observed by Fowler (A., 1926, 650) and Bowen (this vol., 285) in the O II spectrum. A complete list of the combinations of quadruplets and of doublets of terms of the O II spectrum, corresponding with the 3α-orbit of the emission electron, has thence been compiled.
J. Grant.

Origin of the nebulium spectrum. A. Fowler (Nature, 1927, 120, 617).—Whilst Bowen's estimate for the $^4S_2$ term of O II was 283,366, the new data indicate a value of 283,028; this is in remarkable agreement with the value 283,020 for the nebular spectrum. It appears that the conditions in nebulæ which facilitate the occurrence of irregular combinations of deep spectroscopic terms are such as to prohibit the regular combinations which produce the ordinary laboratory spectra of the same elements.
A. A. Eldridge.

Natural width and broadening of the absorbed *D*-line in sodium vapour as a function of the partial pressure of the vapour and of other gases. W. Schütz (Z. Physik, 1927, 45, 30—66).—The theory of Voigt has been used to develop an analysis of the Righi effect in gases as a function of the partial pressure of the absorbing gas, that of any other gas present, and the strength of the magnetic field; this has been employed to interpret data obtained on the width of the *D*-line absorbed by sodium vapour alone, and in the presence of hydrogen, helium, nitrogen, neon, and argon. At pressures of sodium vapour below 4×10^{-3} mm. the natural width approaches a limiting value in agreement with the classical half-width $\omega_0'=0{\cdot}64\times10^{-8}$ sec.$^{-1}$ The widths observed at higher pressures, and due to the addition of other gases, are in quantitative agreement with the theory.
R. W. Lunt.

Spark spectra of high order of sulphur and selenium. L. Bloch and E. Bloch (Compt. rend., 1927, 185, 761—763).—By means of an oscillating electrodeless discharge in a highly evacuated silica tube the spark and arc spectra of sulphur and selenium have been separated. Lists of intense rays of the spark spectra corresponding with S II, S III, Se II, and Se III are given. Above the wave-length 4900 Å. only the rays of S II and Se II exist.

J. Grant.

Intensity of the forbidden potassium line 4642 A. F. Rasetti (Atti R. Accad. Lincei, 1927, [vi], 6, 54—55).—From measurements of the magnetic rotation, in a field of 1000 gauss, of the $^2S_4$—$^2D_3$-doublet of potassium in absorption, and from known data relating to the doublet 7665, 7699 Å., the number of electrons per cm.^{3} responsible for the observed dispersion is found to be $2{\cdot}7\times10^{11}$ (probable error 50%). This number is approximately 10^{-6} that corresponding with the doublet 7665, 7699 Å.

R. W. Lunt.

Multiplets of the nickel and cobalt arc spectra in the chromospheric spectrum. C. R. Davidson and F. J. M. Stratton (Month. Not. Roy. Astr. Soc., 1927, 87, 739—747).—A number of unclassified lines of nickel appearing in the chromospheric spectrum between 3100 and 4000 Å. have been identified with arc multiplets. One line (3769·47) may belong to the ionised atom. A number of fresh multiplets in cobalt lines have also been identified in the chromospheric spectrum.

R. A. Morton.

Second spark spectrum of zinc, Zn III. O. Laporte and R. J. Lang (Physical Rev., 1927, [ii], **30**, 378—386).—Accurate wave-lengths (1839·40—677·55 Å.) of the spectrum of the high-potential spark between zinc electrodes are tabulated, together with a classification of the lines of Zn III. The ionisation potential of the shell of ten equivalent 3_3 electrons is 40 volts.

A. A. Eldridge.

Spectral lines of trebly-ionised germanium. S. Smith (Nature, 1927, **120**, 728).—The first members of the second principal series, $5S_1-5P_{1,2}$ were observed at 3554·14 and 3676·61 Å., and a triplet resulting from combinations between $4D_{2,3}$ and $5P_{1,2}$ at 2788·41, 2736·09, 2717·41. A doublet, the second member of the first principal series, is at 441·95, 440·11 Å.

A. A. Eldridge.

Series of the first spark spectrum of tin (Sn I). A. L. Narayan and K. R. Rao (Z. Physik, 1927, **45**, 350—363).—A number of lines in the spark spectrum of tin have been determined in the range 6844·26—2449·79 Å. by a grating with a dispersion of 5·6 Å./mm. These lines together with those observed by other workers have been classified in a doublet system. It is shown that the spectra of C II, Si II, Pb II, and Sn II are very similar and are capable of interpretation on Hund's theory.

R. W. Lunt.

Low-voltage arcs in iodine. H. F. Fruth and O. S. Duffendack (Physical Rev., 1926, [ii], **27**, 248).—It is concluded that 6·5 volts is the minimum radiating potential of the atom, 8·0 the ionising potential of the atom, and 9·5 the ionising potential of the molecule. The spectrum of the abnormal 4·9-volt arc contained only the lines 2062, 2535, and 3135 Å., the continuous band 3460 Å., and several groups of bands. The strongest spark lines commence at 8 volts. Continuous bands at 4080, 4300, and 4800 Å. are present in molecular, but disappear in atomic, iodine. A band system between 2224 and 2050 Å. was observed, and two groups of four bands each at 2880, 2833, 2776, 2716 Å. and 2480, 2379, 2290, and 2243 Å.

A. A. Eldridge.

Intensity of spectral lines. G. I. Pokrowski (Z. Physik, 1927, **45**, 140—145).—The relationship between the intensity of the barium spark and arc lines 4930, 5540, and 5850 Å. has been investigated as a function of the concentration of barium for low concentrations, for which a satisfactory theoretical expression has been derived. With increasing concentration the apparent width of lines increases; this is due to self-absorption.

R. W. Lunt.

Long wave-length limit of mercury. W. B. Hales (Physical Rev., 1926, [ii], **27**, 809).—The limit is 2735±10 Å., in agreement with Kazda's value for flowing mercury.

A. A. Eldridge.

Absorption of resonance radiation in mercury vapour. A. L. Hughes and A. R. Thomas (Physical Rev., 1927, [ii], **30**, 466—472).—The absorption of radiation 2436 Å. per atom decreases rapidly as the amount of absorbing vapour is increased, indicating that the resonance radiation is not homogeneous. The maximum atomic absorption coefficient was $11{\cdot}2\times10^{-14}$; hence an atom can stop the radiation which falls on an area 110 times as large as its cross-sectional area.

A. A. Eldridge.

Determination of certain outer *X*-ray energy levels for the elements from antimony (51) to samarium (62). K. Chamberlain and G. A. Lindsay (Physical Rev., 1927, [ii], **30**, 369—376).—Direct determinations of the distances between the $L\beta_2$, $L\gamma_1$, and $L\gamma_4$ lines and the L_{III}, L_{II}, and L_I absorption edges, respectively, for antimony, tellurium, iodine, cæsium, barium, lanthanum, cerium, praseodymium, neodymium, and samarium yield values for the N_{IV}, N_V, and O_{II-III} energy levels, respectively. A graph shows the variation of these levels with the atomic number. For antimony, tellurium, and iodine, the L_I absorption edges are at 2631·7, 2503·9, 2383·9, the L_{II} edges at 2821·9, 2679·3, 2547·5, and the L_{III} edges at 2990·7, 2845·7, 2713·9X., respectively.

A. A. Eldridge.

Absorption of *X*-rays in various elements. E. Jönsson (Nature, 1927, **120**, 695).—Experimental evidence leads to the enunciation of the following laws: (1) The jump of the absorption coefficient on passing the *K*-absorption limit is $\delta_K=E_K/E_{L_1}$, where E_K and E_{L_1} are the energy levels corresponding with the *K* and L_1 levels, respectively; similarly, $\delta_L=E_{L_1}/E_{M_1}$ and $\delta_M=E_{M_1}/E_{N_1}$. (2) If the absorption is calculated per electron, μ_e, instead of per mass-unit, μ_e is a function of the product $N\lambda$ (*N* is the atomic number) for every branch of the absorption curve. (3) One single continuous curve can be drawn for the absorption at all wave-lengths for all elements, with μ_e and $N\lambda$ as co-ordinates.

A. A. Eldridge.

Separation of the modified and unmodified scattering coefficients of *X*-rays. O. K. DeFoe and G. E. M. Jauncey (Physical Rev., 1926, [ii], **27**, 102).—An improved method is described.

A. A. Eldridge.

Zeeman effect in the Ångström CO bands. E. C. Kemble, R. S. Mulliken, and F. H. Crawford (Physical Rev., 1927, [ii], 30, 438—457).—The qualitative features of the Zeeman effect in the band lines of rigid diatomic molecules as given by the conventional quantum theory and the new quantum mechanics are the same. The results of measurements of the CO bands at 5610, 5198, and 4835 Å. are in agreement with the theoretical predictions.

A. A. Eldridge.

Zeeman effect in the cerium spectrum between 3000 and 5000 Å. H. Margenau (Physical Rev., 1927, [ii], 30, 458—465).—The lines are tabulated according to the general appearance of the Zeeman patterns. A. A. Eldridge.

Zeeman effect and the structure of the arc spectrum of rhodium. L. A. Sommer (Z. Physik, 1927, 45, 147—193).—The Zeeman effect in fields of 30,000 gauss has been examined by a grating method for some 1600 lines of the arc spectrum of rhodium between 2300 and 8600 Å. Approximately 1000 of these lines have been arranged as combinations of the 136 terms of the arc spectrum; they follow the classification of Russell, Pauli, Heisenberg, and Hund. By extrapolation to the series limit the value of 7·7 volts is obtained for the ionisation potential.

R. W. Lunt.

Resonance and ionisation potentials in mercury vapour. C. W. Jarvis (Physical Rev., 1926, [ii], 27, 808).—The following values (volts) were observed: 1·23, 2·21, 2·80, 3·44, 3·80, 4·21, 4·53, 4·97, 5·22, 5·37, 5·70, 6·05, 6·46, 6·79, 7·13, 7·41, 7·74, 8·02, 8·33, 8·82, 9·33, 9·58, 9·90. A. A. Eldridge.

Excitation of spectra by high-frequency oscillations. J. R. Clarke (Nature, 1927, 120, 727).—The spectrum of mercury can be excited by means of high-frequency oscillations (cf. Wood and Loomis, this vol., 1008). The resonance line 2536·7 Å. appeared first, then lines of the *s* and *d* triplet series, then lines of the *S* and *D* singlet series, and some combination lines involving the arrival and departure levels of the series lines present. The lines 3984·1, 3860·4, 3820·6, 3790·4, 3751·8, 3561·5, 3543·7, 3390·5, 3351·5, 2820·0, 2686·7, 2660·1, and 2540·4 Å., which have not yet been allocated to any series or combination, were also observed.

A. A. Eldridge.

Secondary emission from molybdenum due to bombardment by high-speed positive ions of the alkali metals. W. J. Jackson (Physical Rev., 1927, [ii], 30, 473—478).—An extension of previous work (A., 1926, 1074) to the bombardment of sodium, rubidium, and cæsium ions. In general, heat treatment reduces the secondary emission. When the surface of a target is in a condition to emit electrons due to positive ion bombardment, the percentage secondary emission is a function of the speed of the impacting ion. A. A. Eldridge.

Rotation of electric discharge in a decomposable gas. C. E. Guye and B. Luyet (Arch. Sci. phys. nat., 1927, [v], 9, 191—217, 247—263).—When a discharge from a static induction machine is passed through carbon dioxide in a cylindrical chamber fitted with concentric ring and disc electrodes, and a magnetic field is placed around the chamber, the discharge is seen to rotate. The carbon dioxide begins to decompose as soon as the discharge is set up, so that the system studied is always carbon dioxide–carbon monoxide–oxygen. The speed of rotation falls very rapidly during the first few minutes of the discharge and afterwards more slowly. The diminution in speed is least noticeable (*a*) with low initial pressure, (*b*) at a given initial pressure, after the discharge has been running for a long time. Although the slowing down is ascribed to the decomposition of carbon dioxide, the speed of rotation in the mixture is not intermediate between the speeds for the constituents, and it would appear that the simple theory of the discharge is adequate.

At a pressure of 20 mm. the speed of rotation becomes constant after a few minutes, although decomposition of carbon dioxide is occurring all the time. After 1 hr. the increase in pressure under a discharge of 400×10^{-6} amp. was 9·6, 11·0, and 14·8% at initial pressures of 20, 35, and 50 mm., respectively. The rate of decomposition measured in this way depends on the initial amount of gas as well as on the intensity of the discharge, whilst for pressures between 9 and 30 mm. the speed of rotation also depends on the intensity of the discharge. During the first few seconds the apparent volume of the discharge rapidly increases and the speed of rotation rapidly decreases. R. A. Morton.

Motion of slow electrons in a gas. H. Faxén and J. Holtsmark (Z. Physik, 1927, 45, 307—324).—On the assumption that the rare gases can be considered as possessing a symmetrical central electrostatic field, the motion of slow electrons through these gases has been calculated by Schrödinger's wave mechanics. By deriving the structure of xenon from Thomas' model for the cæsium ion (this vol., 290) a first approximation with experiment is obtained.

R. W. Lunt.

Effective cross-section of the noble gases, argon, neon, helium, against slow electrons. E. Brüche [with (Frl.) D. Lilienthal and (Frl.) K. Schrödter] (Ann. Physik, 1927, [iv], 84, 279—291). —The effective cross-sections of argon, neon, and helium have been very carefully determined for various electron velocities. The neon curve falls off steeply with decreasing small velocities. The relation between cross-section and molecule formation is discussed. R. A. Morton.

Detection of unimolecular ions in air, and the existence of forces between ions and gas molecules. W. Busse (Ann. Physik, 1927, [iv], 84, 327—328).—Schilling's work (this vol., 708) makes certain modifications necessary in the author's earlier views on the rôle of water vapour in ion formation (this vol., 4). R. A. Morton.

Molecular structure and relative mobilities of positive and negative gaseous ions. L. B. Loeb and A. M. Cravath (Physical Rev., 1926, [ii], 27, 811—812).—The mobility of the positive ion in hydrogen sulphide is 0·61, and that of the negative ion 0·55 cm./sec. per volt/cm. In water the mobilities are 0·62 and 0·56, respectively. The mobility values

are relative to air, assuming 1·4 for positive and 1·8 for negative ions in cm./sec. per volt/cm.
A. A. Eldridge.

Isotopes of calcium. E. K. Plyler (Science, 1927, **65**, 578—579).—The selective reflexion of polarised radiation (about 6·5 μ) shows maxima at 6·36, 6·54, and 6·62 μ, of which the relative intensities are in agreement with the assumption of the presence of isotopes of mass 39, 40, and 44 in the ratio 0·2 : 1 : 0·05.
A. A. Eldridge.

Limit of accuracy of physico-chemical at. wt. determinations. I. Normal molar volume and at. wt. of nitrogen. E. Moles (Z. anorg. Chem., 1927, **167**, 40—48).—A method is developed for the calculation of at. wt. from limiting density measurements. The normal molar volume of nitrogen, calculated from the mean of accurate density determinations given in the literature, is 22·4148±0·0007, and the at. wt. is 14·0082±0·0002.
H. F. Gillbe.

Density and at. wt. of nitrogen. E. Moles and J. M. Clavera (Z. anorg. Chem., 1927, **167**, 49—66).—The mean density of nitrogen, obtained from four different sources, is 1·25049±0·00003 g./litre. The most probable value of the at. wt. is 14·0082±0·00042.
H. F. Gillbe.

At. wt. of antimony from different sources. K. R. Krishnaswami (J.C.S., 1927, 2534—2539).—The at. wt. of antimony has been determined in samples from five different sources by the method of Willard and McAlpine (A., 1921, ii, 405). The results range from 121·744 to 121·754, the variation being less than the experimental error.
C. W. Gibby.

Isolation of protoactinium (element 91). A. Grosse (Nature, 1927, **120**, 621).—About 2 mg. of protoactinium oxide has been isolated, having a half-value period of 2×10^4 years. Thus, for each g. of radium in a mineral there is approx. 0·4 g. of protoactinium.
A. A. Eldridge.

Radioactive products present in the atmosphere of Bombay. S. J. Khambata (Indian J. Phys., 1927, **2**, 25—27).—The amount and character of the active deposit collected on an insulated copper wire, suspended 75 feet above the ground in a N.E.—S.W. direction, and at a negative potential of 560—590 volts, have been determined under varying atmospheric conditions and for varying lengths of time. An average of 56% of the initial activity was due to the active deposit of thorium, the rest being attributable to radium deposit. The calculated ratio of the number of atoms of radon to thoron is approximately 3400; this is in agreement with several other values from different parts of the world. The greatest amount of activity was found in May with a S.W. wind. Bright, cloudless days gave more excited activity than dull, cloudy days, and windy days than calm.
M. S. Burr.

Existence of groups of atoms of radio-elements in acid solutions and on surfaces activated by the emanation. (Mlle.) C. Chamié (Compt. rend., 1927, **185**, 770—772).—Photographic experiments have shown the existence of groups of atoms of radio-elements in acid solutions, and on surfaces activated by exposure to emanations or by evaporation of acid solutions. Since the impressions are always the same, and similar to those obtained with activated mercury (this vol., 605), it is concluded that during activation the mercury receives aggregates of atoms which are absorbed by it without dissociating into individual atoms.
J. Grant.

Mobility of the actinium-*A* recoil atom measured by the cloud method. P. I. Dee (Proc. Roy. Soc., 1927, **A**, **116**, 664—682).—The cloud method has been used to measure the mobility of individual actinium-*A* recoil atoms immediately after they have reached the end of their recoil tracks and during an interval equal to the life of an atom. The conditions are more definite than those in Erikson's experiments (A., 1925, ii, 79), since the recoil atom, if charged, is rapidly removed from ions of the opposite sign, and if neutral, both positive and negative ions are rapidly removed from its neighbourhood. Photographs of four main types of grouped tracks are reproduced, corresponding with the double disintegration actinon ⟶ actinium-*A* ⟶ actinium-*B*. The relative positions of the origins of these tracks give the mobility and, in some cases, the life of the actinium-*A* atom. The value obtained for the mobility agrees with that usually accepted, viz. 1·56 cm./sec. per volt/cm., and no cases were found of the additional mobility 4·35 found by Erikson for recoil from an active source (*loc. cit.*). The method gives definite evidence that some of the recoil atoms at the end of their recoil paths are uncharged, and the proportion of positively-charged atoms, 84%, agrees well with Briggs' value of 82%, found for thorium-*A* and radium-*A* in air by activity distribution methods (A., 1925, ii, 922). The mean life of 47 actinium-*A* atoms is found to be $1\cdot8\times10^{-3}$ sec.
L. L. Bircumshaw.

Retardation of α-particles by matter. S. Rosenblum (Compt. rend., 1927, **185**, 851—853).—A continuation of the author's experiments (A., 1926, 879) has resulted in a more exact numerical expression for the retardation of α-particles during their passage through metals. Experimental constants are given for a number of metals; alloys obey the law of additivity. Within certain limits the field of force opposing the motion of the α-particles depends on the atomic number of the absorbing substance.
J. Grant.

Absorption and reduction in velocity of β-rays on their passage through matter. E. Madgwick (Proc. Camb. Phil. Soc., 1927, **23**, 970—981).—Bohr's theory of the absorption of β-rays has been experimentally tested using a magnetic deviation method. There is a close parallelism over a very wide range of energies between the theoretical and experimental results which lends strong support to the general truth of the theory. Disparities are discussed.
W. E. Downey.

β-Ray spectrum of radium-*E*. E. Madgwick (Proc. Camb. Phil. Soc., 1927, **23**, 982—984).—The distribution with velocity of the number of particles in the β-ray spectrum of radium-*E* has been determined by an ionisation method. It is concluded that the particles are ejected from the nucleus with velocities which vary continuously.
W. E. Downey.

Amount of energy emitted in the γ-ray form by radium-*E*. G. H. Aston (Proc. Camb. Phil. Soc., 1927, 23, 935—941).—The energy emitted as γ-rays by radium-*E* has been determined by an ionisation method. The measurement of the energy was derived from that of radium-*B* and radium-*C* by comparing ionisations. It is concluded that only one γ-ray quantum is emitted during about thirty disintegrations of radium-*E* atoms. The bearing of this on the β-ray emission of radium-*E* is discussed.
W. E. Downey.

Scintillation spectra. W. Kutzner (Z. Physik, 1927, 45, 343—349).—The emission spectra of standard preparations of zinc sulphide containing copper, bismuth, or uranium when subjected to irradiation by white light, to α-particles from polonium free from radium-$D+E$, and to friction have been determined in the range 6678—3888 Å. The three methods of excitation produce different but characteristic emission. It is thought that the α-particle emission is due to ionisation. R. W. Lunt.

Series number and decay constants. W. A. Sokolov (Z. Physik, 1927, 45, 409—415).—It is shown that the relation between the radioactive decay constant λ, for substances emitting α-particles, and the number of the element concerned in the radioactive series n can be expressed in the form $\log\lambda = kn+a$, where k is constant for all three radioactive series, and a a constant characteristic of each series. A similar relationship exists for the decay constants of substances emitting β-particles. R. W. Lunt.

Interpretation of the masses of the electron and proton in the five-dimensional universe. A. Schidlof (Compt. rend., 1927, 185, 889—891).—A mathematical paper in which de Broglie's geometrical representation of the electrical charge of a material point in a five-dimensional system (J. Phys. Radium, 1927, [vi], 8, 65) is applied to the proton and electron, and equations are obtained defining their masses. J. Grant.

Spinning electron and the structure of spectra. S. Goudsmit and G. E. Uhlenbeck (Physica, 1926, 6, 273—290).—Theoretical. Chemical Abstracts.

Fundamental equation of quantum chemistry. T. de Donder (Compt. rend., 1927, 185, 698—700).—It is shown mathematically that from the expression defining an Einsteinian conception of gravity, the equation may be deduced for the quantisation of molecular systems containing any number of points having electric mass, and producing a field of gravity $g_{\alpha\beta}$ ($\alpha,\beta=1, \ldots 4$). The fundamental equation of quantum chemistry is thus obtained. J. Grant.

Mutual influence of two hydrogen atoms. S. C. Wang (Physikal. Z., 1927, 28, 663—666).—It is shown mathematically that the mutual potential energy of two hydrogen atoms in the normal state and separated by a distance R is $-243e^2a^5/28R^6$, a being the radius of the first Bohr orbit in the atom. Assuming two dipoles of moment μ and polarisation constants α, the mutual potential energy is $-2\alpha\mu^2/R^6$; this on a quantum basis can be connected with the polarisation effect of two atoms with an electric moment $\mu = 0{\cdot}982ea$ on the classical basis. R. A. Morton.

Spectrophotometry. R. W. Ditchburn (Proc. Camb. Phil. Soc., 1927, 23, 959—969).—For wavelengths below 3200 Å. a Lyman type of hydrogen discharge tube forms a convenient source for spectrophotometry. Various types of reducing sectors are discussed and it is concluded that the radial-aperture sector has many points of advantage over other types.
W. E. Downey.

Absorption measurement in the ultra-violet by photographic photometry. H. Ley and F. Volbert (Z. physikal. Chem., 1927, 130, 308—322; cf. A., 1925, ii, 78).—The more important methods for measuring absorption by photographic photometry are described and criticised, the methods being grouped into: (1) those with equal times of exposure for the absorption and comparison spectra, (2) those with unequal times of exposure, and (3) those involving the use of the rotating sector. The advantages of the authors' combination of Henri's method and Winther's wire-gauge method are discussed. The results obtained from absorption measurements with potassium nitrate by a number of different investigators using different methods are compared, and a mean curve is constructed which might be used as a reference curve for photographic-photometric purposes.
L. L. Bircumshaw.

Molecular constants derived from the Swan bands. J. D. Shea and R. T. Birge (Physical Rev., 1926, [ii], 27, 245—246).—For the initial state, the rotation energy (F) in wave-numbers of the non-vibrating molecule is $1{\cdot}7541m^2-6{\cdot}911\times10^{-8}m^4+1{\cdot}22\times10^{-11}m^6$, where $m=k-\varepsilon=k-(0{\cdot}0989+1{\cdot}746\times10^{-5}k^2)$, k being a half-integer, and representing the resultant molecular momentum; hence the moment of inertia $I_0=15{\cdot}792\times10^{-40}$. For the final state $F=1{\cdot}6295m^2-6{\cdot}594\times10^{-6}m^4+1{\cdot}73\times10^{-11}m^6$, where $m=k-(0{\cdot}0741+0{\cdot}964\times10^{-5}k^2)$; hence $I_0=17{\cdot}000\times10^{-40}$. It is suggested that the molecule HC·CH may be the emitter of the Swan bands.
A. A. Eldridge.

Structure of the ultra-violet spectrum of the hydrogen molecule. G. H. Dieke and J. J. Hopfield (Physical Rev., 1927, [ii], 30, 400—417).—See this vol., 89. A. A. Eldridge.

Rotational distortion of multiplet electronic states in band spectra. E. C. Kemble (Physical Rev., 1927, [ii], 30, 387—399).—Hund's theoretical interpretation of the contracting multiplet type band spectra for diatomic molecules is given quantitative form for the doublet case and for the extreme components of higher multiplicities. The theory is applied to the ultra-violet doublet OH bands, which are interpreted as being of the $^2S \longrightarrow {}^2P$ type with the ^2P doublet inverted. A. A. Eldridge.

Fine structure and electron terms in band spectra. E. Hulthén (Z. Physik, 1927, 45, 331—336).—It is shown that the order of magnitude of the fine structure in band spectra of the types $^2P \longrightarrow {}^2S$ and $^2S \longrightarrow {}^2S$ is in agreement with Hund's theory, and that a simple relationship exists between the ^2S term and the transition $^2P_{\frac{3}{2}}-{}^2P_{\frac{1}{2}}$. These conclusions are discussed with reference to the combination between the atomic and molecular spectra of elements of the second group. R. W. Lunt.

Combination relation in the 3064 Å. OH band. W. W. Watson (Physical Rev., 1926, [ii], **27**, 246).—The P,Q,R combination which holds for any normal band is not satisfied in the MgH and OH bands. New measurements have been made, and satellites of the Q lines have been located which, when combined with the main P and R lines, give the required combination. A. A. Eldridge.

Intensities of the lines in the HCl absorption band at 3·5 μ. D. G. Bourgin and E. C. Kemble (Physical Rev., 1926, [ii], **27**, 802).—Experimental results are in harmony with the theoretical formula (*ibid.*, 1925, [ii], **25**, 1). There is definite evidence of a rotational isotope effect. A. A. Eldridge.

Shape of the carbon dioxide molecule. C. Schaefer (Physikal. Z., 1927, **28**, 667).—The work of Stark and Blüh (this vol., 922) on a linear structure for carbon dioxide is criticised on the grounds that evidence in the opposite sense (A., 1926, 658) is not disproved. R. A. Morton.

Specific heat of carbon dioxide and the form of the carbon dioxide molecule. W. H. McCrea (Proc. Camb. Phil. Soc., 1927, **23**, 890—900).—Theoretical. The specific heats of carbon dioxide based on Dennison's (A., 1926, 222) and Eucken's (*ibid.*, 882) models have been calculated. Neither model is found to be entirely satisfactory; a further hypothesis based on the two models to get better agreement between the calculated and observed specific heats is suggested. The new model explains the fine structure of the infra-red absorption bands better than Dennison's. W. E. Downey.

Sodium and potassium absorption bands. W. R. Frederickson and W. W. Watson (Physical Rev., 1927, [ii], **30**, 429—437).—The band heads of the systems are expressed by the following formulæ: green Na_2, $\nu=20301{\cdot}62+(123{\cdot}84n'-0{\cdot}79n'^2)-(157{\cdot}57n''-0{\cdot}57n''^2)$; red Na_2, $\nu=15006{\cdot}68+(115{\cdot}69n'-0{\cdot}427n'^2)-(157{\cdot}81n''-0{\cdot}538n''^2)$; red K_2: $\nu=15368{\cdot}63+(74{\cdot}58n'-0{\cdot}30n'^2)-(92{\cdot}01n''-0{\cdot}34n''^2)$. There is a new potassium absorption band system situated with respect to the first doublet in the principal series of potassium as is the red sodium band system with respect to the sodium D-lines. Fine-structure analysis indicates that the green sodium and near red potassium bands are both $^1S-^1P$ transitions. For the initial absorption state, the moment of inertia is $7{\cdot}20\times10^{-39}$ g. cm.^{2} for sodium and $8{\cdot}72\times10^{-39}$ g. cm.^{2} for potassium molecules. A. A. Eldridge.

Quantum analysis of the band spectrum of AlO (5200—4650 Å.). W. C. Pomeroy and R. T. Birge (Physical Rev., 1926, [ii], **27**, 107).—The (0,0), (1,0), and (0,1) bands of the blue and green group have been analysed according to the quantum theory. The origin of the (0,0) band is at $\nu_{\text{vac.}}=20635{\cdot}3$, and the limiting values of the moments of inertia for initial (emission) and final states are $(46{\cdot}01\pm0{\cdot}04)\times10^{-40}$ and $(43{\cdot}38\pm0{\cdot}04)\times10^{-40}$, respectively. A. A. Eldridge.

Absorption spectrum of dry chlorine. G. Kornfeld and W. Steiner (Z. Physik, 1927, **45**, 325—330).—The convergence wave-length of the band spectrum of chlorine has been examined by a grating with a dispersion of 2 Å./mm. No difference within the limit of experimental error could be detected between damp chlorine and the gas after drying by careful fractionation. It is therefore concluded that excited and normal chlorine atoms always exist in chlorine irradiated with blue light, and that the influence of water vapour on the reaction between hydrogen and chlorine must be sought in other stages of the reaction. The dryness of the chlorine examined was evidenced by the fact that it did not react with pure hydrogen in blue light. For 3130 Å. the quantum efficiency in a mixture of such dry chlorine and hydrogen diffused through palladium is 6—7 molecules per quantum. R. W. Lunt.

Ultra-violet absorption spectra of aqueous solutions of calcium, strontium, and barium chlorides. E. Viterbi (Gazzetta, 1927, **57**, 615—620).—The work of Pool (Z. Physik, 1924, **29**, 311) and of Getman (A., 1925, ii, 837) is repeated, using the method of Henri, with highly purified salts; tables of the molecular absorption coefficients, and curves, are given for a 3·913M-calcium chloride, a 1·864M-strontium chloride, and a M-barium chloride solution in a thickness of 15—50 to 500 mm. Contrary to the results of Getman (*loc. cit.*), each salt has a selective absorption in the middle ultra-violet, with a maximum which shifts towards the extreme ultra-violet with increasing at. wt., and has the values 2785, 2665, and 2624 Å. for the respective salts. There are also broad but distinct minima at 2579, 2550, and 2359 Å. respectively. The absorption band is somewhat indistinct with strontium, but lies close to that of calcium; that of barium is much stronger, although still small. E. W. Wignall.

Quantum analysis of the rotational energy of certain molecules. R. T. Birge (Physical Rev., 1926, [ii], **27**, 245).—Higher order terms of the rotational energy function are calculated for CuH. A. A. Eldridge.

Absorption spectra of borax glasses coloured with copper salts. P. Lasarev and V. Lazarev (Compt. rend., 1927, **185**, 855—856).—The absorption spectra between the wave-lengths 470 and 590 μμ of glasses prepared by fusion of borax with a small quantity of a copper salt differ from those of solutions of copper sulphate. Annealing the glasses destroys their temper, but does not alter their absorption spectra. J. Grant.

Series of emission and absorption bands in the mercury spectrum. (Lord) Rayleigh (Proc. Roy. Soc., 1927, A, **116**, 702—719; cf. this vol., 496).—An improved method is described for the study of absorption bands in the mercury spectrum, using a silica discharge tube, containing hydrogen at 2·5 mm. pressure, as the source, and an electrically-heated silica absorption tube, of length varying from 45 to 178 cm. In the less refrangible region (3000—2600 Å.), the wave-lengths and frequencies of 42 emission bands and 48 absorption bands are given. The initial spacing of the observed emission bands is 250 cm.$^{-1}$; the point of convergence is found by extrapolation to be near the resonance line 2537 Å. Both the emission and absorption bands are diffuse and symmetrical, without heads. The initial spacing of the absorption bands is 148 cm.$^{-1}$; the convergence point, found by extrapolation, is about 2645 Å. The two band systems appear to be coincident over a part of the range, 2734—2696 Å., for seven or eight periods, but beyond this range the absorption bands are more closely spaced than the emission bands in the long wave-length side, and *vice versa* on the side of short waves. Since no uniform shift on the scale of frequencies could bring the two series into coincidence, it has not been found possible to apply the quantum theory to their classification. In the more refrangible region (2350—2290 Å.), a series of symmetrical emission bands has been observed, which has been resolved for a short distance from 2345 Å. These merge into an apparently continuous spectrum which stops abruptly at the forbidden line 2270 Å. A series of four bands which are nearly the counterpart of the first four emission bands has been observed in absorption, and in part superposed on this structure is a much finer one, of which 48 bands have been observed. The bands are of the normal type with heads, and are definitely degraded to the red. The initial spacing is only 18 cm.$^{-1}$ The convergence point, found by two alternative methods of extrapolation to be 2264 or 2222, probably represents dissociation into a neutral atom and one excited to the 1^3P_2 metastable state.

L. L. Bircumshaw.

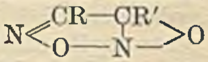
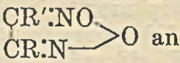
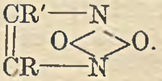
Depolarisation of light by dispersed systems. G. I. Pokrowski (Z. Physik, 1927, 45, 135—139).—From a consideration of the maximum and minimum polarisation characteristic of mercuric sulphide, cadmium sulphide, sulphur, arsenic green, madder, and ultramarine dispersed in water with that of water dispersed in air, it is concluded that: (i) the polarisation in coarsely-dispersed systems is less than that anticipated by theory, (ii) this diminution is specific to the nature of the disperse phase and is also due to the irregular size of the particles, (iii) in high concentrations multiple scattering produces depolarisation. R. W. Lunt.

Spectroscopic investigation of acetylene, methane, and ethylene. F. C. McDonald (Physical Rev., 1926, [ii], 27, 246).—Although no bands have been observed which can be definitely ascribed to the complete molecules, a new band spectrum (three bands, degraded towards the red, with heads at 2263, 2367, and 2395 Å.) has been observed when methane, in a Wood tube, at a pressure of 2 mm., is excited by a violent disruptive discharge. A. A. Eldridge.

Interference method for determining the anomalous absorption of concentrated solutions. E. Adinolfi (Rend. Accad. Sci. fis. mat. Napoli, [iii], 32, 189—193).—Improvements in the technique for determining the anomalous absorption of concentrated solutions by interference methods are described; data obtained with a solution of fuchsin in ethyl alcohol are discussed to illustrate the method.

R. W. Lunt.

Absorption bands of ergosterol and vitamin-*D*. I. M. Heilbron, E. D. Kamm, and R. A. Morton (Nature, 1927, 120, 617—618).—Explanatory, and polemical against Rosenheim and Webster (Lancet, 1927, Sept. 17). Further, for the concentration employed by those authors the persistence of the 247 μμ band is constant over a long period; irradiation behind "vitaglass" screens does not effect the expected increase in vitamin concentration. A. A. Eldridge.

Various spectrochemical observations. K. von Auwers (Ber., 1927, 60, [*B*], 2122—2142).—Optical comparison of the furazans with the furoxans indicates the improbability of the constitution  for the latter, but leaves open the choice between the structures  and . The carbylamines have higher molecular indices of refraction and dispersion than the corresponding nitriles and are therefore to be regarded as more unsaturated substances. The differences, however, are comparatively slight and it appears unlikely that the carbylamines contain a true bivalent carbon atom in which two valencies are completely unsatisfied. Comparison of the optical behaviour of *s*- and *as*-phthalyl chlorides shows that the refractive and dispersive powers of the asymmetric isomeride which contains only one active conjugation are little lower than those of the normal chloride with its two active conjugations. The exaltation of the refractive index of quinones is such that the presence of a true benzenoid derivative is improbable even if it is admitted that the presence of a peroxide linking of the oxygen atoms somewhat enhances the refraction. Contrary to Levy (Diss., Frankfurt, 1920), the optical behaviour of ethylated hydrindenes is exactly comparable with that of similarly constituted benzenoid hydrocarbons except that the exaltations are generally lower, due to the presence of a *gem*-diethyl group. Chloroformic esters appear to be constituted normally.

The following data, among others, are recorded: dimethylfurazan, $d_4^{14\cdot4}$ 1·0528, $n_{\mathrm{He}}^{14\cdot4}$ 1·42829; dimethylfuroxan, $d_4^{14\cdot8}$ 1·1896, $n_{\mathrm{He}}^{14\cdot8}$ 1·48599; methylcarbimide, $d_4^{17\cdot9}$ 0·7337, $n_{\mathrm{He}}^{17\cdot9}$ 1·34393; ethylcarbimide, $d_4^{17\cdot6}$ 0·7425, $n_{\mathrm{He}}^{17\cdot6}$ 1·36321; phenylcarbimide, $d_4^{19\cdot1}$ 0·9823, $n_{\mathrm{He}}^{18\cdot1}$ 1·52828; acetonitrile, $d_4^{21\cdot9}$ 0·7781, $n_{\mathrm{He}}^{21\cdot9}$ 1·34186; propionitrile, $d_4^{21\cdot8}$ 0·7758, $n_{\mathrm{He}}^{21\cdot8}$ 1·36368; *n*-butyronitrile, $d_4^{16\cdot2}$ 0·7951, $n_{\mathrm{He}}^{16\cdot2}$ 1·38588; *n*-valeronitrile, $d_4^{18\cdot9}$ 0·8018, $n_{\mathrm{He}}^{18\cdot9}$ 1·39715; *iso*valeronitrile, $d_4^{19\cdot4}$ 0·7925, $n_{\mathrm{He}}^{19\cdot4}$ 1·39179; toluquinone, $d_4^{77\cdot9}$ 1·0830, $n_{\mathrm{He}}^{77\cdot9}$ 1·51108; *m*-xyloquinone, $d_4^{78\cdot1}$ 1·0479, $n_{\mathrm{He}}^{78\cdot1}$ 1·50740; thymoquinone, $d_4^{99\cdot6}$ 0·9727, $n_{\mathrm{He}}^{99\cdot6}$ 1·48250; β-methyl-Δ^{δ}-pentenal, $d_4^{18\cdot1}$ 0·8588, $n_{\mathrm{He}}^{18\cdot1}$ 1·45132; β-methyl-Δ^{α}-buten-γ-one, $d_4^{22\cdot3}$ 0·8505, $n_{\mathrm{He}}^{22\cdot3}$ 1·42251; Δ^1-menthenone, $d_4^{14\cdot5}$ 0·9376; $n_{\mathrm{He}}^{14\cdot5}$ 1·48678; ethyl *iso*phoronecarboxylate, $d_4^{15\cdot5}$ 1·0342, $n_{\mathrm{He}}^{15\cdot5}$ 1·48126; ethyl *α*-*o*-formylphenoxypropionate, $d_4^{18\cdot5}$ 1·1372, $n_{\mathrm{He}}^{18\cdot5}$ 1·51746; *o*-*iso*butyryl-*s*-*m*-xylenyl methyl ether, $d_4^{16\cdot7}$ 1·0116, $n_{\mathrm{He}}^{16\cdot7}$ 1·51823; *o*-Δ^{γ}-pentenoylphenyl methyl ether, $d_4^{10\cdot9}$ 1·0525, $n_{\mathrm{He}}^{10\cdot9}$ 1·53903; β-*p*′-methylchalkone, $d_4^{100\cdot6}$ 1·0258, $n_{\mathrm{He}}^{100\cdot6}$ 1·61715; *α*-*p*′-methylchalkone, $d_4^{99\cdot6}$ 1·0317, $n_{\mathrm{He}}^{99\cdot6}$ 1·61905; ethyl *α*-methylbenzoylacetate, $d_4^{16\cdot1}$ 1·0895, $n_{\mathrm{He}}^{16\cdot4}$ 1·51355; ethyl *o*-methoxybenzoylacetate, $d_4^{13\cdot1}$ 1·1634, $n_{\mathrm{He}}^{13\cdot1}$ 1·53968; furfurylideneacetone, d_4^{57} 1·0496, n_{He}^{57} 1·58197; ethyl furfurylidenemethyl ketone, $d_4^{17\cdot1}$ 1·0823, $n_4^{17\cdot1}$ 1·59047; ethyl *α*-furfurylidene-ethyl ketone, $d_4^{18\cdot0}$ 1·0573, $n_{\mathrm{He}}^{18\cdot0}$ 1·57593; furfurylidenepinacolin, $d_4^{15\cdot6}$ 1·0088, $n_{\mathrm{He}}^{15\cdot6}$ 1·55263;

difurfurylidene-γ-methyl*cyclo*hexanone, $d_4^{100\cdot1}$ 1·1181, $n_{\mathrm{He}}^{100\cdot1}$ 1·68812; α-bromo*iso*crotonic acid, $d_4^{99\cdot7}$ 1·5809, $n_{\mathrm{He}}^{99\cdot7}$ 1·48546; αβ-dibromocrotonic acid, $d_4^{100\cdot1}$ 1·9963, $n_{\mathrm{He}}^{100\cdot1}$ 1·53522; ethyl α-*cyclo*hexylidenepropionate, d_4^{18} 0·9989, n_{He}^{18} 1·48483; ethyl 4-hydroxy-*m*-toluate, $d_4^{21\cdot1}$ 1·1035, $n_{\mathrm{He}}^{21\cdot1}$ 1·52123; 2 : 2-diethylhydrindene, $d_4^{13\cdot4}$ 0·9295, $n_{\mathrm{He}}^{13\cdot4}$ 1·51820; 2 : 2 : 5-triethylhydrindene, $d_4^{16\cdot2}$ 0·9178, $n_{\mathrm{He}}^{16\cdot2}$ 1·51473; 2 : 2 : 5 : 6-tetraethylhydrindene, $d_4^{14\cdot35}$ 0·9246, $n_{\mathrm{He}}^{14\cdot35}$ 1·51998; 2 : 2 : 4 : 5 : 6-pentaethylhydrindene, $d_4^{14\cdot1}$ 0·9234, $n_{\mathrm{He}}^{14\cdot1}$ 1·52115; 2 : 2 : 4 : 5 : 6 : 7-hexaethylhydrindene, $d_4^{14\cdot3}$ 0·9263, $n_{\mathrm{He}}^{14\cdot3}$ 1·52265; phenheptamethylene, $d_4^{16\cdot2}$ 0·9683, $n_{\mathrm{He}}^{16\cdot2}$ 1·54856; 3-ethyl-4-*iso*propyltoluene, $d_4^{15\cdot7}$ 0·8756, $n_{\mathrm{He}}^{15\cdot7}$ 1·50227; methyl chloroformate, $d_4^{16\cdot85}$ 1·2240, $n_{\mathrm{He}}^{16\cdot85}$ 1·38882; ethyl chloroformate, $d_4^{15\cdot05}$ 1·1418, $n_{\mathrm{He}}^{15\cdot05}$ 1·39861; *iso*butyl chloroformate, $d_4^{17\cdot9}$ 1·0425, $n_{\mathrm{He}}^{17\cdot9}$ 1·40711; *iso*amyl chloroformate, $d_4^{15\cdot0}$ 1·0321, $n_{\mathrm{He}}^{15\cdot0}$ 1·41916; *O*-benzoate of ethyl benzoylmalonate ("ethyl dibenzoylmalonate"), $d_4^{99\cdot3}$ 1·1129, $n_{\mathrm{He}}^{99\cdot3}$ 1·52818.

H. Wren.

Spectrochemical studies of hydroxyazo-compounds. V. T. Uemura and S. Tabei (Bull. Chem. Soc. Japan, 1927, 2, 249—257; cf. this vol., 1006).—The absorption spectra of neutral and alkaline solutions of the azo-dyes from the three toluidines with phenol and with resorcinol, and from aniline and the mononitroanilines with certain cresols have been investigated and the results correlated with the structure of the compounds. In neutral and alkaline solutions the substances exist in *A*- and *R*-forms, respectively. The previously recorded, hyperchromic influence of the methyl group on a previously non-methylated compound is confirmed. Hydroxyl and nitro-groups exert a maximum effect on the absorption when in the *p*-position with respect to the azo-group. Except when the hydroxyl group occupies an *o*-position with regard to the azo-group, when there are two bands, only one band is shown by the absorption curves.

J. S. Carter.

Fluorescence and absorption spectra of iodine. F. W. Loomis (Physical Rev., 1926, [ii], 27, 802).—Mecke's four series without linear terms in Wood's spectrum of fluorescent iodine are due to four lines of the band (26, 0). Values are obtained as follows: $B_0''=0\cdot03835$, $B'=0\cdot02480$ cm.$^{-1}$; $J_0=7\cdot21\pm0\cdot03\times10^{-38}$. The absolute values of m are half-integral. Lines of Mecke's series II belong alternately to the P and R branches of band (27, 0). A. A. Eldridge.

Application of the spectrography of fluorescence to the examination of powdered alkaloids. A. Andant (Compt. rend., 1927, 185, 713—715).—The author has applied his method (this vol., 538) to the spectrographical examination of the fluorescence produced from small quantities of powdered alkaloids excited by the rays of the mercury arc. The spectrograms obtained indicate the degree of purity of the sample, each pure alkaloid having a characteristic fluorescence spectrum for a particular exciting radiation. The differences between the spectra produced by the various alkaloids are most marked when exciting rays of short wave-lengths are used.

J. Grant.

Luminescence produced by bombarding solidified gases with electric rays at the temperature of liquid helium. L. Vegard and W. H. Keesom (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 514—520).—An improved form of the apparatus originally used for the investigation of the luminescence of solidified gases, under the action of cathode and canal rays (Vegard, Onnes, and Keesom, A., 1925, ii, 474), is described. In an attempt to obtain a spectrogram of the luminescence of solidified hydrogen, produced by swift cathode rays, no impression was obtained on the photographic plate, in spite of the intensity of the source of light. Hence, if any line spectrum is obtained in this way, it must be extremely faint compared with the continuous spectrum. Under the bombarding action of hydrogen canal rays, with velocities corresponding with a parallel spark gap of 3 mm., the total intensity of luminescence is smaller than for the swift cathode rays, but the spectrogram shows a well-marked line spectrum of which the strong lines belong to the Balmer series. A number of faint lines between these appear to belong to the ordinary second hydrogen spectrum, but some may be lines characteristic of the solid state. The luminescence of solid nitrogen, produced by canal rays at the temperature of liquid helium, has also been examined. The four bands N_1, N_2, N_3, and N_4, and also a diffuse band series, A, previously found at the temperature of liquid hydrogen (A., 1926, 660), were reproduced, but with a different intensity distribution. In addition, some new lines, *e.g.*, 6004, 5766, 3870, and 3849 Å., were observed. Some of these appear to belong to the positive band spectrum of nitrogen.

M. S. Burr.

Mechanism of chemiluminescence reactions in gases. V. Kondratéev (Z. Physik, 45, 67—82).—The radiation emitted when potassium vapour interacts with that of mercuric chloride has been examined. At temperatures above 350° potassium lines alone are emitted from the apparently homogeneous region in which the gases interact; as the temperature is diminished to 200—250° a bluish-violet glow appears on the walls of the containing vessel in the neighbourhood of the reaction zone. These two phenomena are thought to correspond with two independent reactions, the latter taking place on the surface of the containing vessel. The following scheme is suggested to explain the mechanism of reaction: (1) $HgCl_2+K=Hg+KCl+Cl$, (2) $Cl+K=KCl^*$, and (3) $KCl^*+K=KCl+K'$. From an analysis of the velocity of reaction in terms of the velocity constants of reactions (1) and (2), and of the diffusion coefficients of K, HgCl, and Cl at the measured temperature, an expression is obtained for the length of the luminous reaction zone as a function of temperature which is in agreement with experiment. Since the light emitted by the surface reaction contains a number of bands identical with those of mercuric chloride, it is thought that this is due to monatomic potassium vapour reacting with solid mercuric chloride forming solid potassium chloride and an activated HgCl molecule. This hypothesis leads to a value for the thickness of the luminous layer, derived from the life of an excited HgCl molecule and its mean velocity of thermal agitation, of $2\cdot5\times10^{-2}$ mm., in satisfactory agreement with experiment. Similar phenomena have been observed in the interaction of sodium and of potassium vapours with mercuric bromide and iodide and with cadmium chloride. R. W. Lunt.

Quantitative study of the luminescence of mercury vapour excited by electronic shock. P. Bricout (Compt. rend., 1927, 185, 707—709).—A rapid and convenient method is described for the determination of the relationship between the intensity of the radiation emitted by mercury vapour and the speed of the exciting electrons, for wave-lengths less than 4000 Å. A heated carbon filament is the source of electrons, and the excited radiations pass through a quartz window and are registered spectrographically. The densities of the photographs obtained are compared with those from sources of ultra-violet light of known intensities. An accuracy of about 5% is obtainable if corrections are applied for the variations in the initial speeds of the electrons, the effect of the spatial charge (this vol., 85), variations in the density of the vapour, and the diminution in transparency of the quartz window owing to the deposition of carbon (from the filament) and droplets of mercury. J. Grant.

Quantitative study of the luminescence of mercury vapour excited by electronic shock. P. Bricout (Compt. rend., 1927, 185, 846—849).—A formula for the function of excitation is deduced assuming it to be the product of the probability of shock, which depends on the initial speed and position of the electron, and the probability of the transfer of the optical electron from one orbit to another, as a result of collision with an electron of given initial speed. It is $f=C/U^2\sqrt{\overline{U/U_1-1}}$, where C, U_1, and U are a constant, the resonance potential, and the potential of the exciting electron, respectively. The rule agrees with experiments with the resonance radiation of mercury 2536 (preceding abstract) and with Dauvillier's results for the distribution of energy in the continuous X-ray spectrum. It is therefore suggested as general for all radiations excited by the passage of electrons from a basic orbit at a speed insufficient to produce ionisation. J. Grant.

Lattice constant of calcium sulphide- and strontium sulphide–samarium mixed phosphors. E. Rumpf (Ann. Physik, 1927, [iv], 84, 313—322).—By means of Debye–Scherrer photographs it is shown that the transition between pure calcium sulphide–samarium phosphor and pure strontium sulphide–samarium phosphor is perfectly continuous as far as lattice constants are concerned. The lattice constant increases gradually until the strontium sulphide content has risen from zero to 30% and much more rapidly in the range 40—100% SrS. Similar changes occur with the phosphorescence emission of mixed phosphors. R. A. Morton.

Emission from phosphors. I. Behaviour of samarium in sulphides and sulphates. R. Tomaschek (Ann. Physik, 1927, [iv], 84, 329—383; cf. A., 1925, ii, 12, 354).—The banded emission spectra of samarium phosphors have been measured and tabulated. Sulphide phosphors containing magnesium, calcium, barium, strontium, or zinc sulphide show three band systems in the region 5500—6800 Å., and in each case the fine structure is more easily obtainable at −150° than at 20°. Observations on calcium sulphide–samarium phosphors at 300° and 20° show that rise of temperature not only alters the relative intensities of the bands, but also affects the relative intensities of fine-structure components within a band. A distinct broadening is noticed for the line emission. The influence of changes in the mode of preparation affecting the dielectric constant of a given phosphor has been investigated in relation to the phosphorescence phenomenon.

Similar measurements have been carried out on sulphate phosphors in which the samarium is present with the sulphate of an alkali or alkaline-earth metal, or of magnesium, zinc, cadmium, aluminium, and lanthanum. R. A. Morton.

Absorption spectra of phosphors produced by the addition of lead and thallium to halides of the alkali metals. R. Hilsch (Z. Physik, 1927, 44, 860—870).—The absorption coefficients of the alkali halides containing 0·1—0·01% of lead or thallium (as nitrate or chloride) have been determined in the range 3200—1800 Å. In all cases the maxima of absorption are shifted by the addition of lead or thallium towards the red to the extent of from 180 to 300 Å. R. W. Lunt.

Absorption spectra of alkali halide phosphors containing silver and copper. A. Smakula (Z. Physik, 1927, 45, 1—12; cf. this vol., 917).—The influence of the addition of 0·2—1·0% of silver or copper as chloride on the absorption of the halides of sodium and potassium has been investigated from observations of the extinction coefficient of the substances produced in the range 2000—4000 Å. The following cases have been examined and the data cited refer to the absorption maxima to which the excitation of phosphorescence can be traced, and the half width in Å. of these respectively: sodium chloride–silver 2100, 100; sodium bromide–silver 2190, 100; sodium chloride–copper 2550, 300; sodium bromide–copper 2590, 300; potassium chloride–copper 2650, 400; and potassium bromide–copper 2650, 300. In the same range the extinction coefficients of pure sodium bromide, potassium iodide, 99% potassium chloride —1% potassium iodide, and 85% sodium chloride —15% silver chloride are sensibly zero at 2200, 2100, 3000, 2500 Å., respectively. At shorter wave-lengths rapidly increasing absorption characterises these substances, and the data show that the absorption due to silver chloride commences at a wave-length less than 2500 Å. In potassium chloride and bromide the presence of silver ions produces practically no deviation from the normal continuous absorption. The width of the absorption bands produced by the addition of copper is considerably greater than those due to lead and thallium; for the chlorides the curves indicated the existence of second maxima between those recorded and the wave-lengths at which they normally commence to exhibit absorption (sodium chloride 1700, potassium chloride 1810 Å.). These two bands are thought to be due to (*a*) the formation of mixed crystals and (*b*) the distortion of the alkali chloride grating by copper ions, which is smaller with sodium chloride. The extinction coefficients of the bands produced by the addition of copper are approximately proportional to the copper concentrations, and similarly those produced by the addition of silver either as chloride or nitrate to sodium chloride are approximately proportional to the silver concentrations. R. W. Lunt.

Dielectric constant of helium and oxygen in a magnetic field. B. B. Weatherby and A. Wolf (Physical Rev., 1926, [ii], 27, 252).—For helium (20 cm. pressure), air (76 cm.), and oxygen (76 cm.) at the ordinary temperature there is no change in the dielectric constant on exposure to an electric field (5000—10,000 volts/cm.) parallel or normal to a magnetic field (8000—10,000 gauss).

A. A. Eldridge.

Dielectric constant for very dilute solutions of electrolytes. A. Deubner (Ann. Physik, 1927, [iv], 84, 429—456).—A new technique, based on the application of a new short-wave generator devised by Hollmann to the first Drude method, has been developed so as to ensure values accurate to 0·1% in pure water and 0·2—0·3% in solutions up to a maximum strength of 0·005*N*. The method is discussed critically and results on solutions of sucrose, sodium chloride, and copper sulphate are detailed. The work of Hellmann and Zahn (A., 1926, 778; this vol., 7) is in agreement, but that of Sack (this vol., 409) is not in agreement with that of the author.

R. A. Morton.

Optical constants of single-crystal bismuth. L. H. Rowse (Physical Rev., 1926, [ii], 27, 247).—The index of refraction rises from 1·05 at 470 $m\mu$ to 1·55 at 670 $m\mu$, whilst the extinction modulus rises from 2·7 to 3·6. A. A. Eldridge.

Relation between refractive index and density. D. Burnett (Proc. Camb. Phil. Soc., 1927, 23, 907—911).—Theoretical. The formula proposed by Macdonald (Proc. Roy. Soc., 1926, **A**, **113**, 237) for the dependence of the refractive index of a medium on its density has been examined for water, alcohol, aniline, benzene, and ethyl ether. The formula gives as satisfactory an agreement with experiment as that of Lorenz and Lorentz in most cases and occasionally a better. W. E. Downey.

Natural rotatory dispersion of molybdomalic complexes. E. Darmois and R. Descamps (Compt. rend., 1927, **185**, 705—706).—The rotatory dispersions of solutions of complex molybdomalates of the types $[4MoO_3,2C_4H_5O_5](NH_4)_4+5H_2O$ (dextro-) and $[MoO_3,2C_4H_5O_5]K_2+2H_2O$ (lævo-) have been measured for wave-lengths between 5780 and 3655 Å. The dispersion is least for the lævo-salt, and in each case [α] may be expressed by a formula of the type $[\alpha]=A/(\lambda^2-\lambda^2_1)+B/(\lambda^2-\lambda^2_2)$. Since the values of λ_1 are in the region of the ray 3655 Å., it is probable that the condition of negligible absorption assumed for the purposes of the formula does not hold exactly for this ray, a supposition supported by the results.

J. Grant.

Molecular arrangement of uniaxial optically active crystals. W. G. Burgers (Proc. Roy. Soc., 1927, **A**, **116**, 553—585).—With the object of determining whether optical activity must be ascribed to pseudo-symmetrical intergrowths of biaxial lamellæ or to special arrangements of the atoms within the unit cells, *X*-ray examinations have been made of the following uniaxial optically active crystals: *d*-potassium rhodium oxalate, $K_3[Rh(C_2O_4)_3],H_2O$; sodium metaperiodate, $NaIO_4,3H_2O$; ethylenediamine sulphate, $C_2H_4(NH_2)_2,H_2SO_4$, and guanidine carbonate, $(CN_3H_5)_2,H_2CO_3$. The dimensions of the unit cells and the corresponding space-groups were determined chiefly by means of 20°-oscillation photographs about various crystallographic directions, Laue photographs being taken to confirm the crystal symmetry. For *d*-potassium rhodium oxalate, the space-group is D_3^4 (or D_3^6), the dimensions of the hexagonal unit cell, $a=11·28$, $c=20·25$ Å., the number of groups of $K_3[Rh(C_2O_4)_3],H_2O$ per unit cell is 6, and this group possesses no plane of symmetry. For sodium metaperiodate, the space-group is C_3^4, the dimensions of the orthohexagonal unit cell, $a=10·38$, $b=6·00$, $c=13·13$ Å., the length of the edge of the rhombohedral unit cell, $a'=5·58$ Å., the rhombohedral angle $\alpha=65° 1'$; there are six $(NaIO_4,3H_2O)$ groups in the orthohexagonal cell, one in the rhombohedral cell, and the group has an axis of threefold symmetry. For ethylenediamine sulphate, the space-group is D_4^4 (or D_4^8), $a=5·96$, $c=17·99$ Å., there are 4 molecules in the unit cell, and the molecule possesses an axis of twofold symmetry. For guanidine carbonate, the space-group is D_4^4 (or D_4^8), $a=6·95$, $c=19·45$ Å., there are 4 molecules in the unit cell, and the molecule has an axis of twofold symmetry. The view is held that the rotatory power of the crystals is not due to a spiral arrangement of biaxial lamellæ (cf. definite spiral piles of thin mica plates), but to some definite arrangement of atoms within a unit of structure. This unit is a real unit if the crystal is truly uniaxial, but is a pseudo-unit if the crystal is built up of very many twinned lamellæ which are individually too small to give separate *X*-ray reflexions ("pseudo-paramorphic" structures). It is shown that the similarity between the rotatory dispersion curves of crystals and solutions of *d*-potassium rhodium oxalate is not due to the presence of parallel molecules in the crystalline state. The molecules occupy a spiral arrangement in the crystal, which may account for the movement of the inversion point of the dispersion curve on transition from solution to crystal. The marked difference in rotatory power between tetragonal–pyramidal and tetragonal–trapezohedral crystals is considered in connexion with the spiral arrangements of the molecules. The exceptional place occupied by potassium lithium sulphate as an optically active crystal is discussed.

L. L. Bircumshaw.

Number of dispersion centres in saturated sodium vapour. W. Weingerov (Z. Physik, 1927, 45, 416—429).—The number of dispersion centres in saturated sodium vapour has been determined from measurements of the magnetic rotation of the D_1- and D_2-lines. The necessity for a knowledge of the magnetic resolution is obviated by using a new compensation method. Plane polarised light travels successively through two cylindrical co-axial vessels of different length containing sodium vapour; each vessel is placed symmetrically and coaxially in one of two equal solenoids, the fields of which are equal and opposing, exterior to the furnaces heating the tubes containing sodium. For any given temperature of the longer tube the magnetic rotation in this tube can be compensated by that of the shorter tube, provided that some higher temperature is maintained. Under these conditions the number of dispersion centres per unit volume in each tube is equal. Observations have been made for three different ratios of the lengths of the two tubes containing sodium in the temperature range, and the results show that the number of dispersion centres per unit volume is proportional to the density of the saturated vapour. Using the vapour-pressure data of Haber and Zisch and those of Ladenburg and Minkowski, the chemical constant calculated from the data now cited is, respectively, 0·43, 0·50: the theoretical value of Stern is 0·46. R. W. Lunt.

Relation of Tyndall effect to osmotic pressure in colloidal solutions. C. V. Raman (Indian J. Phys., 1927, 2, 1—6).—Theoretical. The fluctuation theory is applied to the interpretation of the optical behaviour of colloidal solutions. On the assumption that colloidal and strongly scattering molecular solutions are analogous, and that in these solutions the simple Rayleigh theory of scattering cannot be regarded as valid, an expression for the light-scattering power of the former is derived thermodynamically in terms of the variations of osmotic pressure and refractive index with concentration. M. S. Burr.

Scattering of light by liquids at high temperatures. S. R. Rao (Indian J. Phys., 1927, 2, 7—24).—In an apparatus which is described, the variations in the intensity and depolarisation factor of transversely scattered light have been studied for *iso*pentane, *n*-pentane, *n*-hexane, ethyl ether, methyl acetate, and ethyl formate at different temperatures up to the critical point. The depolarisation factor diminishes extremely slowly up to a certain temperature characteristic of the liquid. Beyond this the decrease becomes more rapid until the critical temperature is approached, when it again slows down. Only with *iso*pentane, *n*-pentane, and ethyl ether could values for the intensity ratio between the different temperatures and 30° be compared with calculated values. The results, for all temperatures, agree very closely with Ramanathan's modified formula (*ibid.*, 1927, **1**, 401). The intensity increases with temperature, at first slowly and then rapidly as the critical temperature is approached. The molecular anisotropy at different temperatures, calculated for all six liquids, apparently increases with temperature and tends to attain the value for the vapour state. This change is attributed to the anisotropy of the local polarisation field acting on the molecules at lower temperatures. Since the molecules are less closely packed at higher temperatures, they can approximate more nearly to a perfectly chaotic distribution which is attainable, however, only in the vapour state. Two sources of error, affecting the measurements of the depolarisation factor in the neighbourhood of the critical point, are discussed. One is the strain produced in the glass of the observation window by the great increase of pressure at this temperature; the other is the inefficient background at temperatures near the critical temperature, when the scattered light has considerable intensity and the liquid surrounding the track is illuminated by secondary scattering. M. S. Burr.

Scattering of light by aromatic compounds. A. N. Banerjee (Indian J. Phys., 1927, 2, 51—60).—The methods of measurement of the depolarisation factor and of the relative intensity with respect to benzene of the light scattered by a large number of aromatic compounds are described. The results are tabulated and compared, where possible, with those calculated from the modified Einstein and Smoluchowski's formula, and also from Ramanathan's more recent formula (*ibid.*, 1927, **1**, 420). Agreement with the new formula is slightly better than with the old. M. S. Burr.

Light-scattering data for ten gases and sixty-three vapours of organic compounds. I. R. Rao (Indian J. Phys., 1927, 2, 61—96).—The various methods for the determination of the depolarisation of light scattered by gases and vapours have been experimentally examined, and the method of Cabannes (J. Phys. Radium, 1923, [vi], 4, 429; 1926, [vi], 7, 340; A., 1926, 559), in which the two images of the scattered light, as seen through a double image prism viewed in a common background, is selected as trustworthy. The effect of finite convergence on the incident pencil of light has been determined experimentally. It appears to be unnecessary to correct for this and a theoretical explanation of the null effect is offered. The depolarisation values of a number of gases and vapours are given. The anisotropies in the gaseous and liquid states have been calculated for the vapours. Except for the fatty acids and methyl formate where the converse holds, the anisotropy in the liquid is smaller than in the corresponding vapour. This may be due either to the association of molecules in the liquid state, resulting in the formation of scattering units more isotropic than the individual molecules themselves (Raman, Nature, 1923, **111**, 428), or to the close packing of the molecules in the liquid state, in consequence of which the influence on a single atom, of the atoms in the neighbouring molecules, may be comparable with the influence of the other atoms in the same molecule, thus conducing to greater optical symmetry (Krishnan, A., 1925, ii, 1030). The anomalous behaviour of the fatty acids may be explained as due to the lack of coincidence between the longest geometrical axis of the molecule and the axis of largest refractivity. In the hydrocarbons the depolarisation does not increase regularly with the size of the molecule and the anisotropy is small, but is increased by halogen substitution. Unsaturated compounds show much larger depolarisation than saturated. Alcohols show very small depolarisation and small anisotropy, trimethylcarbinol being almost isotropic. The fatty acids and esters decrease steadily in anisotropy and depolarisation with increasing mol. wt. The cyclic compounds are invariably more anisotropic than the aliphatic, and all benzene compounds examined, except benzylidene chloride, are more anisotropic than benzene. The depolarisation factor of double ring compounds is greater than that of single ring compounds. For water vapour, a depolarisation value of 1·91 has been obtained, which does not agree with Havelock's predicted values (this vol., 189). The anisotropy of the carbon atom is discussed. M. S. Burr.

Relation between shared electrons and valency: principal and contra valencies. W. A. Noyes (Z. physikal. Chem., 1927, **130**, 323—333).—The generalisation is proposed that in balancing the positive charge of the kernel of an atom a pair of shared electrons is equivalent to a single unshared electron. This generalisation is strongly supported by the hypothesis that a covalent link consists of a pair of electrons rotating in opposite directions in orbits which include two positive kernels or two nuclei. Further support is obtained from the following considerations: the ionisation of quaternary ammonium compounds, radioactive changes, dissociation of elements at high temperatures, the Hückel–Grimm law, semi-polar linkings, principal and contra valencies, atoms without full octets, and condensations of carbon compounds. By accepting the evidence of Sugden (A., 1925, ii, 936) and of Phillips (A., 1926, 159) for semipolar linkings, the formulæ under this generalisation agree very nearly with those assumed by Lewis for the sulphate and perchlorate ions, with the limitation that the pair of electrons which are the occasion for the polar part of a semipolar linking are not available for a covalency. The pair of electrons of a covalent link rotate about the kernels of the two atoms which are held together, whilst the electrons of a polar link rotate about the kernel of only one of the atoms. L. L. Bircumshaw.

Electronic theory of valency. Stereochemical representation of the elements. G. Dupont (Bull. Soc. chim., 1927, [iv], **41**, 1101—1137).—A lecture.

Contraction of molecules in the liquid state. S. G. Mokrushin (J. Physical Chem., 1927, **31**, 1581—1583; cf. Richards, A., 1925, ii, 362).—Theoretical. Further evidence is advanced that molecules contract on passing from the gaseous to the liquid state. A change in shape from that of a sphere first to that of a hexahedral prism and finally to that of a honeycomb cell is suggested.
L. S. Theobald.

Rast's micro-method for mol. wt. determinations. J. H. C. Smith and W. G. Young (J. Biol. Chem., 1927, **75**, 289—298).—A description of a slightly modified technique. C. R. Harington.

Crystal structure of carbon steels. I. N. Seljakov, G. Kurdjumov, and N. Goodtzov (Z. Physik, 1927, **45**, 384—408).—*X*-Ray measurements on hardened carbon steels have demonstrated the existence of a tetragonal-centred lattice little different from that of α-iron. The ratios of the lattice parameters are functions of the carbon content, and of the temperature of hardening. The existence of a surface-centred cubical grating has also been established and identified with that of austenite; this grating can be considered as that of a solid solution of carbon in α-iron. The process of hardening is shown to be due to a transition of γ- into α-iron.
R. W. Lunt.

Atomic grouping in "permalloy." L. W. McKeehan (J. Franklin Inst., 1927, **204**, 501—524; cf. A., 1926, 892).—The explanation of the peculiar magnetic properties of "permalloy" which was given previously in terms of an hypothetical atomic grouping, comprising one iron atom with four adjacent nickel atoms and of specified dimensions and orientation, is inconsistent with the known cubic symmetry of iron–nickel alloys unless the lattice unit is very large or the arrangement of the groups random. The probable number of such atomic groupings resulting from a random or partly random arrangement of the component atoms has been studied by a method which involved the preparation of charts representing the sections of a crystal with 1688 atoms (20% Fe) to the various parts of which the atoms were assigned by means of a lottery machine. It is concluded tentatively that the formation of a sufficient number of the groupings to explain the magnetic properties of the alloy is improbable except when the stipulations regarding the dimensions and orientation of the unit group are abandoned and arrangements with more than two adjacent iron atoms discarded.
G. A. Elliott.

Crystal structure of calcium hydroxide. A. Rejna (Atti R. Accad. Lincei, 1927, [vi], **5**, 1008—1010).—By assuming a value for u in the neighbourhood of 0·25 the grating constants of calcium hydroxide are a=3·52, c=4·93; the calcium atom is at (0, 0, 0), the oxygen atoms at 0 ($\frac{1}{3}$, $\frac{2}{3}$, u) and ($\frac{2}{3}$, $\frac{1}{3}$, $\bar{u}$).
R. W. Lunt.

Crystal structure of nickelous and cobaltous chlorides. A. Ferrari (Atti R. Accad. Lincei, 1927, [vi], **6**, 56—59).—Nickelous and cobaltous chlorides have cell structures similar to that of magnesium chloride; the grating constants a and c are, respectively, 7·08, 17·35; 7·07, 17·32.
R. W. Lunt.

Lattice parameters and densities of copper, silver, and tungsten. W. P. Davey and T. A. Wilson (Physical Rev., 1926, [ii], **27**, 105).—New measurements are as follows: copper has side of unit cube 3·605 Å., d 8·95, thus changing Patterson's values for chromium and titanium by 0·3%. Silver has d 10·481; tungsten has side of unit cube 3·155 Å., d 19·32. A. A. Eldridge.

Crystallographic investigation of silver subfluoride. H. Steinmetz and A. Hettich (Z. anorg. Chem., 1927, **169**, 75—76).—The crystals belong to the trigonal system; $a:c=1:1{\cdot}880$; α=71° 52′. H. F. Gillbe.

Grating constant of purple of Cassius. G. R. Levi and C. Fontana (Atti R. Accad. Lincei, 1927, [vi], 5, 996—1000).—With the Debye–Scherrer method values have been obtained for the grating constant of samples of purple of Cassius prepared in different ways and containing varying amounts of stannic oxide. Assuming a cubical cell the mean value of the constant is 36 Å.; the amount of stannic oxide present has no influence on the constant.
R. W. Lunt.

Crystal structure of cæsium mercuric chloride. G. Natta (Atti R. Accad. Lincei, 1927, [vi], 5, 1003—1008).—Cæsium mercuric chloride crystallised from solutions containing excess of cæsium chloride has a cubic lattice of constant 5·44 Å.; the mercuric ion is at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), the cæsium ion at (0, 0, 0), and the chlorine ions at ($\frac{1}{2}$, $\frac{1}{2}$, 0), (0, $\frac{1}{2}$, $\frac{1}{2}$) and ($\frac{1}{2}$, 0, $\frac{1}{2}$), $d_{\text{calc.}}$ is 4·53, $d_{\text{obs.}}$ 4·266. R. W. LUNT.

Crystal structures of mercuric and mercurous iodides. M. L. HUGGINS and P. L. MAGILL (J. Amer. Chem. Soc., 1927, 49, 2357—2367).—The unit tetragonal cell of mercuric iodide contains $2HgI_2$ and has the dimensions $a_0=4{\cdot}34$, $c_0=12.34$ Å. The mercury atoms are at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and the iodine atoms at (0, $\frac{1}{2}$, u), ($\frac{1}{2}$, 0, $\bar{u}$), ($\frac{1}{2}$, 0, $\frac{1}{2}-u$), and (0, $\frac{1}{2}$, $u+\frac{1}{2}$), where $u=0{\cdot}140\pm0{\cdot}003$ (cf. Bijvoet, Claassen, and Karssen, A., 1926, 889). The valency electrons are probably in pairs at the corners of tetrahedra surrounding both mercury and iodine atoms. Each mercury atom is linked to four iodine atoms, each of the latter being linked to two mercury atoms.

The unit tetragonal cell of mercurous iodide contains $2Hg_2I_2$ and has $a_0=4{\cdot}92$, $c_0=11{\cdot}64$ Å. The mercury atoms are at (0, 0, u), (0, 0, $\bar{u}$), ($\frac{1}{2}$, $\frac{1}{2}$, $u+\frac{1}{2}$), and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}-u$); the iodine atoms are at (0, 0, v), (0, 0, $\bar{v}$), ($\frac{1}{2}$, $\frac{1}{2}$, $v+\frac{1}{2}$), and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}-v$), where $u=0{\cdot}117$ and $v=0{\cdot}353$ Å. (cf. Havighurst, A., 1926, 995).

S. K. TWEEDY.

Crystal structure of thallium. K. BECKER (Z. Physik, 1927, 45, 450).—The author maintains his original contentions (this vol., 503) with regard to the crystal structure of thallium and refutes those of Levi (this vol., 1013) in which a hexagonal structure is claimed. R. W. LUNT.

***X*-Ray investigations on the structure of formaldehyde polymerisation products.** J. HENGSTENBERG (Ann. Physik, 1927, [iv], 84, 245—278).—Johner and Signer have studied the polymerisation of formaldehyde and many of their products have been examined by the powder method. Highly polymerised polyoxymethylenes of the types $OH{\cdot}CH_2{\cdot}[O{\cdot}CH_2]_x{\cdot}O{\cdot}CH_2{\cdot}OH$, x being about 60; $HSO_3{\cdot}O{\cdot}CH_2{\cdot}[O{\cdot}CH_2]_x{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}SO_3H$, and $OMe{\cdot}CH_2{\cdot}O{\cdot}[CH_2{\cdot}O]_x{\cdot}CH_2{\cdot}OMe$, etc., all show the same *X*-ray diagram. By heating polyoxymethylenes with acetic anhydride, oxymethylene diacetates of the type $COMe{\cdot}[O{\cdot}CH_2]_x{\cdot}OAc$ are obtained and a number of solid diacetates in which x varies from 8 to 22 have been separated by fractional crystallisation. Using a specially pure diacetate in which $x=9$, the *X*-ray study leads to the cell dimensions (Å.) of $25{\cdot}2\times8{\cdot}30\times4{\cdot}47$ (=935 Å.^{3}), and since the volume of a single molecule is calculated to be 451 Å.^{3}, the number of molecules per unit cell is 2 within the limits of error. Similarly, when $x=15$ the cell dimensions are $36{\cdot}8\times7{\cdot}89\times4{\cdot}56$ with again 2 molecules per unit cell. For every fresh CH_2O-group the length of the unit cell increases by about 1·9 Å. For soluble diacetates it is therefore evident that the molecule is the unit with which the lattice is built up. Similar conclusions follow from the study of the dimethyl ethers, which are built on a pseudo-trigonal form. When mixtures of products of a low degree of polymerisation are examined it is found that molecules of the same length always crystallise together so that mixed crystals are not formed. On the other hand, in the diacetates in which x is high, and in the other highly-polymerised products, molecules of different lengths may be attached end to end and the lattice is not built up with molecules as units.

The work lends support to Staudinger's idea of a relatively simple formaldehyde polymerisation product as the unit in the cellulose structure. In certain lattices it must be assumed that with the $[CH_2O]_x$ alinement, the lattice forces must be chemical in nature in one direction, thus accounting for the fibre structure. With a more complicated unit group, the lattice forces may represent chemical affinity in several directions so that the entire crystallite may be regarded as one large molecule.

R. A. MORTON.

Comparison of *X*-ray spectra of organic compounds in the solid and liquid states. R. O. HERZOG and W. JANCKE (Z. Physik, 1927, 45, 194—199).—The comparison was undertaken by the Debye–Scherrer method. A strong undifferentiated band in the spectrum of a liquid occurred, generally in the neighbourhood of an especially intense interference line in the spectrum of the corresponding solid (but not always *vice versa*). If several intense lines lie close together in the spectrum of the solid, these are converted by liquefaction into a single wide amorphous band. Bands close to the point of intersection of the incident ray with the photographic plate are at a greater distance from that point than the corresponding intense lines of the solids, whilst bands which occur near the periphery are displaced towards the centre. G. A. ELLIOTT.

***X*-Ray liquid diffraction.** C. M. SOGANI (Indian J. Phys., 1927, 2, 97—133; cf. this vol., 924).—*X*-Ray diffraction data for fourteen further liquids, including formic, acetic, butyric, lauric, palmitic, erucic, and brassidic acids, pyridine, piperidine, quinoline, methyl and ethyl benzoate, phenetole, and mercury, have been obtained. All the acids, except formic and butyric acids, have also been studied in the solid state in order to compare the corresponding prominent spacings in the two states of aggregation. On the basis of these and the previous data (*loc. cit.*), the molecular constitution of liquids is discussed. It is shown that there must be fairly regular spacings between the molecules of a liquid, and that the shape of molecules influences considerably their orientation. *X*-Ray haloes of liquids composed of spherical molecules will have a single maximum in the diffraction halo corresponding with the mean distance between neighbouring molecules, the sharpness depending on the compressibility of the liquid. Liquids having elongated or flat molecules are characterised, in general, by two maxima in the diffraction pattern, corresponding with the two principal dimensions of the molecules, in the first case the cross-sectional, and in the second the linear dimensions of the flat surface. In discussing the haloes of molecules in which the distribution of the scattering electrons is very unsymmetrical, it is probably sufficient to regard the optical centre of the molecule as the centre of mass of the electrons. From the point of view of these typical cases the diffraction haloes of all the liquids investigated are discussed and their important features explained.

M. S. BURR.

Diffraction of *X*-rays in liquids. G. W. Stewart, R. M. Morrow, and E. W. Skinner (Physical Rev., 1926, [ii], 27, 104).—Camphor at 21° or 205° shows the same location of intensity peaks when allowance is made for expansion. Liquid naphthalene, α-naphthol, and β-naphthol give broad peaks which are approximately the mean of the peaks given by the solids. For methyl, propyl, hexyl, octyl, and decyl alcohols, a single broad peak is accompanied by smaller ones, indicating a larger "grating" spacing. The phenomena are probably interatomic in origin. A. A. Eldridge.

Magnetic susceptibility of iron–carbon alloys at high temperatures, and the equilibrium diagram of the system. K. Honda and H. Endo (Sci. Rep. Tôhoku Imp. Univ., 1927, 16, 627—637).—The magnetic susceptibility of steels containing up to 5% of carbon has been measured both in the solid and in the molten state, and between about 800° and 1300°. In general, the susceptibility–temperature curves are rectilinear, but points of inflexion may be observed corresponding with the liquidus and solidus points, and with the solubility of cementite, so that from the measurements the equilibrium diagram of the system may be constructed. The susceptibility of cementite, determined by extrapolation of the susceptibility–composition curves, which are also rectilinear, is found to decrease in a linear manner with rise in temperature. The susceptibility of the molten steels does not vary with the temperature. R. Cuthill.

Piezo-electric effect in sodium bromate. J. Valasek (Physical Rev., 1926, [ii], 27, 254).—The change of the lattice constant for sodium bromate with temperature is 0·0000286, whilst the temperature coefficient of the piezo-electric constant is approx. 100 times as great. This is not in accord with simple expansion of all atomic distances. A. A. Eldridge.

Recrystallisation of silver and copper. H. Widmann (Z. Physik, 1927, 45, 200—224).—A study has been made of the changes in the *X*-ray spectra, tensile strength, and extension of silver and copper foil, when rolled to varying extents and subsequently heated. The crystals of a thoroughly rolled foil are oriented in a definite manner, whilst on heating a process of recrystallisation takes place whereby the plane of orientation changes at a more or less sharply defined temperature. Further heating may cause the crystal arrangement to become quite irregular. Cold-rolled copper which has been previously worked at a higher temperature, however, does not change from the recrystallised state on further heating, whilst foil which has been incompletely rolled changes directly to the irregular condition. In the recrystallised state, the (113) plane of silver and the (100) plane of copper are parallel to the plane of rolling. The process of recrystallisation is accompanied by a softening of the metal and an increase of its extension. The influence of small amounts of impurities on the temperature at which recrystallisation begins has also been studied. G. A. Elliott.

Alteration of the crystal orientation of iron on rolling. G. Tammann and A. Heinzel (Z. anorg. Chem., 1927, 167, 173—182).—The influence of rolling on the crystal structure of iron has been determined under various conditions. H. F. Gillbe.

Internal stress [in tungsten wires] as revealed by *X*-ray photographs. (Freiherr) von Göler and G. Sachs (Z. Metallk., 1927, 19, 410—411).—The blurring of the $K\alpha$ doublets in the Debye–Scherrer *X*-ray photographs of drawn tungsten wire gradually disappears with rise in annealing temperature and has totally vanished at about 1000°. The tensile strength of the wires increases slightly to a maximum at about 800°, then decreases fairly rapidly with further rise in the annealing temperature. These results indicate that the blurring of the interference lines by cold work has nothing to do with the hardening action of cold deformation, but is probably caused by internal stresses in the wire which are completely relieved by annealing it at 900° without appreciably reducing its hardness or strength. A. R. Powell.

Photo-elastic properties of transparent cubic crystals. H. B. Maris (J. Opt. Soc. Amer., 1927, 15, 194—200).—The photo-elastic coefficients of rock salt, sylvite, and fluorite have been measured for the mercury lines 436, 546, and 578 $\mu\mu$. Compared with glass the coefficient is positive for rock salt, negative for sylvite; for fluorite stressed normal to a cube face it is positive and when stressed normal to an octahedral face negative. For all cases except the last the relative retardation, Δ, plotted against stress per cm.^{2} gave a straight line for loads between 10,000 and 20,000 g./cm.^{2}; this line extended cut the axis of Δ above zero. The relation between photo-elastic effect and applied force for cubic crystals is therefore not the simple direct relation assumed for non-crystalline materials. C. J. Smithells.

Electrical birefringence of benzil. R. de Mallemann (Compt. rend., 1927, 185, 709—711).—Benzil is the optical analogue of quartz, but is more convenient for electro-optical studies on account of its low m. p. and its solubility. Measurements conducted with solutions of benzil in benzene have shown that the specific birefringence increases with the concentration and that Kerr's constant is negative and higher in absolute value than that of any other known negative substance. The conclusions suggested by the results are the same as those arrived at in the interpretation of the electrical and optical properties of quartz (Rev. gén. Sci., 1927, 38, 474). J. Grant.

Maxwell effect in liquids. C. V. Raman and K. S. Krishnan (Nature, 1927, 120, 726—727).—A molecular theory of the Maxwell effect is presented. A. A. Eldridge.

Influence of *X*-rays on time lags of the Faraday effect and on optical rotation in liquids. F. Allison (Nature, 1927, 120, 729).

Influence of *X*-rays on the crystallisation of antimony. (Sna.) M. Campa (Rend. Accad. Sci. fis. mat. Napoli, 1926, [iii], 32, 170—173; cf. Adinolfi, A., 1925, ii, 485).—*X*-Rays (maximum frequency $\nu=1\cdot46\times10^{19}$) produce a decrease in the Hall coefficient of antimony during solidification similar to that given by mesothorium radiation

(13—17%), causing a thermo-electric current in a circuit containing the unexposed metal, the thermo-electromotive force having a mean value of $2{\cdot}0\times10^{-6}$ volts at 0—18·5°. E. W. Wignall.

Photomagnetic effect in silver chloride and in selenium. C. W. Heaps (J. Opt. Soc. Amer., 1927, **15**, 190—193).—Contrary to the results of Garrison (A., 1925, ii, 371), no change in the magnetic susceptibility of silver chloride and selenium was found when these materials were exposed to the light from a tungsten lamp. This result is considered to support Bohr's theory that free electrons do not contribute to diamagnetic susceptibility. C. J. Smithells.

Determination of the coefficient of magnetisation of certain liquids. G. P. Arcay and M. Fallot (Compt. rend., 1927, **185**, 849—851).—Solutions of gelatin (0·1 and 0·4%), gum arabic (0·2%), albumin (0·1%), gelose (0·02%), casein (0·01%), and of silica gel behave abnormally during the determination of the coefficient of magnetisation by compensating the change in level produced in the arms of a **U**-tube, one of which is placed in a magnetic field, by the addition of a measured quantity of liquid from a burette. A secondary change of level, often of the same order as that produced initially, was observed, the effect being greatest and least for gum arabic and gelose, respectively. Collodion (28%), glycerol (at 30°), sulphuric acid (*d* 1·825), benzene, "vaseline," and olive oil behaved normally. The phenomenon is associated with the same substances as the Schwedoff effect, and may be related to the rigidity of the liquid. J. Grant.

Magnetic susceptibilities of vapours of organic liquids. V. I. Vaidyanathan (Physical Rev., 1927, [ii], 30, 512—515).—The following values of the molecular (volume) susceptibility ($\times10^6$) of vapours are tabulated: methyl acetate 51, ethyl formate 50, carbon tetrachloride 79, chloroform 73, ether 70, *n*-pentane 82, *n*-hexane 89, *n*-heptane 97, methyl formate 38, acetone 34, carbon disulphide 75, benzene 83. A. A. Eldridge.

Specific heats of solid substances at the temperatures attainable with the help of liquid helium. I. Measurements of the atomic heat of lead. W. H. Keesom and D. H. Andrews (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 434—443).—The specific heat of lead has been determined by the method of Nernst and Eucken (cf. Keesom and Onnes, A., 1915, ii, 83; 1916, ii, 12) between 2° and 20° Abs. The results are much less accurate at the lower temperatures than at the higher, the average deviation from the mean being 20% at 2—4°, 7% at 4—8°, and 2% at 8—16° Abs. There is satisfactory agreement with the results of Keesom and Onnes (*loc. cit.*) in the liquid hydrogen range. The atomic heat of lead at the lower temperatures is several times as great as that calculated from the formula of Debye, if the value $0=88$ which reproduces approximately the observed values at higher temperatures be adopted. It is not possible to decide from the measurements whether, on approaching 0° Abs., the atomic heat capacity approaches zero or a positive value. It may approach zero at a smaller rate than Debye's T_3 rule suggests. M. S. Burr.

Specific heat of water vapour and the theory of the dissociation of water vapour at high temperatures. W. H. McCrea (Proc. Camb. Phil. Soc., 1927, 23, 942—950).—Theoretical. The theory of the vibrational specific heat together with the theory of the dissociation of the H_2O molecule at high temperatures accounts for the observed facts. At temperatures near 100° an effect due to polymerisation is found. W. E. Downey.

Thermal properties of butane, *iso*butane, propane, and ethane. L. I. Dana (Physical Rev., 1926, [ii], 26, 819).

F. p. [and b. p.] of organic compounds. X. J. Timmermans (Bull. Soc. chim. Belg., 1927, 36, 502—508).—The f. p. and, wherever possible, the b. p. of a large number of organic compounds are listed. J. S. Carter.

Has pure aluminium an allotropic transformation point? M. Haas (Z. Metallk., 1927, 19, 404—406).—Dilatometric experiments with rods of pure aluminium containing only 0·044% Si, 0·040% Fe, and 0·07% Cu failed to indicate any allotropic transformation at temperatures up to 610°. A. R. Powell.

Vapour pressure of liquid mercury. A. W. C. Menzies (Z. physikal. Chem., 1927, **130**, 90—94).—The temperature scale employed by Smith and Menzies in reporting the vapour pressure of mercury (A., 1910, ii, 1037) has been revised from the sulphur b. p. value of 445° to the new figure 444·6°. Taking into account the new data of Menzies (A., 1920, ii, 11), new values for the constants of the Kirchoff–Rankine–Dupre–Hertz equation, $\log p=A-B/T-C\log T$, have been evaluated, giving $B=3283{\cdot}92$ and $C=0{\cdot}665240$. The average divergence of the pressure measurements of Smith and Menzies from this equation is 0·10%, whilst the measurements of other workers show in general considerably larger differences. Despite this, the equation holds from 0° to 1200°, *i.e.*, over a pressure variation of 1—2,000,000,000, within the limits of experimental error. S. J. Gregg.

Atomic volumes of zirconium and hafnium. A. E. van Arkel (Z. physikal. Chem., 1927, **130**, 100—104).—Hafnium and zirconium apparently violate the usual rule that in a given group of the periodic table atomic volume increases with increasing atomic weight. Hence accurate determinations of their atomic volumes are of importance. The metals were obtained in pure condition by thermal dissociation of their iodides, and were then drawn into wires suitable for *X*-ray examination by the Debye–Scherrer method. The following results were obtained: the density of zirconium is $6{\cdot}53\pm0{\cdot}01$, of hafnium $13{\cdot}08\pm0{\cdot}05$; the atomic volume of zirconium is $13{\cdot}97\pm0{\cdot}02$, of hafnium $13{\cdot}66\pm0{\cdot}06$. S. J. Gregg.

Thermal expansion of silver between +101° and −253°. W. H. Keesom and (Miss) A. F. J. Jansen (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 576—580).—The coefficients of linear expansion of silver over the temperature ranges −252·8° to −182·8°, −182·8° to −102·5°, −102·5° to 0°, and 0° to 101·1°, determined by the method previously described (A., 1926, 1197), are 9·81, 15·89, 17·61, and $19{\cdot}15\times10^{-6}$, respectively. As with copper, an equation involving powers of t up to the fourth is necessary to represent the expansion over the whole temperature range. J. S. CARTER.

Relation between temperature and energy of a gas. II. E. WERTHEIMER (Z. Physik, 1927, 45, 231—260; cf., A., 1926, 1088).—The previous calculation of the energy of a rarefied gas—considered as the sum of the internal molecular energy, the kinetic energy of the molecules, and the energy associated with the black-body radiation from the walls of the enclosure and with the individual temperature spectrum of the gas—as a function of temperature, has been extended to gases of finite concentration. The latter energy term is considered to arise from radiations associated with the elastic collisions of the molecules with the walls of the enclosure or with one another, and it has the form $u'=\phi(v)T$, where v is the specific volume of the gas or vapour. $\phi(v)$ may be expressed as: const. T_S^z (z=6, 9, 12, 15), where T_S is the b. p. corresponding with the given value of v and z depends on the nature of the gas. For a saturated vapour, in which case there is a state of equilibrium between the kinetic and internal molecular energies, the discussion has been simplified by means of considerations based on the law of corresponding states and on Trouton's rule. The resulting vapour-pressure equation has the form $p+Ap_2=CT^n$ (n=13 for normal vapours, and 16 for anomalous vapours), where A and C are constants. This equation is in good agreement with experiment (usually within 5%) for *iso*pentane and water vapours, and the deviations of the calculated from the experimental values are explained qualitatively in terms of the variation of the curvature of the molecular paths with the specific volume, and of the average angle of collision against the enclosure with the mean free path of the molecules.
G. A. ELLIOTT.

Dependence of surface tension on the electric charge. E. BOGOSLOVSKI (Ann. Physik, 1927, [iv], 84, 323—326; cf. Ruff, Niese, and Thomas, this vol., 402).

Surface tension of sodium. F. E. POINDEXTER (Physical Rev., 1926, [ii], 27, 820).—The surface tension of sodium is 222 dynes/cm. at 100°, and 211 dynes/cm. at 250°, the temperature gradient being 0·072 dyne per 1°. The results indicate that the molecules of liquid sodium are polyatomic.
A. A. ELDRIDGE.

Diffusion of non-electrolytes. E. N. GAPON and G. E. MUCHIN (Ukraine Chem. J., 1926, 2, 459—473).—A new empirical formula for the rate of diffusion in solution has been derived from a study of the various factors which affect diffusion. For various organic substances the formula yields results in fair agreement with experimental figures. Assuming that the rate of diffusion is a linear function of temperature, an equation for the temperature coefficient for normal and associated liquids is obtained.
A. RATCLIFFE.

Diffusion. E. N. GAPON (Ukraine Chem. J., 1926, 2, 474—496; cf. preceding abstract).—The formula deduced for the rate of diffusion has been applied to solutions of indifferent substances. It is shown that the empirical equation can be applied to the determinations of mol. wt. The results obtained are in good agreement with values obtained by cryoscopic methods. A. RATCLIFFE.

Dielectric constants of binary mixtures. III. Electric moments of certain organic molecules in carbon tetrachloride solution. I. J. KRCHMA and J. W. WILLIAMS (J. Amer. Chem. Soc., 1927, 49, 2408—2416).—The dielectric constants and densities at 25° of solutions of eight organic compounds in carbon tetrachloride are recorded (cf. this vol., 819). In the case of benzene and toluene, the molecular polarisation of the solute is independent of the concentration. The electric moments of the solute molecules are calculated and compared with the results of previous workers. S. K. TWEEDY.

Dielectric constants of binary mixtures. IV. Benzene as solvent for certain solid substances. J. W. WILLIAMS and R. J. ALLGEIER (J. Amer. Chem. Soc., 1927, 49, 2416—2422).—The dielectric constants and densities at 25° of benzene solutions of benzoic acid, phenol, iodine, antimony iodide, stannic iodide, and silver perchlorate are recorded. The molecular polarisation of the solutes is proportional to the mol. fraction; this could not be confirmed for antimony iodide because of its low solubility. Stannic iodide has a zero electric moment in benzene solution. The values calculated for the other solutes are discussed in the light of recent solubility work.
S. K. TWEEDY.

Properties of mixtures of hexane and nitrobenzene. V. TIMOFÉEV and K. STACHORSKI (Ukraine Chem. J., 1926, 2, 395—407).—In large concentrations, the mol. wt. of hexane, as calculated from the observed depression of the f. p. of its solution in nitrobenzene, is twice its normal mol. wt. In general, this method of determining mol. wt. is not applicable when the determination is made with almost saturated solutions. When the mixture is almost saturated the fluidity curves show a change of curvature as the temperature approaches the saturation temperature. The addition of benzoic, butyric, or valeric acid increases the solubility of hexane in nitrobenzene, whereas *o*-nitrophenol and resorcinol decrease it. The addition of the last two substances does not greatly decrease the solubility unless a large proportion of hexane is present, when the saturation temperature rises rapidly.
E. ROTHSTEIN.

Eutectic f.-p. depression in binary mixtures. II. E. KORDES (Z. anorg. Chem., 1927, 167, 97—112; cf. A., 1926, 798).—From the author's previous equations relationships have been deduced between the eutectic temperature and concentration of a binary system and the m. p. of the pure components. The relative eutectic depressions of the f. p. of the components are related to one another inversely as the ratio of the concentration of the components in the eutectic mixture. Eutectic melting is ascribed to the reciprocal breaking down of the crystal lattices as a result of diffusion in the solid state.
H. F. GILLBE.

Relation between the turbulent internal friction and the constitution of binary liquid mixtures.

R. Kremann, R. Springer, and H. Roth (Z. physikal. Chem., 1927, **130**, 415—421).—An apparatus is described by means of which the rate of hydraulic or turbulent streaming of liquids can be measured, and it has been used to obtain the internal friction curves of the following binary liquid mixtures: acetone–chloroform, aniline–phenol, aniline–nitrobenzene, and benzaldehyde–ethyl alcohol. A comparison with the true internal friction curves shows that in the case of turbulent friction the positive deviations are greater, the negative deviations smaller, and no minimum is found with the alcohol–benzaldehyde mixture (cf. Dunstan, A., 1904, ii, 805). The existence of compounds is readily shown by this method. L. L. Bircumshaw.

Distillation and rectification of complex mixtures. L. Gay (Chim. et Ind., 1927, **18**, 381—393; cf. this vol., 928).—The study of the five possible methods for working a set of three fractionating columns for the separation of a mixture of four alcohols is continued and the minimum heat consumption necessary to effect the separation of a mixture of given composition by each method is calculated from the tetrahedral diagrams previously given. These minimum heat values presuppose a column of infinite height, but the results bear a definite relationship to those attainable in practice. The " domains " of the five methods in the composition tetrahedron are then mapped by calculating the points at which the frontier planes cut the edges (*i.e.*, binary mixtures). Certain of the lines made by the planes cutting the faces are exactly calculable, others are approximations. The positions of these boundary planes within the tetrahedron are further partly worked out. C. Irwin.

New binary azeotropes. VII. M. Lecat (Ann. Soc. scient. Bruxelles, 1927, **47**, *B*, [i], 108—114; cf. this vol., 819).—A further list of binary azeotropic mixtures and non-azeotropic systems is given. R. Cuthill.

Azeotropism in the binary systems alcohols–organic halides. M. Lecat (Ann. Soc. scient. Bruxelles, 1927, **47**, *B*, [ii], 39—62; cf. this vol., 405).—The published data for azeotropic mixtures in the above systems, supplemented with some new determinations, have been used to derive empirical formulæ connecting the difference in b. p. of the constituents, Δ, with the azeotropic lowering, δ, on the one hand, and with the alcohol concentration on the other. In every instance the azeotrope is more volatile than either of its constituents. For a given value of Δ, δ decreases with increase in the number of carbon atoms in the alcohol, but the curves connecting Δ and δ are the same for isomeric substances. R. Cuthill.

Fluidity of metals and alloys in the liquid state. II and III. L. Losana (Notiz. chim.-ind., 1927, **2**, 63—66, 121—125).—II. Values are recorded of the coefficient of fluidity of tin (250—950°), lead (350—900°), cadmium (360 750°), zinc (450—900°), lead–tin alloys (250—900°), tin–antimony (0—20%) alloys (250—600°), tin–copper (0—10%) alloys (300—600°), tin (86—96%)–copper (2—8%)–antimony (2—12%) alloys (300—600°), and tin (10—85%)–copper (4—5%)–antimony (5—20%)–lead (4—80%) alloys 300—500°).

III. An examination of zinc–tin, zinc–aluminium, aluminium–silicon, aluminium–iron, aluminium–copper, aluminium–magnesium, aluminium–copper–silicon, aluminium–silicon–magnesium, aluminium–copper–magnesium, aluminium–copper–zinc, copper–tin, copper–tin–lead, copper–tin–zinc, and copper–zinc alloys, special brasses, and aluminium. The copper–cupric oxide eutectic has m. p. 25° below that of pure copper. Chemical Abstracts.

Hardness, micro-structure, and electrical conductivity of platinum–silver alloys. N. S. Kurnakov and Y. A. Nemilov (Ann. inst. platine, 1926, No. 4, 306—316).—Brinell hardness (kg./mm.^{2}), tensile strength (kg./mm.^{2}), and conductivity values are given for platinum, silver, and 15 alloys. The tensile strength of platinum is 28·56, and of silver 18·04; the conductivity of platinum is $7{\cdot}291\times10^4$ at 25°, $6{\cdot}012\times10^4$ at 100°, and that of silver is $62{\cdot}973\times10^4$ at 25°, $48{\cdot}828\times10^4$ at 100°. Photomicrographs show the absence of compound formation. Chemical Abstracts.

Solubility of non-irradiated cholesterol in liquid ammonia. R. G. Gustavson and J. B. Goodman (J. Amer. Chem. Soc., 1927, **49**, 2526—2528).—The solubility of cholesterol in liquid ammonia from −38° (0·00) to +49° (0·545 g. per 100 c.c.) has been determined (cf. Frank and Gustavson, J. Amer. Med. Assoc., 1925, **84**, 1715). F. G. Willson.

Fractional crystallisation of radioactive substances. II. Equilibrium in the system barium bromide–radium bromide–hydrogen bromide–water at 0° and 25°. V. Chlopin and B. Nikitin (Z. anorg. Chem., 1927, **166**, 311—338; cf. A., 1925, ii, 438).—The distribution of radium bromide between solid barium bromide and a saturated solution of barium bromide containing varying amounts of hydrogen bromide at 0° and 25° has been investigated. Although with increasing concentration of acid the distribution coefficient ultimately increases in favour of the solid phase, yet in view of the variation in the composition of the aqueous phase, the distribution as a whole must be regarded as obeying the Nernst distribution law, and neither Schlundt's empirical formula (U.S. Bur. Mines, Tech. Paper, 1922, No. 265) nor the formula of Doerner and Hoskins (A., 1925, ii, 381) is applicable. The distribution constant does not vary greatly with the temperature. Measurements on the system barium bromide–hydrogen bromide–water at 0° and 25° show that the addition of hydrogen bromide to a saturated solution of barium bromide precipitates an approximately equivalent amount of the salt. R. Cuthill.

Electrolyte adsorption on pure ash-free charcoal. I. M. Kolthoff (Rec. trav. chim., 1927, **46**, 549—573).—The ash-containing charcoals which have usually been employed by past workers on adsorption from solution are undesirable, as the ash exerts a disturbing effect. The charcoal used in this investigation was therefore prepared from pure commercial sugar, by precipitating an aqueous solution with alcohol, its ash content then being less than 0·001%. It was then carbonised by heating in a platinum basin, roughly powdered, heated for 20 hrs. (Meker burner) in a quartz crucible with tightly-fitting lid, and sieved (sample *A*). Sample *B*, obtained by activating *A* in a porcelain tube with free access of air at 920—1000°, exhibited hydrolytic adsorption (the acid only being adsorbed from solutions of salts), whereas *A* did not, the difference between them being due to the volatile impurities which are only expelled at the higher temperature. The usual procedure of washing the charcoal first with hydrochloric acid and then with water until neutral was proved unsatisfactory, for on further heating and washing more acid was liberated. Activation of the charcoal is due to enlargement of the surface by oxidation, mere heating in a closed tube at 900—1000° being insufficient. Heating in a hydrogen stream for 24 hrs. has no effect, showing that activity is not due to the presence or removal of products formed by the reaction of the charcoal with the activating gas.

The adsorption of inorganic acids is purely molecular, equal quantities of both ions being adsorbed. The order of adsorption is $HCNS > HI > HNO_3 > HIO_3 > HCl = HBr = HClO_4 \gg H_2SO_4$; $H_3PO_4 = 0$, and between $0{\cdot}1N$ and $0{\cdot}005N$ the adsorption isotherm follows the Freundlich equation, the exponent $1/n$ usually being larger, the greater the adsorbability of the acid. The adsorption is greatly increased by the presence of the corresponding neutral salts, the Freundlich exponents being then all changed to about 0·20. This increase is due to the fact that in strong electrolytes there is equilibrium between the pseudo-form of the molecule (responsible for capillary activity) and the ionogen form, which equilibrium is displaced towards the former by the presence of the neutral salt. Capillary-active non-electrolytes, being in general more active than inorganic acids, tend to displace the latter from adsorption.

Of basic substances, alkali hydroxides are not adsorbed, whilst ammonia, primary aromatic and aliphatic amines, diphenylamine, piperidine, and pyridine are well adsorbed; the alkaloids, however, although strongly capillary active at the water–air interface, are not adsorbed by the charcoal. Inorganic neutral salts are only hydrolytically adsorbed, the acid alone being taken up; their order of adsorption is the same as that of the free acids, the nature of the cation being immaterial. The general rules of hydrolytic adsorption are (1) salts of capillary-active acids and capillary-inactive bases are only hydrolytically adsorbed (*e.g.*, inorganic salts of the alkalis); (2) salts of capillary-active acids and capillary-inactive bases are adsorbed both hydrolytically and molecularly if the acid exhibits well-marked polar and apolar portions (*e.g.*, salts of most organic acids); (3) salts of capillary-active acids and capillary-active bases are adsorbed molecularly and also hydrolytically, if the base possesses a strong polar group; (4) salts of capillary-active acids and capillary-active bases, both containing strong polar groups, are adsorbed mainly molecularly.

Hydrolytic adsorption (of potassium thiocyanate) at the air–water interface has also been demonstrated by drawing a current of air through an aqueous solution of the substance and collecting the bubbles; these showed greater, and the remaining liquid less, acidity than the original solution. S. J. Gregg.

Heat of adsorption of oxygen on charcoal. II. W. E. Garner and D. McKie (J.C.S., 1927, 2451—2457).—The heat of adsorption of oxygen on charcoal has been measured between 18° and 200° in a vacuum calorimeter. The heat varies with the amount of oxygen adsorbed and reaches a maximum value of 70 kg.-cal. for $1{\cdot}5\times10^{-5}$ g.-mol. of oxygen per g. of charcoal. The maximum value has a large positive temperature coefficient. The bearing of the results on the constitution of the C_xO_y complex is discussed.

C. W. Gibby.

Sorption of ammonia by glass. (Time, pressure, and temperature relationships.) M. Francis and F. P. Burt (Proc. Roy. Soc., 1927, A, 116, 586—602; cf. Bangham and Burt, A., 1925, ii, 284).—A continuation of previous work (*loc. cit.*). By heating glass wool at 200° for long periods of time in an atmosphere of ammonia, until further treatment produces no more change, the glass may be maintained indefinitely in such a condition that its behaviour towards ammonia can be closely reproduced. The shape of the sorption curve depends on the water content of the sorbent. For a state of maximum dryness it is S-shaped, but at higher temperatures the upper part only of the S curve is observable. The sorption process can be divided into two parts, represented by straight lines by plotting log (sorption rate) against log time. The slope of each line is independent of pressure and varies only slightly with temperature. Their points of intersection lie on a straight line and correspond with 50% sorption. The first half of the sorption process is probably of a different nature from the second, where the rate of change of log ds/dt with log t is more than doubled. The complete sorption process can be represented as a single-valued continuous function of temperature, pressure, and time, by a suitable choice of co-ordinates. As regards temperature variation, this is only approximately true. At 50% sorption, the rate of sorption is very nearly directly proportional to the pressure at constant temperature, and $d \log (ds/dt)/d \log p = 0{\cdot}9$. At constant pressure, the rate of sorption is approximately doubled for every 20° rise in temperature. At constant temperature, log sorption, in the limit, is a linear function of log pressure between 0·5 and 1 atm. Below about 300 mm. there appear to be alternative values for the sorption. At constant pressure, sorption, in the limit, is a linear function of the reciprocal of the absolute temperature. An outstanding feature of the phenomenon investigated is the extraordinary slowness of the later stages of the process, making the experimental attainment of equilibrium quite impracticable. L. L. Bircumshaw.

Reduction of weights of powders in air to weights in a vacuum. II. R. Ruer and J. Kuschmann (Z. anorg. Chem., 1927, 166, 257—274; cf. A., 1926, 1089).—The study of the removal of adsorbed air from various powders by heating in a vacuum has been continued. Cupric oxide prepared from the basic nitrate has a very small adsorptive power, which is a maximum when the temperature of ignition has been about 500°, but the adsorbed air is not completely removed by evacuation at the ordinary temperature. The oxide obtained by precipitating the nitrate with potassium hydroxide adsorbs much larger amounts of air, and if the preparation is heated at 440° in a vacuum its adsorptive power at the ordinary temperature is further increased, apparently owing to the removal of adsorbed water. This latter phenomenon is also manifested by ceric oxide, the adsorptive power of which is considerable, but varies with the mode of preparation. Silicic acid ignited at 600° has the greatest adsorptive power of any of the oxides examined, but this is almost completely destroyed by ignition at 1220°. In confirmation of Scott's results (Proc. C.S., 1909, 25, 286), it is found that thoroughly dried potassium chloride adsorbs a very small amount of air, which is removed satisfactorily by evacuation at the ordinary temperature. Lead sulphate behaves like potassium chloride, but cerous sulphate has an appreciable adsorptive power when quite dry. Reduced copper and iron do not adsorb nitrogen and argon to any appreciable extent, and their apparently large adsorptive power in respect of air involves oxidation effects. R. CUTHILL.

State of moisture adsorbed on acid earth. H. ISOBE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 155—190).—Measurements of the vapour pressure of specimens of Japanese acid earth containing varying amounts of adsorbed moisture showed that from 2 to 20% the vapour pressure increased linearly with the amount of adsorbed moisture, and by applying the Clausius–Clapeyron equation the heat of vaporisation of the adsorbed moisture was found to be greater than that of pure water, but to approach it with rise of temperature. Microscopical observations showed that the earth contained cracks or cavities amounting to 55·7% of the total volume, and with 20% adsorption the water layer is several molecules thick. Density determinations over a range of temperature showed that part of the adsorbed water is denser than unadsorbed moisture, and by heating the earth to high temperatures it was found that 42% by weight of the moisture is combined with the earth, and is not evolved at temperatures below 200°.

F. S. HAWKINS.

Influence of water on the solidity of powdered substances after heating. B. GARRE (Z. anorg. Chem., 1927, 167, 77—80).—Pellets of inert material containing various percentages of water and of benzene have been prepared and their mechanical strength after heating for 30 min. at 900° has been studied. Those prepared with benzene are easily crushed, the solidity being altered but little with change of the benzene content of the powder. Pellets prepared with water are much more stable, their solidity increasing with increase of water content up to about 30%.

H. F. GILLBE.

Adsorption and chemical nature of some organic compounds. N. SCHILOV and B. NEKRASSOV (Z. physikal. Chem., 1927, 130, 65—72).—The adsorbent was Merck's "Carbo medicinalis," 0·05 g. being shaken for 20 min. with 15 c.c. of an aqueous solution of the substance in question, usually of 0·01—0·005*M* concentration. After filtering, the concentration of the dissolved substance was determined acidimetrically or iodometrically. It was found that (1) in homologous series, the increase in adsorption due to the introduction of a CH_2 group reaches a maximum at about the fifth or sixth member; (2) the substitution of most radicals for hydrogen increases the adsorption, whilst the hydroxyl and sulphonic groups lower it; (3) the optically active isomerides and the racemic form have about equal adsorption, whilst the inactive form has lower adsorption; (4) differences are shown in the adsorptions of the stereoisomeric benzene derivatives and of the α- and β-substituted aliphatic compounds; (5) the *trans*-form of compounds which contain a double linking is more strongly adsorbed than either the *cis*-form or the corresponding saturated compounds; (6) for an equal number of carbon atoms, an aliphatic compound is more strongly adsorbed than the corresponding aromatic compound.

S. J. GREGG.

Surface area and sorption. M. TARLÉ (Bull. Chem. Soc. Japan, 1927, 2, 243—245).—Sameshima's conclusion (this vol., 304) that the sorption of carbon dioxide by charcoal is independent of the surface area and is hence to be regarded as a dissolution phenomenon is not supported by the actual experimental numbers recorded. Since charcoal is a very porous substance, powdering has a negligible effect on the surface area. Sameshima's figure for the density of his charcoal (2·1) is held to be too high. J. S. CARTER.

Surface area and sorption. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1927, 2, 246—249; cf. preceding abstract).—Pointing out that uncertainty regarding his density figure, which incidentally is in agreement with values recorded by Howard and Hulett (A., 1924, ii, 823), has but a negligible effect on the nature of the results, and producing evidence to show that powdering of charcoal produces an appreciable increase in surface area, the author defends the plausibility of his original conclusion.

J. S. CARTER.

Adsorption on dissolved molecules. N. S. MARINESCO (J. Chim. physique, 1927, 24, 572—585).—A review of measurements of the dielectric constants, viscosities, and coefficients of diffusion for various coloured substances in solution. Theoretical considerations show that these data may be used to estimate the degree of adsorption of the solvent on the molecules of the solute. G. A. ELLIOTT.

Electrical condition of hot surfaces during the adsorption of gases. I. Gold and silver surfaces at temperatures up to 850°. G. I. FINCH and J. C. STIMSON (Proc. Roy. Soc., 1927, A, 116, 379—400).—A gold or silver surface becomes charged when heated either in contact with a gas or in a high vacuum. The magnitude of the charge is independent of the gas pressure. Gold in the presence of oxygen or air and silver in the presence of oxygen, air, or hydrogen lose their charges slowly on evacuation but rapidly in the case of other gases. The lingering charges on gold or silver may be rapidly removed by burning off with the appropriate gas. It is suggested that the charge on a hot gold or silver surface in contact with a gas is due to activation of the gas, whereby its molecules become electrically charged; also, that the activation of a compound molecule such as water vapour or carbon dioxide involves its dissociation.

W. E. DOWNEY.

Gibbs on adsorption. W. D. Bancroft (J. Physical Chem., 1927, **31**, 1501—1506).—From the work of Gibbs (Scientific Papers, 1906, **1**, 235), it follows that the criterion for the applicability of the Freundlich equation to the case of the adsorption of a gas by a liquid in which it is practically insoluble is that the change in surface tension is proportional to the change in adsorption. The exponent in this equation is a measure of the change in surface tension with adsorption. L. S. Theobald.

General theory of absorption and distribution phenomena. W. Sementschenko (Z. physikal. Chem., 1927, **129**, 176—185).—Boltzmann's e theorem has been applied to the statistical consideration of the distribution of a substance between two phases and the boundary relations. An expression equivalent to Henry's law is derived and this shows that the solubility of a gas runs parallel with the generalised electric moment of its molecules, some measure of which may be afforded by the excess of its dielectric constant over unity. For solutions, an expression is obtained which leads to a relation similar to Gibbs' equation, from which it appears that if the moment of the solute molecules is less than that of the solvent molecules the concentration of the solute will be greater in the surface layer than in the main body of the solution, and *vice versa*. This explains the connexion between the dielectric constants of solvent and solute and the surface activity of the former, previously observed by Rehbinder (A., 1926, 674). For two solutions with the same solute but different solvents in contact with each other, the solute will be concentrated at the surface of separation, with resulting lowering of the surface tension, if the moment of the solute molecules is intermediate between those of the molecules of the solvents. Nernst's distribution law also follows, but the theory requires that the distribution ratio shall be a function of the concentration, and of the difference between the dielectric constants of the solvents. Where a substance is distributed among any number of other substances, the maximum concentration of the solute will occur in that solvent for which the value of the dipole moment is nearest to its own. R. Cuthill.

Diffusion in a gravitational field. R. Fürth (Z. Physik, 1927, 45, 83—85; cf. A., 1926, 21).—A reply to a criticism by Weaver (Z. Physik, 1927, 43, 296), in which it is conceded that the previous calculation of the sedimentation time for the metal hydrosol used by Burton (Proc. Roy. Soc., 1922, A, **100**, 414) gave a value which is much too large. Further calculation shows, however, that Burton's sol either comprised particles of varying sizes, or else these particles were not metallic. The author's previous statement that the time of sedimentation of finely-dispersed colloids is so great that no sedimentation can be observed in large vessels, is maintained. G. A. Elliott.

Boundary surface activity and dielectric constants. I. Dependence of boundary surface activity and adsorption at various surfaces of separation on the polarity and dielectric constants of the two phases forming the boundary surface, and of the adsorbed substance. P. Rehbinder (Z. physikal. Chem., 1927, **129**, 161—175).—It is suggested that the properties of a surface of separation of two phases are functions of the difference in polarity of the two species of molecules, which may be represented by the difference in the dielectric constants or by the free surface energy, although for single liquids there does not seem to be any simple relation between the dielectric constant and the surface tension. In accordance with this theory, it is found that the adsorption of a substance with surface activity at the surface of separation of two phases increases with increase in difference in polarity of the phases (cf. this vol., 930). The rule is formulated that if the added substance is adsorbed by both sides of the surface of separation it will tend to reduce the difference in the polarity and dielectric capacity of the phases. It is found experimentally that, in general, the greater the difference between the dielectric constant of the more polar phase and of the active substance dissolved in it, the greater is the surface activity of the latter. R. Cuthill.

Ring method for surface tension measurement. J. M. Johlin (Science, 1926, **64**, 93—94).—A criticism of the ring method; the accuracy attained is not so great as is assumed. In particular, no method can yield " absolute " values for the surface tension of colloidal solutions. A. A. Eldridge.

Compressibilities of aqueous solutions of some fatty acids. S. Venkateswaran (J. Physical Chem., 1927, **31**, 1521—1525).—Data for the adiabatic compressibilities of aqueous solutions of formic, acetic, propionic, and butyric acids, and for water, at a pressure of 1—2 atm. are given. The isothermal compressibilities for water and for the first two acids have been calculated. The values of the adiabatic compressibility for water ($45{\cdot}66\times10^{-6}$ at 22°) and for acetic acid are in good agreement with those of Tyrer (J.C.S., 1914, **105**, 2534). The compressibility of formic acid is lower than that of the other acids, and in all cases investigated the adiabatic compressibilities increase at first slowly with the concentration, and more rapidly at higher concentrations. L. S. Theobald.

Molecular structure in solution. II. Refractive indices and surface tensions of aqueous solutions of cobalt chloride and hydrochloric acid. O. R. Howell (J.C.S., 1927, 2039—2051).—The surface tension and refractive index of solutions containing a fixed quantity of cobalt chloride and varying amounts of hydrochloric acid have been compared with the corresponding data for a series of hydrochloric acid solutions. The curves obtained by plotting the differences of the constants of corresponding solutions against the concentration of the hydrochloric acid show inflexions near the concentration where the colour change of red to blue occurs. The colour change is explained by a change in the groups co-ordinated with the cobalt atom, the red complex being $Co(H_2O)_6^{\cdot\cdot}$, and the blue $CoCl_4''$, the inflexions on the curves occurring when the two complexes are present in equal numbers. The surface-tension measurements show that there should be a greater concentration of blue complexes in the surface layer, and, in support of this, it is found that the inflexion on the surface-tension curve occurs at a slightly smaller concentration of acid than the inflexion on the refractive index curve. The colour change is somewhat indefinite, and, as the blue form has the more intense colour, the maximum colour change occurs at a smaller acid concentration than the inflexions. F. S. Hawkins.

Synthesis and properties of uranium colloids. S. J. Diachkovski (Ukraine Chem. J., 1926, 2, 340—352).—Stable colloidal suspensions have been prepared by hydration of insoluble uranium salts. Analyses of the progressive hydration products point to the formation of complex intermediate compounds during the process. Complete hydration is obtained after continuous dialysis in running water. Dehydration leads to coagulation of the sol resulting in the precipitation of a hydrate of uranic acid. When hydration is incomplete the precipitate formed on coagulation corresponds with $Na_2U_2O_7$. In either case on treatment with water a colloidal solution is again formed. The whole synthesis can be represented: $n\mathrm{Na_2U_2O_7} \rightleftharpoons [\mathrm{Na_2U_2O_7,H_2UO_4}]_{n-1} \rightleftharpoons [\mathrm{H_2O(UO_3)_2UO_2(OH)_2}]_n \rightleftharpoons [\mathrm{UO_2(OH)_2}]_{n+1}$, the equilibrium being disturbed if sodium diuranate or uranic acid is removed from the sphere of reaction. The particles are negatively charged and their velocity in an electric field corresponds with a charge of $1{\cdot}984\times10^{-8}$ e.s.u. The density of the sol is 7·45 and the size of the particles varies from $1{\cdot}144\times10^{-15}$ to one amicron, showing that the system is polydisperse. The effects of hydrochloric acid, barium chloride, and aluminium chloride on the coagulation were studied. The sign of the charge changes after treatment with aluminium chloride. A. Ratcliffe.

Formation of colloid systems by trituration. H. Neugebauer (Kolloid-Z., 1927, 43, 65—67).—The production of colloid systems by grinding substances in a machine mortar, both alone and in the presence of 0·1%, 1·0%, and 10% of lactose, was studied. The amount of colloid formed increased with the concentration of the lactose. The substances used can be arranged in the following order, representing a decreasing tendency to dispersion by this means: indigo, selenium, sepia, graphite, antimony sulphide, silver, gold, copper. The curves which connect the quantity of colloid formed with the duration of grinding show that dispersion takes place rapidly during the first 2 or 3 hrs., after which further production of colloid is slow. E. S. Hedges.

Preparation of colloidal solutions. S. Roginski and A. Schalnikov (Kolloid-Z., 1927, 43, 67—70).—For the preparation of colloidal solutions a method is developed which is based on the following principle. If a metal is distilled in a vacuum and the vapour is allowed to condense on a surface cooled by liquid air, the condensate is almost entirely amorphous, consisting of a highly disperse system of aggregated particles. By distilling simultaneously in this way a metal and a substance which is liquid at the ordinary temperature, a condensate is obtained which, when melted, produces a highly dispersed sol of the metal in the liquid employed. An apparatus is described for this work, in which the relative amounts of the substances in the condensate can be varied by suitable control of their distillation temperatures. The method has been employed successfully for the preparation of hydrosols of mercury, cadmium, selenium, sulphur, and phosphorus, and for organosols of mercury, cadmium, sodium, potassium, rubidium, and cæsium (using benzene, hexane, xylene, toluene, and in some cases ether and alcohol as dispersion media). The method is particularly suitable for the production of sols of the alkali metals, since no carbonisation of the organic medium occurs. The solid sols (condensates) have characteristic colours (sodium, reddish-violet; potassium and rubidium, bluish-green; cæsium, brownish-green), which disappear shortly after the sol is melted. The colour is considered to be due to atoms of the alkali metal, which later undergo aggregation. Examination showed the systems to be polydisperse. E. S. Hedges.

General colloid chemistry. XXII. Aluminium oxide sols. W. Pauli and E. Schmidt (Z. physikal. Chem., 1927, 129, 199—222; cf. A., 1926, 901).—Alumina sols obtained by boiling solutions of aluminium chloride with amalgamated aluminium have been titrated conductometrically with solutions of various silver salts. It is found in this way that the chloride ion in the sol may be completely replaced by the anion of the added salt, the conductivity being depressed by an amount which, for univalent anions, varies from anion to anion, and affords some measure of the extent to which the substituent ion is deactivated. Activity measurements show that when hydrochloric or sulphuric acid is added to alumina sols such as the above it is taken up rapidly at first but the amount soon tends to a limit, which is much less than would be equivalent to the total amount of aluminium present. The conductivity changes in this process suggest that the colloid particles undergo partial disintegration, the surface layers probably being removed, leaving the nucleus unattacked. With increasing dilution, the hydrogen-ion activity falls considerably, but the dissociation of the colloid particles does not change very much.

R. Cuthill.

Constitution of colloidal platinum. S. W. Pennycuick (J.C.S., 1927, 2600—2613).—The conductivities of platinum sols prepared by sparking under conductivity water have been measured. A variation in conductivity with time was observed, and specific conductivities as high as 66·1 gemmhos were obtained by boiling sols. It is suggested that some of the platinum is oxidised, and forms an ionic micelle $[\mathrm{Pt}_x(\mathrm{PtO_4})_y]''$, in equilibrium with an equivalent amount of hydrogen ion (cf. Pauli, Trans. Faraday Soc., 1921, 16, 14). Pure platinum sols contain free hydrogen ions, which form a layer on the surface of the sol particles. Equilibrium is disturbed by temperature changes, and the redistribution proceeds with measurable velocity. Consideration of titration curves with various bases shows that platinum sols behave as weak acids, but that the equilibria are not reached instantaneously. The bearing of the equilibrium between free and adsorbed ions on the coagulation of colloids is discussed.

C. W. Gibby.

Amorphous carbon or graphite ? O. Ruff, P. Mautner, and F. Ebert (Z. anorg. Chem., 1927, **167**, 185—189).—Although the adsorptive activity of graphite increases with increase of surface area there is no simple relationship between the state of division and activity. Further, specimens differing in activity give the same Debye–Scherrer diagrams. The existence of active corner atoms is postulated; the number of such atoms which are exposed, and therefore active, depends on the method of preparation of the specimen and on the degree of subdivision. H. F. Gillbe.

Optical properties of disperse mercuric sulphide. G. P. Voronkov and G. I. Pokrovski (Kolloid-Z., 1927, 43, 78—81).—Substances which are coloured red or yellow in the massive form are observed to change in colour when finely divided, whilst blue substances remain unchanged by subdivision. A formula was derived theoretically for the intensity of light of definite wave-length scattered by the particles, and was tested experimentally with suspensions of red cinnabar. The experiments showed that the optical properties of mercuric sulphide change gradually from those of the massive substance to those of the colloidally dispersed material. The change becomes noticeable in particles of size about 1 μ.

E. S. Hedges.

Consistence of mixtures of true fluid and of a fluid with solid particles. A. Mallock (Nature, 1927, 120, 619—620).

***X*-Rays and colloids.** G. L. Clark (Fourth Colloid Symposium Monograph, 1926, 145—173).—*X*-Radiation, hydrogen peroxide, or ozone coagulates cerous hydroxide and albumin sols; the radiation may therefore cause formation of peroxide. Heterogeneous rays may inexplicably fail to produce the effects of homogeneous radiation. Colloidal platinum, when exposed to radiation, exhibits a variable increase in catalytic power in the oxidation of sulphur dioxide. Biological colloidal systems, polymerisation, crystalline and sub-crystalline states are discussed. Katz' view that raw rubbers exhibit crystals which disappear on mastication or heating was not confirmed; when *Hevea* rubber is stretched a crystal-like fibre diagram appears, but vulcanised rubber requires much greater extension before the effect appears. The results of *X*-ray examination of balata, gutta-percha, gelatin, collagen, and glue are described. The various kinds of cellulose show a crystal structure; there are profound changes after treatment with 1% sodium hydroxide solution. The maximum spacing is 5·7 Å.

Chemical Abstracts.

Hydrodynamics of systems of variable viscosity. M. Reiner and R. Rivlin (Kolloid-Z., 1927, 43, 72—78).—The indefiniteness of the term involving the virtual volume of the disperse phase in the Einstein–Hatschek viscosity formula is removed by the derivation of the following formula, connecting the virtual volume with the velocity of shear: $f-f_\infty=(f_0-f_\infty)e^{-c_1 G}$, where f_0 and f_∞ are respectively the relative virtual volumes of the disperse phase at rest and at extreme rate of shear, G is the velocity of shear, and c_1 is a constant for the sol. A formula is also derived for the resistance value w of the Couette apparatus: $w=(\eta_0-\eta_\infty)e^{c_1\Omega(R_E^2+R_A^2)/(R_E^2-R_A^2)}+\eta_\infty$, where η_0 and η_∞ are respectively the viscosity coefficients of the sol in a state of rest and under extreme shearing, R_A and R_E the radius of the inner and outer cylinder respectively, and Ω the velocity of rotation of the outer cylinder. E. S. Hedges.

Structural changes in amorphous materials. Silica gel. W. A. Patrick, J. C. Frazer, and R. I. Rush (J. Physical Chem., 1927, 31, 1511—1520).—The structural changes produced in silica gel by heating to various temperatures in the range 100—1150° have been studied by means of the adsorption of carbon tetrachloride. The density of the gel after these heat treatments has also been measured at 30°. Adsorption is unchanged until the pure gel has been heated above 900°, after which it decreases rapidly to a minimum at 1000°. With a gel containing 0·28% of sodium sulphate, the decrease in adsorption begins at about 600°, is more gradual, and reaches a minimum (in this case zero) at 1000°. The density changes correspond qualitatively with the changes in adsorption, increasing at 800° to a maximum value at 1100°. Heating the gel for 2 hrs. at 1000° apparently closes the capillaries of the gel, and on heating at 1100° for 3 days the gel changes definitely to the crystalline form, as the *X*-ray patterns show. This is not in agreement with the findings of van Bemmelen (A., 1899, ii, 84) or of Berl and Urban (B., 1923, 350). An explanation of this structural change is given. L. S. Theobald.

Refractometric measurements on colloidal solutions. Boutaric and (Mlle.) G. Perreau (Compt. rend., 1927, 185, 892—893).—The interference refractometer is used to study the effects on hydrosols of the intermicellular liquid and of the micelles. For the former, which was separated by ultrafiltration, n is similar to that of water. For the sol, n does not alter appreciably during the addition of sufficient electrolyte to produce coagulation, but falls sharply once this has occurred. Adsorption isotherms of the micelles were obtained from a comparison of the value of n for the clear liquid after coagulation with that for a solution containing the coagulating electrolyte in the same concentration.

J. Grant.

Influence of hydrophilic colloids on the conductivity of acids and bases. H. Brintzinger (Kolloid-Z., 1927, 43, 93—106).—The conductivity of solutions of strongly dissociated acids is progressively reduced by increasing amounts of gelatin, gum arabic, salep mucilage, and dextrin. The order of influence of the colloids is that given above, dextrin exerting little effect. The colloids which have a slight effect on the conductivity of strong acids lower the conductivity of sodium hydroxide solutions in a striking manner. This is said to be due to the formation of chemical compounds. The conductivity of acetic acid solutions is raised by the addition of hydrophilic colloids, in consequence of the further dissociation of the acid due to the adsorption of hydrogen ions by the colloid. The hydrogen-ion concentration of all acids and the hydroxyl-ion concentration of bases are diminished by the presence of hydrophilic colloids, the order of influence here being :

gelatin, salep mucilage, gum arabic, dextrin. Dextrin has only a very slight effect on the reaction of acids. The alteration of the conductivity of acids and bases approximates to a linear function of the hydrogen-ion or hydroxyl-ion concentration. The equivalent conductivity of such a system can be represented by the formula $\Lambda=\{(\Lambda'-c)\cdot[H^{\cdot}]+[H^{\cdot}]'\cdot c\}/[H^{\cdot}]'$, where Λ' and $[H^{\cdot}]'$ are respectively the equivalent conductivity and hydrogen-ion concentration of the colloid-free acid, $[H^{\cdot}]$ is the hydrogen-ion concentration of the system, and c is a constant characteristic of the colloid. E. S. HEDGES.

Emulsification by solid powders. A. J. SCARLETT, W. L. MORGAN, and J. H. HILDEBRAND (J. Physical Chem., 1927, 31, 1566—1571).—Photomicrographs of emulsions stabilised by various solids in the form of powder are reproduced and support the explanation previously given by Finkle, Draper, and Hildebrand (A., 1924, ii, 97) that the type of emulsion depends on the angle of contact of the interface with the solid. It is further suggested that in forming the emulsion, droplets having the particles mainly on the outside of the interface would be better protected from coalescence than those having the particles more on the inside. The difficulties encountered in determining angles of contact between solids and liquid interfaces are discussed. L. S. THEOBALD.

Coagulation of smokes and the theory of Smoluchowski. G. NONHEBEL, J. COLVIN, H. S. PATTERSON, and R. WHYTLAW-GRAY (Proc. Roy. Soc., 1927, **A**, **116**, 540—553; cf. Whytlaw-Gray and Speakman, B., 1923, 211).—The use of the Zsigmondy slit ultramicroscope for determining the number of particles in a smoke is criticised and shown to give inaccurate results. A new method, claimed to be free from any serious experimental error, is described, involving the use of a special wedge-shaped cell in which the depth of the observed volume of smoke is limited by the walls of the cell itself. The coagulation of clouds of varying concentrations of ammonium chloride has been investigated, using different types of heater, with a view to discover some method of quantitatively reproducing a cloud; also smokes of antipyrin and arsenious oxide (prepared by sublimation), and of cadmium oxide (prepared by striking an arc between cadmium electrodes). In all cases straight-line graphs of σ, the particulate volume, or the volume containing a single particle, against t, the age of the cloud, were obtained. The constants of the equation $\sigma=\sigma_0+Kt$, calculated by the method of least squares, are tabulated, and it is believed that the results are accurate to about 10%. The experimental data agree as closely as those obtained for sols with the theory of Smoluchowski. The reasons for the fact that K is not a constant, but varies from cloud to cloud, are discussed. L. L. BIRCUMSHAW.

Electrokinetic potential of silica gel. I. Influence of structure of the diaphragm. S. GLIXELLI and J. WIERTELAK (Kolloid-Z., 1927, 43, 85—92).—A method is described for the measurement of the velocity of electro-osmosis through powdered or gelatinous substances in an apparatus which is a modification of that used by Perrin, and experiments were carried out to demonstrate its applicability. A study was made of the electrokinetic potential of silica gel and of ignited silica in dilute nitric acid, and it was established that mechanical deformation of the gel did not affect the values obtained. Although quartz powder and ignited silica gave the usual value for the electrokinetic potential, an abnormally low result was obtained on using silica gel in $10^{-3}N$- and $10^{-4}N$-nitric acid. The low value depends on the silica concentration of the gel, and rises for lower concentrations of silica. This effect is related to the extreme fineness of the capillaries in the stronger gels, which may be less than the width of the electric double layer. E. S. HEDGES.

Molecular association in the liquid state. K. M. STACHORSKI (Ukraine Chem. J., 1926, 2, 408—413).—An expression for the determination of the association factor of liquids has been worked out based on Pavlov's "capillary-chemical law of equimolecular surfaces" (A., 1917, ii, 125). Association factors for various organic liquids have been calculated by means of this expression; the results are found to be in good agreement with those obtained from the equation of Ramsay and Shields.

A. RATCLIFFE.

Chemical equilibrium in a mixture of paraffins. H. A. WILSON (Proc. Roy. Soc., 1927, **A**, **116**, 501—515).—Theoretical. The theory of chemical equilibrium is applied to the hypothetical reaction $C_{n-1}H_{2n}+C_{n+1}H_{2n+4}=2C_nH_{2n+2}$, and it is shown that the equilibrium composition of the vapour and liquid phases can be approximately calculated at any given temperature and pressure. Tables are given of values of the equilibrium pressure at different temperatures and for different values of x (CH_x being the composition of the vapour), and of values of x' ($CH_{x'}$ being the composition of the liquid in equilibrium with the vapour) for different values of x and the temperature, and from these a chart is drawn showing the values of x and x' corresponding with any temperature and pressure. The chart may be used for approximate calculations on vapour at temperatures down to about 260°, provided the vapour was originally produced above 370° or 430° and kept hot long enough for equilibrium to be approximately established between the hydrocarbons present. The theory is compared with the results obtained in large-scale operations on paraffin oils, and gives results which agree approximately with those obtained at temperatures above 320°. L. L. BIRCUMSHAW.

Determination of the dissociation constants of dihydric mono- and di-nitrophenols electrometrically and colorimetrically. F. L. GILBERT, F. C. LAXTON, and E. B. R. PRIDEAUX (J.C.S., 1927, 2295—2308).—Owing to oxidation reactions and tautomeric changes on dilution, some of the dissociation constants show irregularities, but the values for 3 : 5-dinitropyrocatechol, 4 : 6-dinitroresorcinol, 3-nitropyrocatechol, 2-nitroresorcinol, and 4-nitroresorcinol remain fairly constant. When the phenolic form is predominant the dissociation constant may be corrected for the presence of the quinonoid ion by the equation $p_{K'\cdot}=p_H-\log(\alpha-x)+\log(1-\alpha)$, where x is the degree of transformation into the quinonoid form as shown by the colour change, if it is assumed that the quinonoid form is completely ionised. Similarly when the *aci*-form is present in excess, the dissociation constant of this form can be corrected by the equation $p_{K'_a}=p_H+\log(x-\alpha)/\alpha$, if it is assumed that all the ion present is quinonoid. The relation between the dissociation constants and the position of the substituents is generally in accord with the alternate polarity theory. F. S. Hawkins.

Ionisation of sodium acetate. M. Meyer (Chem. News, 1927, 135, 280—281).—The degree of dissociation of sodium acetate in half-neutralised acetic acid is given approximately by the ratio [AcO′]/[AcOH], since the free acid is very slightly dissociated. Measurements of the dissociation of the salt and of the p_H of the solution suffice, therefore, to determine the dissociation constant of acetic acid, or if this is known the degree of dissociation of the salt may be obtained. Data are given which show that values of p_H calculated from the Nernst equation are much too low for concentrations greater than 0·1*N*. G. A. Elliott.

Formation and ionisation of compounds of casein with alkali. VI. Effect of temperature and concentration on the transport numbers of alkali caseinate solutions. D. M. Greenberg (Univ. Calif. Pub. Physiol., 1927, 7, 9—24).—The electrochemical equivalent of casein is, within certain limits, independent of the temperature. The influence of temperature on the mobility of the casein ion or micelle is linear between 5° and 50°; the Kohlrausch temperature coefficient of mobility at 18° is higher than that of any other ion. Solutions of alkali caseinates containing up to 8·65% of casein are to be regarded as completely ionised electrolytes. Chemical Abstracts.

Determination of ionic hydration. (Modification of Remy's method.) G. Baborovský (Z. physikal. Chem., 1927, 129, 129—160).—In order to investigate ionic hydration, transport experiments have been made, in which solutions of sodium, potassium, and lithium chlorides of concentrations from 0·1*N* to *N*, *N*-solutions of the corresponding bromides, and 0·1*N*- and *N*-solutions of hydrogen chloride were electrolysed in an apparatus in which one electrode section was separated from the remainder of the apparatus by means of a diaphragm of parchment-paper. From the weight and composition of the contents of this section before and after electrolysis the amount of water transported may be calculated (cf. A., 1923, ii, 289). The values for the water transport and transport numbers obtained in this way are, however, affected by electro-osmosis at the membrane. Attempts to eliminate this effect have been unsuccessful, but experiments in which no membrane was used indicate that it may be neglected for *N*-solutions, so that in this case the electrolytic transport of water is given by the total transport. In this way, the following absolute hydration numbers, in molecules of water, have been derived: $H^{\cdot}$, 1; $K^{\cdot}$, 5; $Na^{\cdot}$, 8—9; $Li^{\cdot}$, 13—14; Cl', 4; Br', 3. The lack of agreement between these numbers and those calculated from activity data may be due to the present method yielding the dynamic, as distinct from the static, hydration. R. Cuthill.

Activity coefficients of electrolytes. I. Bibivalent salt and the ion attraction theory. U. B. Bray (J. Amer. Chem. Soc., 1927, 49, 2372—2380).—The activity coefficients of zinc sulphate were determined by measuring the *E.M.F.* at 25° of cells of the type Zn,Hg(two phase)|*M*-$ZnSO_4$soln.|$PbSO_4$(solid),Pb,Hg(two phase), where *M* varies from 0·0006 to 3·4. Lead–lead sulphate electrodes are reproducible only in the complete exclusion of oxygen; a definite crystalline form of lead sulphate is essential, which should attain equilibrium with the solution before the electrode is set up. The use of two-phase amalgams, also, is desirable. The preparation of such an electrode is described. The experimental activity coefficients agree with those calculated in accordance with Debye and Hückel's theory within 2% when $M<0·005$; for greater values of *M* the discrepancy increases with great rapidity, indicating that the theoretical equation requires substantial correction before being applicable to ions of higher valency. S. K. Tweedy.

Influence of a foreign substance on the osmotic pressure. F. A. H. Schreinemakers (Z. physikal. Chem., 1927, 130, 120—124).—A mathematical paper in which it is shown that addition of a foreign substance to a solution may either raise or lower the osmotic pressure of the solution; in the latter case the osmotic pressure falls to a minimum and then rises on the addition of further quantities of the substance. If the foreign substance is added to both sides of a semi-permeable membrane with pure water on one side and a binary solution on the other, then the change $d\pi$ in the osmotic pressure depends on the concentration of the substance on both sides of the membrane. S. J. Gregg.

Variations in the b. p. of hydrochloric acid on adding a third substance. A. Mazzucchelli and A. Fatta (Gazzetta, 1927, 57, 584—592).—The method of Schleiermacher (A., 1891, 873) for the determination of b. p. is adapted to the use of 10 c.c. of liquid by fitting a bulb with a U-tube containing a mercury pellet and with another tube through which liquid can be removed to balance the increase due to expansion. In this way the b. p. of hydrochloric acid solutions of 14—22% concentration, containing in addition 5% of ammonium chloride, 4% of lithium chloride, 7% of zinc chloride, or about 10% of sulphuric acid, are determined. The curve obtained by plotting b. p. against the acid concentration is shifted by the addition of the third substance towards lower concentrations of acid, the maximum remaining at about 110°. With zinc chloride the b. p. falls off less slowly than that of the pure solution when the maximum has been reached; this is attributed to the formation of complexes with hydrochloric acid. Somewhat similar results are obtained with ammonium chloride. Sulphuric acid has an opposite effect, and combination with water is suggested as the cause. E. W. Wignall.

Vapour pressure of the binary system methyl alcohol–water. G. Bredig and R. Bayer (Z. physikal. Chem., 1927, 130, 1—14).—The method used was the dynamic method of Zawidski (A., 1901, ii, 6), the mixture being heated electrically in a special flask, the pressure in which was varied until the temperature of the liquid was at the required point. The distillate was collected in a special vessel and analysed pyknometrically. For pressures above atmospheric, a special flask heated in an autoclave was employed. Over the range 40—240°, the total pressure P can be represented by the equation $\log P=J-k/T^n$, where J is a universal constant for all mixtures, and k and n are specific constants for each mixture. With rising temperature, the alcohol content in the vapour over a given mixture decreases, as expected from theoretical considerations.

For mixtures which contain 20—100 mols.-% of methyl alcohol, the isotherms are well represented by Lewis and Murphee's equation (A., 1924, ii, 145). For low alcohol content and low temperatures, the isotherms are straight and follow the equation $x(1-y)/(1-x)y=P_2/P_1'$, where P_2 is the vapour pressure of pure water and P_1' the intercept of the isotherm on the 100% alcohol ordinate. The equation $x(1-y)/(1-x)y=P_2e^{-\lambda/RT.(1-2x)}/P_1$, where P_1 is the vapour pressure of pure methyl alcohol and λ the differential heat of mixing of the components (*i.e.*, the difference between the respective heats of mixing one component with excess of the other), holds over the same range. S. J. GREGG.

Ionic equilibria. II. Equilibrium between calcium fluoride and dilute hydrochloric acid. M. AUMÉRAS (J. Chim. physique, 1927, 24, 548—571; cf. this vol., 312).—The solubility of calcium fluoride in hydrochloric acid has been studied in presence of excess of hydrofluoric acid or of calcium chloride between 15° and 65°, by a method involving the titration of the liquid containing a suspension of the fluoride with hydrochloric acid until the solution became clear. The saturated solutions were, in general, 0·01N with respect to calcium. The solubility of calcium fluoride in water was found by a chemical method to be 0·018 g. per litre at 25°, a result in close agreement with the conductivity measurements of Kohlrausch (A., 1905, ii, 152). On the assumption that the calcium chloride and hydrochloric acid are completely dissociated, the solubility of calcium fluoride has been calculated from mass law considerations and found to be in agreement with experiment. The results show that hydrofluoric acid dissociates in a simple manner in dilute solution, and that the dissociation constant is $16{\cdot}7\times10^{-5}$ at 25°. G. A. ELLIOTT.

The ionic equilibrium $Al(OH)_3+6F'\rightleftharpoons AlF_6+3OH'$. A. TRAVERS (Compt. rend., 1927, 185, 893—895).—This reaction is of importance in the detection of alumina in the presence of silver, and in the determination of fluorine or silica in the presence of alumina. The addition of increasing quantities of potassium fluoride to amorphous aluminium hydroxide, or to potassium aluminate, results in the production of hydroxyl ions. Determinations of the p_H value show, however, that they increase with an increase in the concentration of fluoride, to an extent which corresponds with the above equilibrium. Cryolite is stable over a wide range of p_H values, but potassium fluosilicate and fluotitanate are completely decomposed above p_H 6. J. GRANT.

Salting out, and the ionic electric field. P. DEBYE (Z. physikal. Chem., 1927, 130, 56—64).—Mathematical. An attempt is made to predict quantitatively the salting-out effect from the dielectric properties of the substances in question. If the dielectric constant e of a mixture follows the equation $e=e_1c_1+e_2c_2$, where e_1 and e_2 are the respective dielectric constants of the constituents and c_1 and c_2 their concentrations, and if e_1-e_2 is positive, then it is shown mathematically that the concentration of each constituent in the neighbourhood of the ions of an added electrolyte is reduced. The formula given is in fair agreement with the experimental results for the salting-out effect of potassium chloride on a water–ether solution. S. J. GREGG.

Equilibrium diagram of the copper–zinc system. D. JITSUKA (Z. Metallk., 1927, 19, 396—403).—A reinvestigation of the system zinc–copper by thermal and micrographic methods has confirmed the shape and position of the liquidus and peritectic lines found by Roberts-Austen and others, except in the case of the lines between 0 and 12% Cu and between 20 and 30% Cu. In the first case the horizontal occurs at 425° with 2—12% Cu and is a peritectic and not a eutectic line, since it is above the m. p. of zinc; in the second case the horizontal is at 695°. Considerable variations from earlier work in the solubility limits in the solid state have been noticed; thus the β phase undergoes a transformation between 475° and 450° and a second transformation below 450°, the maximum temperature of each change being found in the alloy with 53% Cu. The solid solution δ is unstable below 550°, being decomposed into the $\varepsilon+\gamma$ eutectoid, and the $\varepsilon+\delta$ and $\delta+\gamma$ fields extend from 590° to 560° only. The limit of solubility of ε in η is 1·5% Cu and of η in ε 14% Cu; the former line is vertical and the latter vertical to 390°, then bending towards the temperature axis. The lines bounding the $\varepsilon+\gamma$ field from the ε and from the γ fields bend towards one another above 500°. The remaining boundary lines correspond fairly closely with those generally accepted. Zinc is appreciably volatile at 470°, so that the outer surfaces of ingots always contain a smaller proportion of zinc than does the interior. A. R. POWELL.

Saturation limit of α-copper–tin solid solution. M. HANSEN (Z. Metallk., 1927, 19, 407—409).—As the result of prolonged annealing tests followed by slow cooling and by quenching and tempering, the limit of solid solubility of tin in copper (α solution) is established at 14% Sn at the ordinary temperature, 16% Sn at 518°, and 13·4% Sn at 800°. The curve joining the first and second points is convex to the temperature axis, whilst that joining the second and third is a straight line. A. R. POWELL.

Systematic doctrine of affinity. XLIII. System cuprous chloride–cupric chloride. W. BILTZ and W. FISCHER (Z. anorg. Chem., 1927, 166, 290—298; cf. this vol., 831).—Extension of Sandonnini's f.-p. measurements with the above system (A., 1912, ii, 918) to higher cupric chloride concentrations has given an extrapolated value of 630±10° for the m. p. of this salt, but has failed to yield any indication of compound formation. This result is confirmed by the fact that cuprous chloride does not affect the dissociation tension of cupric chloride. Density measurements have been made with molten mixtures of the two chlorides, and also with the same mixtures after solidification. Anhydrous cupric chloride has d_4^{25} 3·387. The molecular volumes of both salts are equal to the sum of the zero volumes of the constituents. R. Cuthill.

Vapour pressure of the ternary system methyl alcohol–methyl acetate–ethyl acetate. G. Bredig and R. Bayer (Z. physikal. Chem., 1927, **130**, 15—28).—The apparatus is as previously used (this vol., 1140) and the vapour-pressure measurements were made first on the three binary systems methyl alcohol–methyl acetate, methyl alcohol–ethyl acetate, and methyl acetate–ethyl acetate. Both phases were analysed using the Haber–Lowe interferometer with the aid of standard reference mixtures. The first and second systems give vapour-pressure maxima lying for 40° at 33·7 and 67·4 mol.-% of methyl alcohol, respectively. The third system has an almost rectilinear isotherm, and all three follow the Herzfeld equation, the total pressure P being given by $P=P_1xe^{-\lambda(1-x)^2/RT^2}+P_2(1-x)e^{-\lambda x^2/RT^2}$, where P_1 and P_2 are the vapour pressures of the constituents, and x and $(1-x)$ their respective molecular fractions, λ being the differential heat of mixing.

In the analysis of the ternary mixtures, the free methyl alcohol was determined by esterifying the mixture at 100° with a mixture of pyridine and acetic anhydride, and titrating the excess of acetic acid with alkali. The combined weight of the two esters in the mixture was then found by difference, and their individual proportions by hydrolysing with alcoholic potassium hydroxide and titrating with sulphuric acid. The shape of the "vapour-pressure surface" was fixed by measurements on a mixture of methyl alcohol (18%) and methyl acetate (82%), the quantity of ethyl acetate being varied.

An examination of the results obtained shows that at 760 mm., and using a perfect column, the ternary mixture could be separated into pure methyl acetate and an azeotropic mixture of the other two; the latter can only be completely separated by altering the pressure or distilling in steam. S. J. Gregg.

Ternary systems. VI. Sodium carbonate, sodium hydrogen carbonate, water. A. E. Hill and L. R. Bacon (J. Amer. Chem. Soc., 1927, **49**, 2487—2495).—The isotherms for the above system have been determined at 24·87°, 30°, and 50°. The double salt "Trona," $NaHCO_3,Na_2CO_3,2H_2O$, is stable at all three temperatures and separates out from solutions which contain only 0·16% of sodium hydrogen carbonate at 31·98°; this limiting percentage increases with rise of temperature. Quintuple points are indicated at −3·32°, 21·26°, 31·98°, and 35·17°. The binary eutectic temperatures for sodium carbonate and for sodium hydrogen carbonate with water are −2·05° and −2·33°, respectively, the solid phases in the latter case being sodium hydrogen carbonate and ice. S. K. Tweedy.

System $Fe(NO_3)_3$–KNO_3–H_2O at 25°. G. Malquori (Atti R. Accad. Lincei, 1927, [vi], 5, 1000—1003).—Neither compounds nor mixed crystals are formed at 25°. The solid phases in equilibrium with solution are KNO_3 and $Fe(NO_3)_3,9H_2O$. R. W. Lunt.

Systems $MnSO_4$–K_2SO_4–H_2O and $MnSO_4$–$(NH_4)_2SO_4$–H_2O at 0°, and $CuSO_4$–Na_2SO_4–H_2O at 0°, 25°, and 37·5°. R. M. Caven and W. Johnston (J.C.S., 1927, 2358—2365).—The double salt $MnSO_4,K_2SO_4,4H_2O$ separates at 0°, although this type of salt is usually hexahydrated. The isotherms at 0° and 25° are similar. The double salt $MnSO_4,(NH_4)_2SO_4,6H_2O$ separates at 0° and 25°, and the double salt curve is more extended than that for the corresponding potassium salt. This is due to the greater solubility of the ammonium sulphate, and to the larger amount of water of crystallisation in the double salt. Copper and sodium sulphates would appear to give no double salts at 0°, but the salt $CuSO_4,Na_2SO_4,2H_2O$ separates over a fairly wide range at 25°, and diminishes in solubility with rise of temperature. At 25° the addition of copper sulphate causes an increase in the solubility of sodium sulphate, but at 37·5° the reverse is true. F. S. Hawkins.

Equilibria in systems in which phases are separated by a semi-permeable membrane. XXI. Influence of pressure on osmotic systems and on the osmotic pressure. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 521—531).—Theoretical. A continuation of previous work (this vol., 1031). M. S. Burr.

Equilibria in systems in which phases are separated by a semi-permeable membrane. XXII. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 610—618).—The influence of temperature on osmotic equilibria is discussed. J. S. Carter.

Complete heterogeneous equilibrium. R. Wegscheider (Z. physikal. Chem., 1927, **130**, 44—48).—The term "complete heterogeneous equilibrium" proposed by Roozeboom (Rec. trav. chim., 1887, **5**, 266) is superfluous, since it is synonymous with "univariant system." It should not be used to designate those systems in which volume alterations can take place without disturbance of the equilibrium. S. J. Gregg.

Experimental basis of the third law of thermodynamics. N. de Kolosovski (Z. Physik, 1927, **44**, 756).—Attention is directed to a fundamental error in the author's recent contribution (this vol., 732) in which it was erroneously stated that if $\lim._{T=0}\, dp/dT=0$, then $\lim._{T=0}\, d\log p/dT=0$. Equations 3, 6, and 9 are then invalid, and the analysis is applicable to a degenerated gas only. R. W. Lunt.

Properties at the absolute zero of temperature of the quantities associated with the reversible mixing of substances. R. D. Kleeman (J. Physical Chem., 1927, **31**, 1559—1565).—Mathematical. These properties are deduced from the results already established (this vol., 520, 936). L. S. Theobald.

Standardisation of Richards' thermochemical data. W. Swientoslawski and J. Bobinska (J. Amer. Chem. Soc., 1927, **49**, 2476—2478).—The thermochemical data of Richards and his co-workers are recalculated, taking the heat of combustion of 1 g. of benzoic acid (weighed in air) equal to 6324 g.-cal.$_{15}$. as standard. Data published subsequent to 1915, expressed in g.-cal.$_{18}$., are multiplied by 0·99942; data published previous to 1915, expressed in kilojoules, are multiplied by 238·27. A complete table is appended. S. K. TWEEDY.

Correction of Swarts' thermochemical data. W. SWIENTOSLAWSKI and J. BOBIŃSKA (J. Chim. physique, 1927, **24**, 545—547).—The adoption of more accurate values for the standard substances —benzoic acid and sucrose—indicates that Swarts' values for the heats of combustion of fluorine compounds should be multiplied by 0·9981.

G. A. ELLIOTT.

Systematic doctrine of affinity. XLIV. Heats of formation [and volumes] of ammines, and pyridine compounds. W. BILTZ, K. A. KLATTE, and E. RAHLFS (Z. anorg. Chem., 1927, **166**, 339—350; cf. this vol., 1141).—The apparent heat of neutralisation of ammonia with excess of hydrochloric acid in aqueous solution increases with increase in the acid concentration and with decrease in the ammonia concentration; this is quantitatively accounted for by the fact that the observed heat effect includes the heat of dilution of the acid by the water in which the ammonia is dissolved. In the action of acids on metal ammines, however, the dilution effect is negligible, so that in deriving from the heat of this reaction the heat of formation of the ammine from ammonia and the metallic salt by means of the values for the heat of dissolution of the salt in the acid, and of ammonia in water, and the heat of neutralisation of ammonia, the value taken for the last quantity should be that for very dilute acid. The previous determinations of the heat of formation of the beryllium halides (A., 1925, ii, 1183), in which the apparent heat of neutralisation of the acid of the particular concentration employed was used, therefore require correction, and the new values then agree satisfactorily with the values derived from fresh determinations of the heat of dissolution of the ammines in more dilute acid. Similar corrections have been applied to the heats of formation of the ammines of mercuric chloride (A., 1925, ii, 1184) and of cupric chloride and bromide (*ibid.*, 1182). The volumes of the ammonia molecules in the beryllium halide ammines are approximately equal to the zero volume, but increase with increase in volume of the halogen. In the compounds of pyridine with calcium iodide, the volume of the pyridine molecule is minimal in the compound $CaI_2,2C_5H_5N$.

R. CUTHILL.

Heats of dissolution of acetonitrile in some organic solvents. P. G. POPOV (Ukraine Chem. J., 1926, **2**, 387—390).—The heat of dissolution of acetonitrile in methyl alcohol, ethyl alcohol, ethyl acetate, acetic acid, and benzene is negative, but not in acetone. The heat charge is greater for ethyl alcohol than for methyl alcohol.

A. RATCLIFFE.

Heats of dissolution and dilution of salts from extreme dilutions to saturation. III. Potassium fluoride and potassium fluoride dihydrate. E. LANGE and A. EICHLER (Z. physikal. Chem., 1927, **129**, 258—300; cf. this vol., 1029).—The integral heats of dissolution of anhydrous potassium fluoride at 25° have been obtained from measurements of the intermediate heats of dissolution at lower concentrations and of heats of dilution at higher concentrations up to saturation, and the intermediate heats of dissolution at high concentrations have been calculated from the results. From the data obtained, the values for the first, last, and entire heats of dissolution are found to be 4244, 185, and 2415 g.-cal./mol., respectively. The heat of hydration to form the dihydrate being found to be 5912 g.-cal./mol., the corresponding heats of dissolution for the hydrate are −1668, −4367, and −3497 g.-cal./mol., respectively. R. CUTHILL.

Heats of dissolution and dilution of alkali salts in solutions of electrolytes with the same cation. J. HOLLUTA and H. WERNER (Z. physikal. Chem., 1927, **129**, 262—284).—The integral heats of dissolution of potassium chloride in water and in aqueous solutions of potassium nitrate, and of potassium nitrate in water and in aqueous solutions of potassium chloride, have been measured, and by subtraction from them of the corresponding heats of dilution, the entire heats of dissolution have been obtained. With both salts, the integral heats of dissolution are negative, and decrease numerically with increase in the concentration of the salt solution serving as solvent. The relative lowering of the entire heat of dissolution produced by 1 g.-mol. of the electrolyte with a common ion is an approximately linear function of its concentration in the solution employed as solvent. This variation is probably to be ascribed to ionic hydration, and this assumption leads, in fact, to hydration values which approximate to those obtained by the usual methods. R. CUTHILL.

Stabilisation of chemical compounds by means of exothermic additive reactions. W. BILTZ (Z. anorg. Chem., 1927, **166**, 275—283).—The stability of a chemical compound may be increased by adding to it a substance with which it combines with evolution of heat. In many instances, this involves the conversion of an endothermic into an exothermic compound by such processes as double salt formation, hydration, combination with ammonia, and polymerisation. Exothermic substances, however, may frequently be treated in a similar manner, *e.g.*, silver chloride loses its photochemical sensitivity when combined with ammonia to form the compound $AgCl,3NH_3$. R. CUTHILL.

Conductivity of acids of medium strength in methyl alcohol, and their catalytic action. II. H. GOLDSCHMIDT, E. MARUM, and L. THOMAS (Z. physikal. Chem., 1927, **129**, 223—240; cf. A., 1925, ii, 976).—The conductivity of 2 : 4 : 6-trinitro-*m*-cresol and its salts and of certain picrates in methyl alcohol and mixtures of methyl alcohol and water has been measured, and the affinity constants and degree of dissociation have been calculated by application of Bjerrum's theory. In pure aqueous solution, the dissociation of the trinitrocresol is considerable, being much greater than in alcoholic solution. The influence of trinitrocresol and of trichloroacetic acid on the rate of esterification of acetic and phenylacetic acids in methyl alcohol containing varying amounts of water or free from water has also been examined. In the esterification of a particular acid, the quotient of the velocity coefficient by the hydrogen-ion concentration of the catalyst is somewhat different for different catalysts, so that it appears probable that the rate of esterification is influenced by another factor in addition to the concentration of hydrogen ions and alcoholated hydrogen ions. For water concentrations up to $0{\cdot}5N$, the retarding effect of water can be represented satisfactorily by the formula previously proposed (*loc. cit.*). At higher concentrations, however, the velocity coefficient diminishes rather more rapidly than the formula indicates, but for acetic and phenylacetic acids the ratio of the observed to the calculated values is practically the same for all the catalysts. The effect of water on the affinity constant of trinitrocresol in methyl alcohol is much the same as it is with trichloroacetic and trichlorobutyric acid, so that it is primarily the hydrogen ion which is affected, in accordance with the equation (alcohol, H)$^{\cdot}$+water=(water, H)$^{\cdot}$+alcohol.

R. CUTHILL.

Conductivity of salt solutions containing agar. E. IWASE (Kolloid-Z., 1927, **43**, 70—72).—The salt solutions studied were copper sulphate, potassium sulphate, chloride, thiocyanate, and iodide, and sodium chloride. Measurements of the conductivity of these solutions were made at a series of dilutions, and were repeated after 0·5% of agar had been added. A further measurement of conductivity was made when the agar had set to a gel. In every case the conductivity of the salt solution+gel was greater than that of the salt solution+sol. It is concluded that in the process of gelation a decrease in specific volume of the particles of colloid occurs, causing desorption of some of the electrolyte, which thus produces the rise in conductivity. E. S. HEDGES.

Potential of a proposed standard form of copper and the activity of copper sulphate. R. F. NIELSEN and D. J. BROWN (J. Amer. Chem. Soc., 1927, **49**, 2423—2426).—Copper electrodes prepared by Lewis and Lacey's method (A., 1914, ii, 521) do not give reproducible potentials in copper sulphate solution. Two-phase copper amalgam is recommended as an alternative standard electrode material. From the *E.M.F.* at 25° of the cells Cu amalgam|$CuSO_4$,xMsoln.|Hg_2SO_4|Hg, where x=0·05, 0·1, 0·2, 0·4, and 0·5, and combinations of these cells, the activity coefficients of copper sulphate over a limited concentration range were calculated, Lewis and Randall's value at $0{\cdot}05M$ being assumed. The results are about 3% lower than those of Lewis and Randall. The standard potential of the amalgam is calculated to be —0·3502 volt, independent of the composition within fairly wide limits.

S. K. TWEEDY.

***E.M.F.* of the cell with transference and theory of interdiffusion of electrolytes.** P. B. TAYLOR (J. Physical Chem., 1927, **31**, 1478—1500).—Mathematical. A general expression for the *E.M.F.* of a cell with transference has been derived in terms of the corresponding cells without transference, and the integral obtained has been extended to include the effect of solvent transfer. The differential equation for the diffusion of electrolytes is derived rigorously, and is shown to depend only on molecular free energies and to be independent of ionic free energies. It is shown from this that the *E.M.F.* of the cell with transference is independent of these latter, which may be chosen for each solution so as to satisfy any single arbitrary function, not a function of molecular free energies, without thermodynamic error. A method of general application is given for finding the distribution of concentrations through a junction. Henderson's formula (A., 1908, ii, 655) for liquid junction *P.D.* is extended to provide for variable mobilities and activity coefficients, and the theory when applied to the tenth-normal HCl|KCl cell, gives better results. The bearing of these results on the determination of $p_{\rm H}$ is discussed.

L. S. THEOBALD.

Electronic theory of the voltaic cell. O. M. CORBINO (Phil. Mag., 1927, [vii], **4**, 436—446).—With the acceptance of the existence of the Volta effect between two metals a basis is provided for the explanation of the working of a voltaic cell. It is shown that this basis of explanation does not lead to any of the substantial contradictions inherent in the usual theories. A. E. MITCHELL.

Cells with identical, unchangeable electrodes. V. KARPEN (Compt. rend., 1927, **185**, 766—768).—Pairs of electrodes of various types of carbon, or of metals unattacked by alkalis, give an *E.M.F.* when one is completely immersed in a saturated solution of sodium hydroxide and the other only partly. The former electrode is negative, and the *E.M.F.*, which is of the order of 0·7 volt for platinum, decreases with diminution in the concentration of the solution, with agitation of the electrodes, or when the positive electrode is gradually submerged. It also depends on the nature of the electrode surface, but once established, is independent of the time or of the passage of a current. The rapid and almost complete polarisation obtained (99%) supports the evidence for the absence of any reaction in the cell, the *E.M.F.* of which is unexplained. J. GRANT.

***P.D.* in the double layer at the surface of a simple electrolyte and of pure water.** A. BÜHL (Ann. Physik, 1927, [iv], **84**, 211—244).—The drop method for measuring the *P.D.* at a liquid surface has been refined and applied to the chlorides of potassium, sodium, and lithium and hydrochloric acid. For the alkali chlorides a maximum *P.D.* is observed at a concentration which is smaller as the mobility of the cation is greater. The diffusion potential is discussed in terms of Nernst's theory. The comparison of experimental data with calculated diffusion potentials leads, especially for hydrochloric acid, to a proof of complete dissociation in dilute solutions of strong electrolytes; it shows also that it is the ionic mobility only which changes with concentration. On the assumption that two separate effects enter into the observations it is calculated that the *P.D.* in the double layer of pure water is 5·5±0·5 millivolts. R. A. MORTON.

Thermodynamic evaluation of the contact potentials of two fused salts. R. LORENZ (Z.

physikal. Chem., 1927, 130, 39—43).—It has been found experimentally that the *E.M.F.* of a Daniell cell containing fused salts is equal to the difference between the *E.M.F.* of the two corresponding “salt formation cells,” *i.e.*, cells in which *E.M.F.* is developed by the formation of a salt from its elements, *e.g.*, $Pb|PbCl_2|Cl_2$. Using this fact, it is readily shown that the contact potential π between two fused salts is given by $\pi=[n\mu(Cl')_2-n\mu(Cl')_1]/rF'$, where n is the valency of the metals, $\mu(Cl')_2$ and $\mu(Cl')_1$ the thermodynamic potentials of the chlorine ions in the respective fused salts, and r and F have their usual meanings. S. J. Gregg.

Theory of overpotential. J. Heyrovský (Rec. trav. chim., 1927, 46, 582—585).—At cathodes where a large overvoltage is present, molecular hydrogen is formed according to the equation $H'+H^{\cdot}=H_2$, at a rate v_{H_2} given by $v_{H_2}=k[H']c=K'i$, where c is the concentration of the hydrogen ions, i is the current, and k and K' are constants. Sand's objections to this theory (this vol., 735) are refuted, and his modification of it involving the formation of ions $H_3^{\cdots}$ and $H_4^{\cdots}$ is criticised as leading to a constancy of overpotential with changing acidity at the mercury dropping electrode, which is contrary to experiment. S. J. Gregg.

Overvoltage in alkaline solution. P. Herasymenko (Rec. trav. chim., 1927, 46, 586—587).—The author re-affirms his criticism of Sand and Weeks' investigation of the overvoltage at the antimony cathode in alkaline solution (A., 1924, ii, 152). The experiments of Sand, Grant, and Lloyd (this vol., 317) confirm the validity of the Nernst formula for the relationship between cathode potential and the sodium-ion concentration. S. J. Gregg.

Influence of perchlorate ion on the anodic overvoltage during the electrolysis of sulphuric acid. A. Mazzucchelli and B. Romani (Gazzetta, 1927, 57, 574—583).—Experimental evidence is adduced for the view previously suggested (A., 1925, ii, 214) that the increased yield of persulphuric acid obtained by the electrolysis of sulphuric acid in presence of small quantities of perchloric acid is due to an increase in the anode overvoltage. Curves are given showing the variation of the anode potential with the time, before and after the addition of perchloric acid. After the perchloric acid is added there is a small increase of short duration in the anode potential. The addition of small quantities of chloride ion during the electrolysis of sulphuric acid, or of fluoride ion during the electrolysis of potassium hydrogen sulphate, has a similar result. The fluoride ion, however, has an abnormal effect on the electrolysis of pure sulphuric acid and causes a decrease in the anode potential in spite of the fact that the yield of persulphuric acid increases. O. J. Walker.

Anodic behaviour and passivity of nickel. W. J. Müller (Monatsh., 1927, 48, 559—570).—The development of passivity in nickel immersed in *N*-sulphuric acid is dependent on time, and the behaviour resembles that of iron and chromium in that a close connexion exists between the time effect and the current strength. The initial polarisation observed with nickel is a property of active bivalent nickel which passes into solution, and is due to anodic overvoltage. A voltage–current density diagram is shown which gives a fairly complete account of the behaviour of a nickel anode. The first stage is a superficial passivity bound up with the dissolution of bivalent nickel; later something approaching true passivity sets in at higher current densities and oxygen is liberated, but the passive state is not yet permanent and the nickel is alternately active and passive. At considerably higher current densities the alternation disappears and the nickel remains passive so long as the circuit is complete. The initial polarisation recorded by many observers corresponds with an anodic overvoltage and has nothing to do with passivity as such. R. A. Morton.

Electrometallurgy of magnesium and its alloys. Pressure of the binary system lithium fluoride–magnesium fluoride. V. P. Hyniski and P. F. Antipine (Trav. inst. russe chim. appl., 1925, No. 84, 3—8).—Lithium fluoride has m. p. 837°; magnesium fluoride has m. p. 1225°. The eutectic, containing 53% of the latter, has m. p. 718°. Between 0 and 53% of magnesium fluoride there is no eutectic. At 90% of magnesium fluoride there is another eutectic point. All the mixtures contract on cooling. The fused eutectic readily dissolves 10% of magnesium oxide. Crystallisation in the system magnesium fluoride–lithium fluoride–magnesium oxide commences at 753°; hence the magnesium oxide may be electrolysed in the eutectic at 753°. Chemical Abstracts.

Electrolytic decomposition of glass. P. Selényi (Ann. Physik, 1927, [iv], 84, 111—118).—If glass is electrolysed with an anode consisting of an ionised gas, sodium is set free at the cathode and oxygen at the anode. A feebly-conducting layer of silicic acid is formed on the anode side. W. E. Downey.

Valve effect shown by a silicon anode, and its mechanism. R. Audubert (Compt. rend., 1927, 185, 768—770).—It is shown theoretically and by experiments with cells of the type $Si|10\%\ H_2SO_4|Pb$ that the anodic valve effect (unilateral conductivity) is associated with an oxidation–reduction process. The silicon, which may be in the pure or alloyed state, is probably oxidised by anodic polarisation, and forms a non-conducting layer of silica which is subsequently reduced by cathodic hydrogen. The effect is an exponential function of temperature and occurs in acid or alkaline solutions. J. Grant.

Theories of the velocity of chemical reactions. F. Giordani (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 32, 70—82).—A theoretical discussion of various formulæ and their application to some reactions. M. Carlton.

Inflammability of hydrogen. V. Influence of tin tetramethyl and lead tetramethyl on the limits of inflammability of hydrogen–air mixtures. Y. Tanaka and Y. Nagai (Proc. Imp. Acad. Tokyo, 1927, 3, 434—436).—Tin tetramethyl and lead tetramethyl lower the upper limit of hydrogen concentration necessary to cause inflammability. The presence of 0·125% of tin tetramethyl in the mixtures lowers the upper limit from 71 to 54 mol.-% of hydrogen, whilst 0·5% of lead tetramethyl is necessary to produce the same effect.

W. E. Downey.

[Flame and combustion.] G. I. Finch (Nature, 1927, 120, 694).—The combustion of the mixture $2CO+O_2$ in a steady high-tension direct-current discharge has been studied. In the cathode zone the rate of combustion is independent of the gas pressure or of the presence of moisture, but is proportional to the current. In the positive column region, however, the presence of moisture greatly accelerates the combustion. The results support Bone's view that moisture is not essential to the combustion of carbon monoxide, and that if it accelerates the process its effect is electrical, and not chemical.

A. A. Eldridge.

Gaseous combustion at high pressures. VIII. Explosion of methane with up to its own volume of oxygen at initial pressures up to 150 atm. D. T. A. Townend (Proc. Roy. Soc., 1927, **A**, **116**, 637—663; cf. Bone, Phil. Trans., 1915, **A**, **215**, 275).—A systematic study has been made of the pressure–time curves obtained by exploding (1) a number of methane–oxygen mixtures of compositions between $5CH_4+2O_2$ and CH_4+O_2, at initial pressures of 6—150 atm., and (2) mixtures corresponding with $CH_4+O_2+3{\cdot}76R$ (where $R=N_2$, A, or He), at initial pressures of 10, 50, 100, and 150 atm. The results obtained confirm previous observations (*loc. cit.*) and are in agreement with the "hydroxylation" theory of hydrocarbon combustion. It is found that, although at atmospheric pressure it is not possible to explode methane with less than two thirds of its own volume of oxygen, at high pressures mixtures containing much lower proportions of oxygen can readily be exploded. With mixtures containing more than 60% of methane, the effect of increasing the initial pressure is not only to decrease the violence of the explosion, but also to diminish, and in some cases to suppress altogether, carbon deposition. The results are attributed to the influence of pressure in suppressing the thermal decomposition of methane. Contrary to its behaviour in carbon monoxide–air explosions at high initial pressures (cf. A., 1924, ii, 398; 1925, ii, 800), nitrogen is not activated in explosions of $CH_4+O_2+3{\cdot}76N_2$ mixtures, but appears to behave normally as a diluent only. Reasons for this are discussed. The general influence of helium, as compared with argon, as a diluent in the explosion of $CH_4+O_2+3{\cdot}76R$ mixtures, is to hasten the rate of pressure development and to increase the subsequent rate of cooling, effects attributable to the greater mobility of the helium molecule. The corrected P_m/P_i ratios are in most cases, however, about 6 or 9% higher with the argon-diluted mixtures than with the corresponding helium-diluted mixtures.

L. L. Bircumshaw.

Explosions in gaseous mixtures of acetylene, of hydrogen, and of pentane. A. Egerton and S. F. Gates (Proc. Roy. Soc., 1927, **A**, **116**, 516—529; cf. this vol., 318).—An arrangement is described by means of which the velocities of detonation waves can be measured to an accuracy of at least 0·5%, and the velocities and positions of detonation for various mixtures of acetylene, of hydrogen, and of pentane with oxygen, nitrogen, or argon are recorded for initial pressures up to 6 atm. The results are in fair agreement with those obtained previously (*loc. cit.*), and the fact that detonation occurs earlier as the pressure increases up to a certain limiting value is confirmed. Experiments in which the steel explosion tube (diameter 1·5 cm.) was virtually shortened by the insertion of steel rods showed that the length of the tube does not appreciably affect the position of detonation, except in the case of the weak mixture ($1C_2H_2:2{\cdot}5O_2:6N_2$), where shortening the tube caused later detonation. The photographic record of flame travel in a short bomb of large diameter (10·7 cm.) gave some evidence of autoignition during the progress of combustion of a vibratory nature in certain acetylene mixtures. The addition of the "anti-knock" compound, lead tetraethyl, has a definitely delaying effect on the rate of travel of flame in the case of slow-burning pentane mixtures, but with acetylene mixtures the only effect is an accelerating one. The results obtained in general support the inference that "knock" is associated with a vibratory type of combustion, not necessarily involving autoignition, and is not due to the establishment of a detonation wave (cf. Morgan, this vol., 630).

L. L. Bircumshaw.

Gaseous combustion in electric discharges. II. Ignition of electrolytic gas by direct current discharges. G. I. Finch and L. G. Cowen (Proc. Roy. Soc., 1927, **A**, **116**, 529—539; cf. A., 1926, 690).—An investigation of the conditions of ignition of electrolytic gas by direct-current discharges has been carried out, precautions being taken to eliminate as far as possible any conditions favourable to ignition, particularly heat and catalytic combustion at the electrodes, other than those due to ionisation of the gas. Four series of measurements were made with water-cooled platinum electrodes, three over concentrated sulphuric acid with gap-widths of 3·8, 7·5, and 15 mm. respectively, and one with a gap-width of 15 mm., but without sulphuric acid, gas-pressure and igniting current readings being taken simultaneously at the moment of explosion. Ignition occurs without lag immediately on attainment of the igniting current, and it was found that the igniting current varies with the pressure over a considerable range in a hyperbolic manner. The reasons for the observed deviations of the pressure–igniting current curves from rectangular hyperbolæ at the two extremes of the curve are discussed, and it is concluded that the value of the igniting current is raised by either an excess or a deficiency of water vapour in the gas in the ignition zone. The fact that a reduction in the gap-width results in an increase in the igniting current is ascribed to the widening of, and thus the lowering of the ionic concentration in, the two bright positive glows, in the brighter of which ignition probably originates. In an attempt to obtain direct experimental evidence for this, it was found that the velocity of flame propagation was at least ten times as great along the path of the discharge as elsewhere in the explosion vessel. The view is held that, under the given experimental conditions, ignition is determined solely by the attainment in some portion of the gas traversed by the discharge of a certain definite concentration of suitable ions or electrically charged particles, in the building up of which water vapour materially assists, and that flame propagation is also essentially an electrical phenomenon. L. L. Bircumshaw.

Combustion of mixtures of hydrogen with air or oxygen in a eudiometer. T. Terada, K. Yumoto, and U. Nakaya (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 81—128).—In mixtures containing a small percentage of hydrogen, when there is a small volume of gas in the eudiometer tube combustion is complete, but with an increasing volume of gas the proportion burnt becomes less and less until a critical volume is reached, when combustion is again complete. If the original volume of gas be increased still more, combustion may be complete or almost complete until a second critical volume, almost double the first, is reached. After this volume is passed, combustion is only partial, the proportion of gas burnt being the same as before the first critical volume. If the oscillation of water in the bend of the eudiometer tube be stopped, combustion is complete until a certain volume, dependent as before on the size of the tube and the position of the electrodes, is reached, when the gas is only partly burnt. This suggests that the effects at the critical volumes are caused by cooling due to adiabatic expansion of the gas caused by movement of the water column, but photographic studies show that the effect is complicated by the cooling and contraction caused by condensation of moisture in the burnt gas. Experiments with mixtures containing a high percentage of hydrogen showed no evidence of the two critical volumes, but with large volumes of gas the flame was extinguished before combustion was complete. By igniting mixtures in a spherical bulb, it was shown that the volume of gas burnt at each spark was greatly dependent on the construction of the electrodes, and by means of a mathematical analysis, it was shown that the mass velocity of combustion could be assumed to be constant. F. S. Hawkins.

Ignition of carbon monoxide and oxygen. A. K. Brewer (Proc. Nat. Acad. Sci., 1927, 13, 689—694).—In a moist explosive mixture of carbon monoxide and oxygen, the ignition at any one pressure is determined by the energy of the spark and not by the voltage, whilst the ignition points at various pressures are related not as the energy ($\frac{1}{2}CV^2$) but as the voltage (V). Using a constant pressure of 14 cm. of explosive gas dried by means of sulphuric acid, and adding known amounts of water vapour, the ignition voltage varied from 262 with a partial pressure of 0·4 mm. of water vapour to 46 at a partial pressure of 20 mm. Addition of argon, nitrogen, carbon dioxide, chloroform, alcohol, *iso*propyl nitrite, and ether showed that these impurities are inert in the explosion except in that they absorb energy, thus increasing the ignition voltage. Other impurities act similarly to water, *i.e.*, they greatly reduce the ignition voltage and cause the oxidation to go to completion. Sufficient oxygen must be added to burn the impurity. It would appear from the partial pressure–voltage curves that the catalytic properties of hydrogen, alcohol, and ether are derived from their ability to furnish water on oxidation, and furthermore, the freshly-formed water must be more potent than ordinary water. It is shown that the two explosive gases in an explosive mixture may ignite more readily than will either gas separately under similar conditions. R. A. Morton.

Ignition of gases by hot wires. W. C. F. Shepherd and R. V. Wheeler.—See B., 1927, 803.

Active nitrogen. R. Rudy (Physical Rev., 1926, [ii], 27, 110).—Argon has little influence on the rate of decay of the afterglow. The decay follows a bimolecular law for the first 100 sec.; the temperature coefficient of the reaction, between 20° and 130°, is much smaller than that of ordinary chemical reactions. Band spectra excited by active nitrogen show vibrational energy as if at high temperature, whereas the rotational energy indicates low temperature. A. A. Eldridge.

Behaviour of oxygen in the reaction between carbon monoxide and chlorine. H. J. Schumacher (Z. physikal. Chem., 1927, 129, 241—261).—The rate of formation of carbonyl chloride at 160° in the dark from carbon monoxide and chlorine is not affected by the presence of free oxygen, the reaction velocity being given by the equation $d[COCl_2]/dt=k[Cl_2]^{3/2}[CO]$. In light, at the ordinary temperature, however, carbon dioxide is formed to the almost complete exclusion of the formation of carbonyl chloride until the oxygen pressure becomes very small, so that in these circumstances the main reaction is the photosensitised formation of carbon dioxide. The rate of this reaction is represented by the equation $d[CO_2]/dt=k'[Cl_2]^{0\cdot71}[CO]^{1/2}$, the velocity coefficient, k', being independent of the carbon dioxide concentration, but tending to fall somewhat with the oxygen concentration for concentrations below 100 mm., and having a temperature coefficient of 0·95 per 10°. With light of wave-length greater than 405 μμ, there are formed about 1000 molecules of carbon dioxide per quantum in a mixture of carbon monoxide, oxygen, and chlorine in which the concentration of each is 0·5 atm., and 3000 molecules of carbonyl chloride in a mixture of carbon monoxide and chlorine, each under 0·5 atm. pressure.
R. Cuthill.

Chemical kinetics of the reaction between tetrathionate and cyanide. F. Ishikawa (Z. physikal. Chem., 1927, 130, 73—81).—Kurtenacker and Fritsch (A., 1921, ii, 502) give the equations $S_4O_6'' + CN' + H_2O = CNS' + SO_4'' + S_2O_3'' + 2H$ (1); $2H^{\cdot} + 2CN' = 2HCN$ (neutral solution) (2*a*); $2H^{\cdot} + 2OH' = 2H_2O$ (alkaline solution) (2*b*). In neutral solution, since reaction (2*a*) is instantaneous, the velocity of the whole reaction depends on (1), so that $dx/dt=k_2(a-3x)(b-x)$, where a is the initial concentration of potassium cyanide, b the initial concentration of the tetrathionate, and x the number of reacted molecules of tetrathionate per litre during the time t. Hence $k_2=(1/t)[1/(a-3b)]\log_e[b(a-3x)/a(b-x)]$. This has been confirmed by measurements at 0°, the reacting liquids being placed in the respective limbs of a Y-tube and mixed at a given moment; after a definite interval, 20 c.c. were withdrawn and treated with dilute sulphuric acid and the whole was titrated with 0·1N-iodine solution to determine the thiosulphate. The value of k_2 varies linearly with the initial concentration of either reactant, for a constant concentration (*i.e.*, large excess) of the other.

For alkaline solution, from (1) and (2*b*), $k_2=(1/t)[1/(a-b)]\log_e[b(a-x)/a(b-x)]$. From the experiments, k_2 is found to increase somewhat with increasing concentration of sodium hydroxide; with ammonia, k_2 diminishes with increasing time, probably because ammonia is too weakly basic to neutralise the whole of the hydrogen ions, which therefore react with the cyanide so that excess of the latter is removed. S. J. Gregg.

Conditions controlling oxidation of organic molecules. I. C. Fromageot (J. Chim. phys., 1927, 24, 513—544).—The progress of oxidation of acetic and propionic acids and the corresponding α-amino-acids, of acetaldehyde and propaldehyde and the corresponding alcohols, and of pyruvic acid, by ceric, thallic, and ferric salts and by chloric and permanganic acids has been followed potentiometrically. Pyruvic acid is alone oxidised by the metallic salts, whilst the remaining acids and amino-acids are not sensibly oxidised by any of the agents used. In general there is no relation between the oxidising potentials of the reagents and the occurrence of oxidation, nevertheless for oxidisers of similar type the speed of oxidation increases with the oxidising potential. For chloric and permanganic acids, the order of increasing ease of oxidation is : acid, alcohol, aldehyde. Pyruvic acid, however, is oxidised at approximately the same rate as the alcohols by chloric acid, and almost instantaneously by permanganic acid. G. A. Elliott.

Kinetics of the hydrolysis of vinyl acetate. A. Skrabal and A. Lahorka (Monatsh., 1927, 48, 459—473).—The velocity of hydrolysis of freshly-prepared, unimolecular vinyl acetate by acids and alkalis in aqueous solution and by water has been studied at 25°. The velocity coefficient for hydrolysis with hydrochloric acid with the minute as the unit of time is 0·00813, whilst for hydrolysis with sodium borate the value is 620. A much lower value is obtained with sodium carbonate as hydrolysing agent, but this is due to the greater degree of polymerisation in the presence of the stronger alkali, the polymerised ester being hydrolysed much more slowly. The value of the coefficient for hydrolysis by water alone varies from 6·8 to $9·7\times10^{-6}$ according to the concentration of sodium acetate present. In all three cases hydrolysis is much more rapid than in the case of the related saturated ester, ethyl acetate. The remainder of the paper is mathematical and it is shown that by integration of the differential equation of the secondary effect of hydrolysis in a buffer solution the values of all three hydrolysis coefficients may be determined. J. W. Baker.

Velocity of hydrolysis of stearolactone with alcoholic alkali. A. Kailan and A. Blumenstock (Monatsh., 1927, 48, 529—536).—The velocity of hydrolysis of stearolactone in concentration of 0·025 mol./litre with sodium hydroxide and ethoxide in queous and absolute alcohol at 25° has been measured. Only in alcohol containing relatively large concentrations of water does the bimolecular coefficient approach constancy, and in alcohol containing only 0·036 mol. of water/litre it diminishes rapidly, due to the diminishing concentration of water as the reaction proceeds. In the latter case the termolecular coefficient, based on consideration of the participation of water in the reaction, approaches constancy. As the water content of the alcohol is increased from 0·025 to 1·6 mol./litre this termolecular coefficient decreases to one third of its original value. This may be due either to the alteration in the composition of the medium or to the variation in the relative proportions of sodium hydroxide and ethoxide present as hydrolysing agents. As the water content of the alcohol is increased from 1·6 to 4·8 mol./litre the value of the termolecular coefficient remains approximately constant. J. W. Baker.

Velocity of hydrolysis of acetonals. A. Skrabal and F. Bilger (Z. physikal. Chem., 1927, 130, 29—32).—The reaction, which is catalysed by hydrogen ions, was arrested at the required moment by addition of excess of sodium hydroxide; iodine solution was then added in excess in order to determine the acetonal remaining undecomposed. The excess of iodine was determined by neutralising and titrating with thiosulphate, sodium acetate being added to reduce the hydrogen-ion concentration and thus prevent the reaction of the iodine with the acetone produced by the original hydrolysis. The following velocity coefficients were obtained for unit hydrogen-ion concentration (25°) : dimethylacetonal $3·7\times10^4$, diethylacetonal $1·35\times10^5$. S. J. Gregg.

Dynamic isomerism of the reducing sugars. T. M. Lowry (Z. physikal. Chem., 1927, 130, 125—145).—The unimolecular form of the mutarotation curves for dextrose has been established for dextrose in water, in pure methyl alcohol, and in aqueous methyl alcohol, and also for tetramethylglucose in aqueous pyridine. This unimolecular form is quite compatible with the occurrence of a chemical change subsequently to mutarotation, provided this is not accompanied by any marked change of rotatory power. The existence of such a change is proved by a comparison of the mutarotation curves, which depend only on the rotatory powers of the isomerides, with the solubility curves, which depend on the concentrations of the products in solution; with aqueous methyl alcohol as solvent, the half-change period calculated from the mutarotation is almost twice as long as that calculated from solubility measurements, showing that concentration changes last much longer than changes of rotatory power. These views are further confirmed by the observations of Riiber and Minsaas (A., 1926, 1228). S. J. Gregg.

Velocity of esterification of nitrobenzoic acids in glycerol. A. Kailan and L. Lipkin (Monatsh., 1927, 48, 501—519).—The velocity of esterification of *o*-, *m*-, and *p*-nitrobenzoic acids in anhydrous and moist glycerol with hydrogen chloride as a catalyst at 25° has been measured. In all cases esterification is almost complete, but the velocity of esterification of the *ortho*-acid is so slow that chlorohydrin formation must be taken into account, the value of the latter coefficient being 5×10^{-5} in anhydrous glycerol. In all cases the unimolecular coefficient is proportional to the concentration of the hydrogen chloride (c). The relationship of the velocity coefficient to the concentration of the water (ω) in each case is expressed by intrapolation formulæ. The velocities in glycerol are compared with those of the same acids in alcohol (Kailan, A., 1907, ii, 242). The effect of water is less in glycerol than in alcohol. When $\omega=0{\cdot}03$ and 0·065 mol./litre the esterification coefficients in alcohol are respectively 41—66% and 24—42% greater than in glycerol. When $\omega=0{\cdot}733$ mol./litre and $c=0{\cdot}66$ mol./litre the velocities in the two media are approximately equal; when $c=0{\cdot}33$ and 0·166 the coefficients in alcohol are, respectively, only 65—68% and 46—48% of the values in glycerol, whilst when $\omega=1{\cdot}346$ and $c=0{\cdot}66$, 0·33, and 0·166, the coefficients in alcohol are respectively only 63—75%, 36—44%, and 25—31% of the values in glycerol. The differences in the velocity of esterification of benzoic acids and the three nitrobenzoic acids are smaller in glycerol than in alcohol. Thus for $\omega=0{\cdot}065$ and $c=0{\cdot}166$ the ratios of the velocity coefficients of benzoic acid and *o*-, *m*-, and *p*-nitrobenzoic acids in glycerol are 1 : 0·068 : 0·63 : 0·80, whilst in alcohol the ratios are 1 : 0·054 : 0·57 : 0·70, the values for *o*-, *m*-, and *p*-nitrobenzoic acids themselves in the two media being, respectively, 1 : 9·27 : 11·7 and 1 : 10·7 : 13·0.

J. W. BAKER.

Chemical kinetics in mixed solvents. Velocity of formation of quaternary ammonium salts in mixtures of nitrobenzene and benzene. G. E. MUCHIN and H. M. MOISEEV (Ukraine Chem. J., 1926, 2, 430—436).—Velocity coefficients for the interaction of pyridine and allyl bromide in various mixtures of benzene and nitrobenzene were determined at 25°, 45°, and 55°. The observed coefficients were lower in every case than those calculated from the additive rule, and this difference diminished with rise of temperature when the mixture contained a large proportion of nitrobenzene. The curve showing the change of velocity coefficient as a function of the percentage composition of the solvent was continuous; no definite compounds were formed.

A. RATCLIFFE.

Chemical kinetics in mixed solvents. Velocity of formation of quaternary ammonium salts in mixtures of nitrobenzene and heptane. G. E. MUCHIN, L. E. KARLSON, and L. M. STEIN (Ukraine Chem. J., 1926, 2, 437—442).—Velocity coefficients for the interaction of allyl bromide with pyridine in a mixture of heptane and nitrobenzene were determined; the results were analogous to those obtained when benzene was used instead of heptane (cf. preceding abstract). A. RATCLIFFE.

Chemical kinetics in mixed solvents. Influence of various substances on the velocity of formation of quaternary ammonium salts. R. B. GINSBURG and G. E. MUCHIN (Ukraine Chem. J., 1926, 2, 443—458).—The effect of compounds containing electro-negative groups, *e.g.*, phenol and nitronaphthalene, and indifferent solids, *e.g.*, paraffin and naphthalene, on the velocity of reaction of (1) triethylamine and allyl bromide and (2) pyridine and allyl bromide in solution in benzene was studied. The addition of the solids gave results from which no conclusions could be reached. The presence of the electro-negative groups caused an increase in the velocity of reaction. Fairly conclusive evidence has been obtained showing that this influence is due to the formation of an unstable intermediate compound between the base and the substance containing the electro-negative group. A. RATCLIFFE.

Rate of absorption of hydrogen chloride in aqueous solutions. H. O. ASKEW.—See B., 1927, 813.

Velocity of oxidation of white phosphorus with gaseous oxygen. J. ZAWIDSKI (Z. physikal. Chem., 1927, 130, 109—119).—Russell's results (J.C.S., 1903, 83, 1263) do not fit any one mathematical equation. If x is the original concentration of oxygen and a that at time t, and $(1-x')$ its relative concentration (measured by the ratio, pressure at time t : pressure at zero time), then $dx'/dt=(k_1/a^2)/(1-x')$ for oxygen dried over sulphuric acid. For oxygen dried over calcium chloride, $dx'/dt=(k_2/a^{5/2})[1/(1-x')(x')^{\frac{1}{2}}]$; for very moist oxygen, $dx'/dt=(k_3/a^3)[1/x'(1-x')]$; and for a mixture of dry oxygen and nitrogen, $dx'/dt=k_4\sqrt{a}\sqrt{x'}(1-x')$. Slightly moist oxygen (over 44% sulphuric acid) follows the same equation as the very dry gas.

These apparently contradictory results are difficult to explain. S. J. GREGG.

Passivity of iron mirrors. II. H. FREUNDLICH, G. PATSCHEKE, and H. ZOCHER (Z. physikal. Chem., 1927, 130, 289—307; cf. this vol., 1037).—The passivity of iron mirrors, deposited on glass surfaces by thermal decomposition of the pentacarbonyl, has been examined by following the changes in the condition of polarisation of the light reflected from the mirrors before and after exposure to air. The measurements show that the phase-changes and loss of amplitude corresponding with greater or lesser transparency of the iron mirrors were smaller to a greater or lesser degree than with massive iron when the mirrors were brought into contact with air, a diminution in the relative phase change and a small increase in the amplitude ratio resulted. This change occurred instantaneously at the first contact of the surface of the iron with air. Withdrawal of the air to a pressure of 10^{-4} mm. did not lessen the effect. These optical changes can be explained by the formation of a surface layer on the iron, and the close correspondence between the optical and chemical behaviour of iron mirrors before and after the first admittance of air permits the conclusion that these surface layers are layers of oxide which cause passivity.

L. S. THEOBALD.

Corrosion of iron in tap water. J. TILLMANS, P. HIRSCH, and W. WEINTRAUD.—See B., 1927, 843.

How do acids attack metals? R. GAUS, A. ELIÇABE, and Z. WEINSTOCK (Contrib. estudio Ciencias fys. mat. [La Plata], 1925, 3, 341—357).—Silver–gold alloys containing less than 50 at.-% of silver are not attacked by nitric acid. The rate of dissolution of silver in alloys containing more than 50 at.-% Ag is a function of the time and of the concentration of the silver; the gold remains as a reddish-brown sponge. On exposure of silver to hydrogen sulphide, the rate of thickening of the sulphide film rapidly decreases, then rises to a constant value. CHEMICAL ABSTRACTS.

Saponification of fats in heterogeneous systems. L. LASCARAY (Anal. Fís. Quím., 1927, 25, 332—348).—The saponification of fats in heterogeneous systems occurs exclusively at the boundary of the phases, and its course agrees with the theories of Harkins and Langmuir on the vectorial structure of such boundaries. The velocity of saponification depends on the degree of dispersion of the system, and is inversely related to the percentage of unsaturated glycerides present. G. W. ROBINSON.

Theory of dislocation from the point of view of thermodynamics and kinetics. J. BÖESEKEN (Rec. trav. chim., 1927, 46, 574—581; cf. A., 1926, 806).—Two factors influence the catalysis of reactions, viz., energy and entropy. A molecule decomposes when it has acquired the necessary amount of energy, which may be received in various ways, *e.g.*, by external radiation, collision, etc. However, the mean internal energy of the molecule is insufficient to account for the observed velocity of reactions, since the number of molecules uniting is a negligibly small fraction of the number of collisions. Only those few molecules which have reached the "intermediate" or "critical" state by receiving the necessary amount of energy by a series of collisions, will react. The effect of the two factors is given by the equation of Scheffer and Marcelin, viz., $\log_e k=(\varepsilon_i-\varepsilon)/RT+(\eta_i-\eta_{c-1})/R+C$, where k is the velocity coefficient, $\varepsilon_i-\varepsilon$ the difference between the mean energy of the reacting molecules and that of the total mass of molecules present, $\eta_i-\eta_{c-1}$ the difference of the corresponding entropies, that of the total mass being calculated for unit concentration. In some cases the addition of a catalyst does not change the first term (energy of activation), so that the acceleration of the reaction must be attributed to change in the second (entropy of activation); this type of catalysis is called "ideal" or "physical" catalysis, whilst "chemical" catalysis is characterised by the formation of intermediate compounds, and change also in the energy of activation. If the intermediate compounds dissociate on heating, then a chemically catalytic reaction will become physically catalytic at high temperature. Thus the catalysis of the reaction $C+2H_2 \rightleftharpoons CH_4$ by nickel is chemical below and physical above 420°, since the intermediate compound nickel carbide is unstable above that temperature.

The processes operative in physical catalysis are termed dislocations. S. J. GREGG.

Neutral salt effect in decomposition of hydrogen peroxide catalysed by iron ions. A. VON KISS and (FRL.) E. LEDERER (Z. physikal. Chem., 1927, 129, 186—198; cf. this vol., 837).—The effect of salts on the catalysed decomposition of hydrogen peroxide in acid solutions in presence of iron ions has been studied. With certain sulphates, the unimolecular velocity coefficient, k, calculated from the equation $dx/dt=k(a-x)$, where a is the initial concentration of peroxide and x the amount decomposed in time t, first falls with increasing salt concentration, then passes through a minimum, and ultimately rises again. Potassium and magnesium chlorides, however, at concentrations up to about N cause k to increase, but at higher concentrations they have the reverse effect, so that a change in the mechanism of the reaction must occur. Potassium nitrate has an accelerating effect at concentrations up to $3N$, but the effect is greatest at about $0{\cdot}5N$. The results as a whole are in harmony with the activity theory, but there are anomalies at lower concentrations. No satisfactory reaction mechanism can be formulated, but the experimental results show that it is not an ionic reaction. R. CUTHILL.

Acid and salt effects in catalysed reactions. XI. Hydrolysis of ethyl acetate and the catalytic catenary. H. M. DAWSON and W. LOWSON (J.C.S., 1927, 2444—2451).—The rate of hydrolysis of ethyl acetate in presence of mixtures of acetic acid and sodium acetate has been investigated. With increasing salt content in $0{\cdot}1N$-acid solutions the velocity falls to a minimum and then rises as a linear function of the salt concentration. The observed effects are connected with the catalytic activities of the undissociated acetic acid molecules, and of the acetate, hydrogen, and hydroxyl ions. The connexion between the hydrogen-ion concentration and the reaction velocity can be represented by a catenary curve. C. W. GIBBY.

Dynamic isomerism. XXIV. Neutral-salt action in mutarotation. T. M. LOWRY and G. F. SMITH (J.C.S., 1927, 2539—2554).—The catalytic catenaries for the mutarotation of dextrose in acid, neutral, and alkaline solutions have been determined at 20°. The reaction is catalysed by acids and bases; definite catalytic activity was detected in the undissociated molecules of a strong or weak acid, the anion of a weak acid, and the cation of a weak nitrogenous base. The velocity is unaffected by neutral salts.

The following catalytic coefficients are recorded: [HCl] about 0·5, $[NH_4^{\cdot}]$ 0·0012, [AcOH] 0·0065, [OAc′] 0·069. C. W. GIBBY.

Dynamic isomerism. XXV. Mechanism of catalysis by acids and bases. T. M. LOWRY (J.C.S., 1927, 2554—2565).—An electrolytic theory of catalysis is propounded, involving the formation of a "zwitterion" by addition and subtraction of a proton by an amphoteric molecule. Isomeric change depends on a process similar to electrolysis of the prototropic compound, and involves a displacement of valency electrons between two alternative points of attachment of the proton. This theory is applied to catalysis in isomeric change by water, acids, and bases. C. W. GIBBY.

Catalytic synthesis of water vapour in contact with metallic gold. A. F. BENTON and J. C. ELGIN (J. Amer. Chem. Soc., 1927, 49, 2426—2438; cf. this vol., 118).—The kinetics of the above catalytic synthesis were investigated at 130—150°. When oxygen is in excess the "steady state" is reached after a much longer time than when hydrogen is in excess. Neither gas is continuously taken up and retained by the catalyst in any considerable amount. The rate of the reaction varies as the square of the hydrogen pressure and the first power of the oxygen pressure, and is approximately inversely proportional to the pressure of water vapour. The average temperature coefficient is about 1·9 per 10°. The maximum yield occurs when the mixed gases are approximately in stoicheiometric ratio. Preliminary heating of the catalyst in oxygen produces a large but transitory increase in yield. Gold adsorbs considerable amounts of oxygen at a very slow rate which decreases with falling temperature and is practically independent of the gas pressure (cf. Sieverts, A., 1907, ii, 741). The quantity adsorbed increases with rising temperature but is almost independent of the gas pressure. No simple mechanism will account for the observed facts; possibly two gaseous hydrogen molecules must strike an adsorbed oxygen molecule simultaneously for combination to occur. Bone and Wheeler's observations that the kinetics of the reaction is independent of the oxygen pressure and that previous oxygen treatment of the catalyst decreased the reaction rate are probably to be attributed to the higher temperature at which they worked (cf. A., 1906, ii, 434). S. K. TWEEDY.

Catalytic combination of ethylene and hydrogen in presence of metallic copper. IV. Kinetics at 100° and 200°, temperature coefficient between 0° and 220°, and summary. R. N. PEASE and C. A. HARRIS (J. Amer. Chem. Soc., 1927, **49**, 2503—2510; cf. A., 1923, ii, 842, 862).—The above reaction is very nearly bimolecular at 220°; at 100°, between the ethylene partial pressures of $\frac{1}{8}$ and $\frac{3}{4}$ atm., it is unimolecular with respect to hydrogen and of zero order with respect to ethylene. The reaction rates were measured between 0° and 220°; the conventional expression for the heat of activation applies from 0° to 100°, but above this the temperature coefficient and therefore the heat of activation decreases. The kinetics of the reaction, which is interpreted on the basis of Langmuir's adsorption theory, is similar to that of the hydrogen–oxygen reaction in the presence of platinum (Langmuir, A., 1922, ii, 629). S. K. TWEEDY.

Methyl alcohol catalysts. I. H. S. TAYLOR and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1927, **49**, 2468—2476).—The methyl alcohol catalysts, zinc oxide and especially zinc oxide mixed with chromium oxide, adsorb very large quantities of hydrogen, carbon monoxide, and carbon dioxide at 0° and 100° after the surface has been cleaned of adsorbed water vapour and carbon dioxide by evacuation at 400°. The adsorption isotherms are of the type shown by metal catalysts in hydrogenation reactions, but the adsorption capacities are many times those of most metal catalysts under the same conditions. Strong adsorption of hydrogen and of carbon monoxide occurs at very low pressures; relative saturation is attained, since there is little increase in adsorption with a many-fold increase in pressure. This implies a considerable active surface per unit weight of material and a corresponding comparative insensitiveness to poisons. The heat of adsorption exceeds the heat of liquefaction of the gases and reaches values characteristic of heats of adsorption on metal catalysts. S. K. TWEEDY.

Catalytic oxidation of hydantoins. O. BAUDISCH and D. DAVIDSON (J. Biol. Chem., 1927, **75**, 247—249).—The rapidity of oxidation of 5-substituted hydantoins in presence of trisodium amminoferropentacyanide varies with the nature of the substituent in the order phenyl > (hydrogen) > methyl > benzyl; oxidation does not take place with 5 : 5-dimethylhydantoin, and therefore probably depends on enolisation on the 4-carbon atom; hydantoic acid, glycylglycine, and glycine anhydride were not oxidised under these conditions. C. R. HARINGTON.

Chain reaction theory of negative catalysis. II. Two stages in auto-oxidation reactions. III. General characteristics of auto-oxidation reactions. H. L. J. BÄCKSTRÖM (Med. K. Vetenskapsakad. Nobelinst., 1927, **6**, Nos. 15 and 16; cf. this vol., 737).—II. Iodometric and acidimetric titrations of benzaldehyde, after shaking with oxygen while exposed to light from a mercury lamp, indicate that perbenzoic acid is at first formed. Previous work has shown that the quantum efficiency of this reaction is high (about 10,000) and that, like the corresponding thermal reaction, it shows strong negative catalysis. The perbenzoic acid subsequently reacts with benzaldehyde, forming benzoic acid. This secondary thermal reaction is pseudo-unimolecular, although the half-life period varied between 30 and 8 min. without apparent cause. It is accelerated by light, but the quantum efficiency of the photochemical reaction is certainly less than 0·5% of that for the primary reaction. The secondary reaction shows little or no negative catalysis. The total reaction, which was studied by measurement of the volumes of oxygen absorbed by the benzaldehyde, shows pronounced auto-catalysis in the absence of light; in presence of light the quantum efficiency decreases during the progress of the reaction. These phenomena indicate that the secondary reaction, although probably less effective than the primary reaction in this respect, causes the activation of benzaldehyde molecules which may then react with oxygen or with perbenzoic acid and so establish reaction chains. This activation probably occurs in both the thermal and the photochemical reaction. The absorption of oxygen by sodium sulphite solutions is considerably accelerated by the addition of potassium persulphate or hydrogen peroxide. This acceleration is attributed to the activation of sulphite molecules during the very rapid pseudo-unimolecular reaction (half-life period, 0·53 min.) between the peroxide and the sulphite.

III. A review of auto-oxidation reactions, including those previously studied by the author, and a discussion of the mechanisms of chemi-luminescence, photo-sensitisation, negative catalysis (inhibition), and certain side-reactions, which are in many cases associated with auto-oxidations, from the point of view of the Christiansen theory of chain reactions. The photochemical and thermal reactions are considered to be identical, except when, as in the case of benzaldehyde, a relatively stable intermediate peroxide is formed. It is concluded that the thermal reaction produces sufficient energy for the excitation of additional molecules, and that it may be followed by a photochemical reaction, or side-reaction, produced by radiation from these excited molecules. The theory also leads to a new explanation of the maximum oxidation pressure of phosphorus which connects it with the formation of ozone. Experiments are described which show that the reactions previously studied (*loc. cit.*) may be photo-sensitised with respect to ultra-violet light, but the results were negative in the case of visible light; the photo-sensitisation is attributed to the formation of activated molecules during the photochemical oxidation of the sensitiser. The decomposition of ozone is also considered in terms of reaction chains of the Christiansen type. G. A. Elliott.

Inhibition of auto-oxidation of benzaldehyde. M. Brunner (Helv. Chim. Acta, 1927, **10**, 707—728; cf. Reiff, this vol., 57).—Reaction between benzaldehyde and gaseous oxygen occurs at the surfaces of the reaction vessel and of the added catalyst (pumice, sand, glass, etc.), and apparently only in presence of traces of water. Oxygen and benzaldehyde activated at a polar water layer on the catalytic surface react to form an unstable ring compound which is rapidly transformed into the more stable perbenzoic acid. The latter then reacts with unchanged benzaldehyde to form benzoic acid. Of the reactions involved only the first is influenced by the catalysts mentioned. The present measurements show that, in general, the rate of absorption of oxygen first increases to a well-defined maximum and then rapidly falls to a value which for a considerable time is roughly constant. The maximum rate is roughly proportional to the amount of catalyst and hence to the catalytic surface. Of this surface only an extremely small fraction is active in promoting oxidation. The shape of the velocity–time curve is markedly dependent on the concentration of benzaldehyde and on its purity. Old samples, *i.e.*, containing benzoic acid, and dilute benzene solutions show periods of induction and a flattened maximum at a much lower value. The duration of the period of induction is primarily dependent on the time taken by benzaldehyde and oxygen to reach the active portions of the catalytic surface. Using *cyclo*hexane as solvent in place of benzene the effect is more pronounced, possibly on account of higher viscosity. The existence of a period of induction when the benzaldehyde contains benzoic acid is due to the fact that the acid is adsorbed on the active surface and is only slowly replaced by oxygen. In all cases where benzene solutions were examined small quantities of phenol were detected amongst the products of reaction. Since the phenol thus formed appears to be without inhibitory effect it is apparently formed at a fairly late stage in the scheme of reactions and is prevented from reaching an active centre on the catalytic surface by oxidation or mechanically.

Inhibitors (iodine, diphenylamine, quinol, etc.) exert their effect when present at extremely low concentrations. They are adsorbed on the active centres and thus retard activation. In all cases a period of induction, the duration of which is primarily dependent on the ratio of the concentration of inhibitor to the area of the catalytic surface, is followed by sudden reaction, the rate of absorption of oxygen rising to a sharp maximum, and then rapidly decreasing. The period of induction is much longer when benzaldehyde which has been exposed to the air is used. Rise of temperature shortens the period. With benzene solutions containing iodine, the colour of the latter disappears on commencement of the reaction and further addition has little or no inhibitory effect. The solutions eventually become colourless and contain iodobenzene. During the induction period some of the adsorbed iodine is displaced by oxygen and formation of peroxide ensues. Iodine molecules at the surfaces and in the solution are converted into less strongly adsorbed iodobenzene etc. and further activation of oxygen follows. Florida earth and blood charcoal have an inhibitory effect. With blood charcoal the duration of the induction period increases with increasing quantity of charcoal and the maximum in the absorption–time curve is considerably flattened. It is suggested that positive and negative catalytic centres are present and evidence is put forward which indicates that the negative centres are progressively poisoned before the positive reaction commences. J. S. Carter.

Electrolysis of potassium chloride solutions by alternating currents. A. J. Allmand and H. C. Cocks (J.C.S., 1927, 2626—2639).—The electrolysis of potassium chloride solutions by alternating current has been investigated at the ordinary temperature with regard to the efficiency of hypochlorite production. The current efficiency diminishes with decreasing current density to zero at a critical value of the latter, and rises from zero above a threshold value of the frequency. The maximum hypochlorite concentration obtained was about $0{\cdot}3N$. Measurements of average electrode potentials were made during electrolysis. The different behaviour of polished platinum and graphite electrodes is investigated. G. W. Gibby.

Electrochemistry of beryllium. II. S. Bodforss (Z. physikal. Chem., 1927, **130**, 82—89).—The beryllium salts were prepared in two ways: (1) commercial beryllium chloride solution was precipitated with ammonia, the hydroxide dissolved in acetic acid, evaporated to dryness, and the salt recrystallised from boiling glacial acetic acid. This was decomposed by refluxing with alcohol and 25% sulphuric acid, when the compound $BeSO_4,4H_2O$ crystallised on cooling. (2) The sparingly soluble, easily crystallisable compounds of ammonium beryllium fluoride with the aromatic amines were decomposed by means of concentrated sulphuric acid.

Measurements of the potential of the cell pure $Be|xN$-$BeSO_4,yN$-KCl against the normal calomel electrode were made in an atmosphere of carbon dioxide. The potential of beryllium in such a solution $0{\cdot}1N$ with regard to beryllium sulphate increased in a negative sense on ten-fold dilution, and was greater (in a negative sense) the greater was the original concentration of the potassium chloride. Thus the potential behaves in a " normal " fashion.

Beryllium passes into solution as a univalent ion, readily forming complex ions, which fact explains the effect of halogen salts, *e.g.*, potassium chloride, on the potential. If the solution of beryllium salt with potassium chloride be diluted with water, the complexes are split up, the concentration of beryllium ions is thus increased, and the potential becomes more positive. If the solution be diluted with a solution of potassium chloride, the formation of the complex ions is promoted and the potential becomes more negative.

The univalency of beryllium ions is supported by the fact that a mixture of beryllium and beryllium iodide reduces aromatic ketones in a similar way to a mixture of magnesium and magnesium iodide, where, as Gomberg and Bachmann (this vol., 245) have shown, magnesium subiodide is formed.

Beryllium stands in the electro-chemical series between cadmium and zinc. S. J. GREGG.

Electrochemical reduction of solid electrodes. K. FISCHBECK and E. EINECKE (Z. anorg. Chem., 1927, **167**, 21—39).—The cathodic reduction of a number of insoluble powders at a lead electrode in 2% sulphuric acid solution has been studied. Titanium dioxide and tungsten trioxide are reduced to the ter- and quinque-valent condition, respectively. Red lead and lead monoxide yield crystals of lead, from which hydrogen is evolved as the reduction proceeds. Manganese dioxide, although largely used as a depolariser, is reduced to only a slight extent. Neither the crystalline nor the amorphous forms of aluminium, ferric, or chromic hydroxides are reduced to any appreciable extent. Silver cyanide and the silver halides are reduced at the interface between the salt and the electrolyte to silver, without evolution of hydrogen. Mercuric oxide, sulphide, and thiocyanate are reduced at the cathode to mercury. Chromium carbide, Cr_3C_2, yields, not chromic ions, but chromic acid and carbon dioxide; the nitride CrN yields chromic acid and ammonia.

Artificial cuprous, ferrous, cobaltous, nickelous, manganous, cadmium, zinc, calcium, and magnesium chromites have been prepared by heating the appropriate oxide with chromic oxide at 1000—1500°, and extracting the product with acid. Cathodic polarisation of the ferrous, cuprous, calcium, and magnesium compounds produces chromic acid, whilst the other chromites are unaffected. Natural chrome ironstone behaves in a like manner, but other commercial chromites are reduced on cathodic polarisation, and yield chromic acid on anodic polarisation. A study of the conditions of formation of chromic acid and of the increase in the amount of gas evolved at higher current strengths indicates that the chromite behaves as an intermediate electrode. H. F. GILLBE.

Effect of high voltages on tantalum anodes. E. M. DUNHAM (Science, 1927, **65**, 525).—Tantalum anodes, used with high voltages, sometimes acquire permanent, coloured surface films; similar films have not been reproduced by heating or other means.

A. A. ELDRIDGE.

Electrolysis of copper pyrites. R. SAXON (Chem. News, 1927, **135**, 263—264).—Copper pyrites is regarded as iron thiocuprate (cf. following abstract).

A. A. ELDRIDGE.

Electrolysis of copper pyrites. R. SAXON (Chem. News., 1927, **135**, 310).—The use of lead salts as electrolyte to remove the sulphur from the ore was unsuccessful; thus lead chloride gives a deposit of lead sulphide, lead, and lead chloride, with ferric hydroxide, but no copper. Ammonium, sodium, or potassium chloride gave good results as electrolyte. R. A. PRATT.

Anodes for chromium plating. O. P. WATTS.—See B., 1927, 849.

Electrolytic preparation of *p*-aminophenol. D. CAESER.—See B., 1927, 849.

Detection of organic diacyl peroxides at the anode. F. FICHTER (Z. physikal. Chem., 1927, **130**, 49—55).—Diacyl peroxides are probably formed as intermediate compounds in the Kolbe synthesis of hydrocarbons by electrolysis of solutions of the alkali salts of the corresponding fatty acids. In order to detect their formation, the following conditions must be fulfilled: (1) the electrolyte and anode must be kept very cool to avoid thermal decomposition of the peroxide, (2) hence the salt must be very soluble so that freezing can be prevented by using a very concentrated solution, (3) the molecule of peroxide must be large enough to withstand thermal decomposition.

Hexoic acid fulfils these conditions, and by covering the solution with a layer of light petroleum to remove the peroxide from the anode, the presence of a small quantity of dihexoyl peroxide, $C_5H_{11}\cdot CO_2\cdot CO_2\cdot C_5H_{11}$, and of perhexoic acid ($C_5H_{11}\cdot CO_2\cdot OH$), giving together about a 0·73% yield, were detected in this layer. A theory explaining their formation is given.

S. J. GREGG.

Electrodeposition of rubber. S. E. SHEPPARD.—See B., 1927, 852.

Photosensitisation. I. J. R. BATES and H. S. TAYLOR (J. Amer. Chem. Soc., 1927, **49**, 2438—2456; cf. this vol., 217).—A cooled mercury arc for use in mercury-sensitised and general photochemical reactions is described; by increasing the energy input into a high-pressure hydrogen discharge a continuous ultra-violet spectrum to 1900 Å. can be obtained. The hydrogenation of ethylene does not proceed solely as $C_2H_4+H_2\longrightarrow C_2H_6$, since the reaction does not cease when the original partial pressure of hydrogen is reached. This is due to polymerisation of the ethylene by excited mercury atoms (Berthelot and Gaudechon, A., 1910, i, 349). An initial pressure increase is attributed to the reaction $C_2H_4+Hg'\longrightarrow C_2H_2+H_2+Hg$; this increase is controlled by the diffusion of the products from the zone of excited mercury atoms. Acetylene is polymerised both by excited mercury atoms and by ultra-violet light, but it cannot be hydrogenated by hydrogen activated by excited mercury. The photosensitised reaction between oxygen and excess of hydrogen yields hydrogen peroxide as the sole product if the rate of gas flow is fairly rapid. Many substances (water, ethyl and methyl alcohols, benzene etc.) are decomposed by excited mercury atoms. The decomposition products of ammonia show an excess of hydrogen over the stoicheiometric proportions; a provisional mechanism is suggested. Leifson's absorption band for ammonia at 2260 Å. (A., 1926, 991) is resolved into two bands at 2266—2262 Å. and at 2262—2259 Å.; the next band begins at 2254 Å. Excited mercury atoms decompose formic acid in two ways: $H{\cdot}CO_2H \longrightarrow H_2O+CO$ and $H{\cdot}CO_2H \longrightarrow H_2+CO_2$.

S. K. Tweedy.

Photochemical decomposition of hydrogen peroxide solutions. F. O. Rice and M. L. Kilpatrick (J. Physical Chem., 1927, **31**, 1507—1510).—Solutions of hydrogen peroxide in dust-containing and dust-free water decompose at different rates, the rate of decomposition being approximately proportional to the dust content. Removal of dust reduced the rate to 1/18 of that of the control solutions, indicating that the deviation of this reaction from the law of photochemical equivalence is much less than the results of Henri and Wurmser (A., 1913, ii, 819), and of Kornfeld (A., 1921, ii, 670) appear to show. Previous melting of the apparatus used greatly reduces the number of distillations required to produce dust-free water by the method of Martin (A., 1922, ii, 335).

L. S. Theobald.

Photochemical studies. V. Photochemical decomposition of ammonia by relatively short wave-lengths. L. S. Kassel and W. A. Noyes, jun. (J. Amer. Chem. Soc., 1927, **49**, 2495—2503; cf. Noyes and Kouperman, A., 1923, ii, 527).—The above reaction was investigated between 190 and 160 mμ, the light intensity being measured by streaming oxygen through the reaction vessel and determining the amount of ozone produced by a special colorimetric method. On the assumption that two molecules of ozone are produced from oxygen for each quantum absorbed (cf. Warburg, Sitzungsber. Preuss. Akad. Wiss., 1914, 872; 1915, 230) it is found that 1·4 quanta are absorbed per molecule of ammonia (cf. Kuhn, A., 1926, 920). A satisfactory mechanism cannot be suggested, although the consideration of thermal data indicates which reactions might be possible.

S. K. Tweedy.

Photochemical formation of carbonyl chloride. I. M. Bodenstein [with Bütefisch, Kahle, Süssenguth, E. Heisenberg, and Harteck] (Z. physikal. Chem., 1927, **130**, 422—448; cf. Bodenstein and Plaut, A., 1925, ii, 135).—The photochemical combination of chlorine and carbon monoxide has been investigated from the ordinary temperature up to 300°. At the ordinary temperature, it takes place according to the equation $+d[COCl_2]/dt=kJ_{\mathrm{Abs.}}^{\frac{1}{2}}[Cl_2][CO]^{\frac{1}{2}}$ (1), with a yield of the order of magnitude of 3000 mols. per quantum. The reaction is retarded by the presence of oxygen, which appears to be sensitised by the illuminated chlorine. In this case, the principal reaction is the formation of carbon dioxide. The reaction (1) takes place more slowly with rising temperature, until at about 260° it is completely replaced by another, which follows the law $+d[COCl_2]/dt=kJ_{\mathrm{Abs.}}[Cl_2][CO]$. The presence of oxygen has now no retarding effect, and does not lead to the formation of carbon dioxide. The same reaction probably occurs at the ordinary temperature in place of reaction (1) if the gases are thoroughly dried. A scheme is suggested for reaction (1), by means of which the absolute reaction velocities can be calculated from the data for the dark reaction (*loc. cit.*). The suggested explanation is modified to bring it into line with the work of Franck (A., 1925, ii, 1077) and others on the connexion between light absorption and the dissociation of the chlorine molecule.

L. L. Bircumshaw.

Similarities in the darkening of photographic plates at various exposures. E. F. M. van der Held and B. Baars (Z. Physik, 1927, **45**, 364—368).—From experiments on the relative darkening of photographic plates as a function of the time of exposure it is shown that a constant darkening coefficient is obtained for Ilford rapid chromatic and special rapid plates for exposures in the range 1 : 1000 if "rodinal" (1 : 20) be used as developer.

R. W. Lunt.

Decomposition of silver bromide per quantum of *X*-radiation. J. Eggert and W. Noddack (Z. Physik, 1927, **44**, 155).—The authors indicate minor corrections to their recent paper (this vol., 841) necessitated by the more accurate data of Rump (this vol., 706) on the energy density of *X*-rays produced by a tube working under specified conditions.

R. W. Lunt.

Mechanism of formation of the latent photographic image. A. P. F. Trivelli (Nature, 1927, **120**, 728).—It appears that high-sensitivity photographic materials contain the system silver, silver halide, silver sulphide, in which the silver and silver sulphide are in contact, representing a photo-electric cell of the Becquerel type. In light, the *P.D.* between the electrodes increases, the conductivity of the silver halide increases, and an electric current flows in the system. Electrolysis of the silver halide results, the cations moving towards the cathode, and the anions losing their charge and remaining in the crystal-substance.

A. A. Eldridge.

Decomposition of hydrogen peroxide and the mechanism of latent photographic image intensification. E. P. Wightman and R. F. Quirk (Science, 1927, **66**, 92).—It is considered that when the photographic plate is treated with an acid hydrogen peroxide solution, the trace of bromide formed from the soluble bromide in the plate attacks the silver sulphide of the sensitivity or latent image speck (where it has not all been converted into silver during exposure to light) and thus renders the grain developable.

A. A. Eldridge.

Photo-bromination of *cyclo*hexane. B. J. Wood and E. K. Rideal (J.C.S., 1927, 2466—2477).—The photo-bromination of *cyclo*hexane in the presence of radiation of wave-length 5460 Å. has been investigated at 30°. The thermal and photochemical reactions both conform to the unimolecular law, and the latter has no temperature coefficient between 30° and 40°. The velocity of the photo-reaction is proportional to the light-intensity, independent of the *cyclo*hexane concentration, and reduced by the presence of oxygen. The inhibition by oxygen is independent of the pressure of *cyclo*hexane.

It is concluded that the primary photoactive constituents are excited bromine molecules, and the mechanism of the reaction is discussed (cf. Pusch, A., 1919, ii, 208; Noddack, A., 1921, ii, 568).

C. W. Gibby.

Reaction of sodium chloride if added to a solution of litmus and mercuric chloride. W. O. Moor (J. Amer. Chem. Soc., 1927, 49, 2355—2357).—The addition of 4—5 drops of 2% aqueous mercuric chloride solution causes neutral, violet litmus solution to become reddish; on subsequent addition of 1 c.c. (excess) of saturated (neutral) sodium chloride solution, the mixture turns blue, but regains its original violet colour after a few seconds. The formation of the neutral salt, $HgCl_2,NaCl,H_2O$, fails to explain this reaction, which occurs only when the litmus and mercuric chloride come into contact first. The addition of zinc sulphate to blue litmus solution gives a solution of the same violet colour as neutral tincture of litmus.

S. K. Tweedy.

Decomposition pressure of cupric metaborate. N. Parravano and G. Malquori (Z. physikal. Chem., 1927, **130**, 167—169).—Copper metaborate glass changes colour from blue to yellowish-red at 800—900°; this is attributed to its conversion into cuprous salt, boric anhydride, and oxygen. Copper oxide does not appreciably lose oxygen under these conditions. A curve was obtained showing the logarithm of the oxygen tension as a function of temperature for the metaborate prepared by two processes. The (linear) curve differs from that for copper oxide. It is calculated that the affinity for oxygen at the atmospheric pressure is 9027 g.-cal. for the oxide and 1159 g.-cal. for the metaborate.

A. A. Eldridge.

Triple iodides of rubidium and gold with other metals. E. S. Burkser, S. G. Rublov, and A. M. Scharnovsky (Z. anorg. Chem., 1927, **167**, 87—96).—Triple iodides containing gold, rubidium, and zinc, copper, silver, mercury, or cadmium have been prepared by adding rubidium iodide and the iodide of the third metal to a solution prepared by dissolving gold in aqueous hydriodic acid containing free iodine and ether as a catalyst. Simple formulæ for the complex salts are obtained only on the assumption that both aurous and auric iodides are present in the molecule. The *silver, cuprous, zinc*, and *cadmium* salts have the general formula $4RbI,MI$ (or $M_{0.5}I$),Au_4I_6, and, with the exception of the silver salt, which is black, form non-hygroscopic crystals with a golden lustre. The crystals break up under the action of water, and the dry salts begin to decompose with evolution of iodine vapour at 170—190°. *Zinc, cadmium, mercury*, and *thallium* form a series of bluish crystalline salts, having the formulæ $16RbI,9ZnI_2,4AuI,2AuI_3$; $8RbI,2CdI_2,AuI,3AuI_3$; $9RbI,4HgI_2,2AuI,AuI_3$; $RbTlI_4,RbAuI_4$.

H. F. Gillbe.

Silver subfluoride. A. Hettich (Z. anorg. Chem., 1927, **167**, 67—74).—Electrolysis of concentrated silver fluoride solutions yields at the cathode with high current density pure silver, whereas at low current density pure silver subfluoride is obtained. *X*-Ray investigation of the product shows it to contain neither silver nor silver fluoride. The crystals are decomposed by water into silver and silver fluoride, but are unattacked by concentrated silver fluoride solutions. When heated, silver subfluoride decomposes, even in total absence of water, leaving pure silver; this reaction, therefore, furnishes a basis for the chemical preparation of fluorine. The subfluoride crystals, *d* 8·57, conduct electricity, and in contact with a silver wire act as rectifiers.

H. F. Gillbe.

Silver sulphate–carbon monoxide. W. Manchot and J. König (Ber., 1927, 60, [*B*], 2183—2185; cf. A., 1924, ii, 609).—The absorption of carbon monoxide by silver sulphate dissolved in sulphuric acid increases with increasing sulphur trioxide content of the solution, with fall of temperature and increase of pressure of the gas, approximating to but never exceeding that required for the formation of the compound, Ag_2SO_4,CO.

H. Wren.

Purification of beryllia. E. Chauvenet and E. Duchemin (Compt. rend., 1927, **185**, 716—717).—The powdered beryllium oxide is placed between two perforated plates in a silica tube and heated in a current of carbonyl chloride at 450° for 1—2 hrs. This removes the volatile chlorides of iron and aluminium; treatment of the residue with water dissolves the calcium chloride and any beryllium chloride present, leaving 80—85% of the original sample as pure beryllium oxide.

B. W. Anderson.

Action of calcium, magnesium, and aluminium on beryllia. C. Matignon and (Mlle.) G. Marchal (Compt. rend., 1927, **185**, 812—814; cf. this vol., 430).—Well-calcined beryllia may be reduced to the metal when heated either with an excess of lime (at about 800°), magnesia (at 675—690° for 3—6 hrs.), or with alumina (at 1270° for 4 hrs. in a vacuum). The yields obtained were 30—33%, 14%, and 0·8%, respectively. With lime or magnesia these yields could be increased by promoting more intimate contact between the reagents (*e.g.*, by means of a flux), but with alumina the small quantity of metal corresponds with the formation of an alloy of low beryllium content. The reduced beryllium was separated from the mixture by means of dilute hydrochloric acid, in which well-calcined beryllia is insoluble.

J. Grant.

Chemical equivalence of carbon monoxide and nitric oxide. W. Manchot and W. Pflaum (Ber., 1927, 60, [*B*], 2180—2182).—Mutual replaceability of carbon monoxide and nitric oxide is exhibited when nitric oxide, alone or in the presence of methyl alcohol vapour, is passed over the substance $RhCl_2,RhO,3CO$ whereby the *compound* $RhCl_2,RhO,3NO$ is produced. The reverse change is readily effected at 130—140°. The carbonyl and nitrosyl groups in these compounds appear to be attached to the metallic atom by subsidiary valencies.

H. Wren.

Interaction between sodium metasilicate and salts soluble in water. P. N. Grigorjev (Z. anorg. Chem., 1927, 167, 137—144).—Three groups of water-soluble salts are recognised, in regard to their reactions with sodium metasilicate solution. (1) Solutions of the alkali metals precipitate silica, the action being purely one of coagulation. (2) Calcium, strontium, and barium salts precipitate completely the corresponding metasilicate, but on washing the precipitate hydrolysis takes place. (3) Salts of more weakly basic metals require for neutralisation of their acid reaction more silicate solution than is theoretically necessary. At moderately high temperatures and pressures the reaction is quantitative, *e.g.*, for aluminium sulphate at 215° and 22 atm. pressure the reaction is expressed by the equation: $Al_2(SO_4)_3+3Na_2O,2SiO_2=3Na_2SO_4+Al_2O_3,3(2SiO_2)$. H. F. Gillbe.

Germanium. XXII. Dihalides of germanium. F. M. Brewer and L. M. Dennis (J. Physical Chem., 1927, **31**, 1526—1538).—The continued fractionation of the mixture of germanobromoform and germanium tetrabromide, produced by the action of hydrogen bromide on germanium, yields *germanium dibromide.* Reduction of the mixture by zinc, under special conditions, is more effective and gives a colourless, crystalline solid which decomposes when heated, presumably according to the equation $2GeBr_2=Ge+GeBr_4$. The dibromide is insoluble in hydrocarbons, but is soluble in alcohol and acetone: it is hydrolysed by water to yellow, hydrated germanous hydroxide. Bromine is absorbed, but not vigorously, forming the tetrabromide. *Germanobromoform* (m. p. −24° approx.) results from the action of hydrogen bromide on this product. Germanium di-iodide (cf. Dennis and Hance, A., 1923, ii, 172) is prepared by the action of concentrated hydriodic acid on an excess of a mixture of hydrated mono- and di-oxides of germanium below 40°. The yellow solid obtained is crystallographically similar to lead iodide; it is insoluble in hydrocarbons, slightly soluble in chloroform and in carbon tetrachloride, and it can be recrystallised from hydriodic acid. Solutions in dilute acids and in water possess reducing properties. Exposure to air results in slow hydrolysis to the dioxide, and on heating in air, oxidation to the dioxide and tetraiodide occurs rapidly at 210°; in a vacuum, germanium and germanium tetraiodide are formed. Attempts to prepare the dichloride by the reduction of the tetrachloride with various metals and amalgams, and by the removal of hydrogen chloride from germanochloroform, failed. L. S. Theobald.

Combinations of zirconium oxychloride with the alkali chlorides. E. Chauvenet and E. Duchemin (Compt. rend., 1927, **185**, 774—776).—Determinations of the heats of mixture of equimolecular solutions (A., 1920, ii, 757) indicate the existence in solution of the compounds $7ZrOCl_2,5NH_4Cl$, $ZrOCl_2,RbCl$, and $8ZrOCl_2,5CsCl$. The corresponding compounds of lithium, sodium, and potassium do not exist, and the *cæsium* compound only could be isolated. A solution of the mixed salts, evaporated slowly, yielded large crystals containing 64 mols. of water, of which 53 were lost at 80° and the remainder at 100°. J. Grant.

Reaction of active nitrogen. P. Jolibois and H. Lefebvre (Compt. rend., 1927, **185**, 853—855).—The decomposition by a powerful electric discharge of carbon monoxide into carbon dioxide and carbon at low pressures (about 4—5 mm. of mercury) is increased seven-fold by the addition of a large excess of pure nitrogen. This phenomenon, Rayleigh's experiments with nitrogen dioxide, and the formation of ammonia in the electric arc may be explained by the catalytic properties of nitrogen passing from the active to the normal state. J. Grant.

Preparation of hypophosphoric acid. M. Speter (Rec. trav. chim., 1927, **46**, 588—589).—When 5 g. of red phosphorus are warmed with 1 litre of 10% filtered bleaching-powder solution, only 1·8 g. of phosphorus remains unoxidised. On filtering and nearly neutralising the solution with solid sodium carbonate crystals, calcium hypophosphate is precipitated, and is dried at the pump. It is dissolved in the least possible quantity of dilute sulphuric acid, and on keeping, calcium sulphate is precipitated, leaving a solution of the hypophosphoric acid in sulphuric acid. This solution, which can be used directly for the thorium test, remains stable for years. The residual phosphorus appears to contain a new allotropic modification. S. J. Gregg.

Tetraphosphorus di-iodide triselenide. J. Mai (Ber., 1927, **60**, [*B*], 2222—2223).—*Tetraphosphorus di-iodide triselenide*, $P_4I_2Se_3$, m. p. 154—155° when rapidly heated, is prepared by the addition of iodine to a solution of phosphorus selenide in carbon disulphide. The isolation of *phosphorus sulphide selenide* is mentioned. H. Wren.

Formation of complexes by the arsenate anion. A. Rosenheim and S. Thon (Z. anorg. Chem., 1927, **167**, 1—20).—Isotherms at 0° of the system $Na_2O-As_2O_5-H_2O$ do not indicate the existence of complex arsenate anions. In acid and neutral solutions there exist the compounds $As_2O_5,4H_2O$, NaH_2AsO_4,H_2O, and $Na_2HAsO_4,12H_2O$. The solubility curve of disodium hydrogen arsenate has been determined between 0° and 34°; the transition of the dodecahydrate to the heptahydrate occurs at 22°. In presence of alkali hydroxides arsenic pentoxide forms with the hydroxides of aluminium and tervalent iron and chromium complex metalloarsenates analogous to the ferriphosphates; the structure of these compounds is discussed on the assumption of a co-ordination number of two for the anion $HAsO_4''$. The following *ferriarsenates*, *aluminiarsenates*, and *chromiarsenates* are described: $NaH_2[Fe(AsO_4)_2],H_2O$, $KH_2[Fe(AsO_4)_2]$, $Ba_3H_6[Fe(AsO_4)_3]_2$, $NaH_2[Al(AsO_4)_2],0{\cdot}5H_2O$, $BaH_4[Al(AsO_4)_3],H_2O$, $NaH_2[Cr(AsO_4)_2],H_2O$, $KH_5[Cr(AsO_4)_3]$,7 and $12H_2O$. The corresponding bismuth, cobaltic, thallic, and lanthanum compounds are not formed under the same conditions. *Tripyrogallolarsenates* of *ammonium* ($3H_2O$), *barium* ($12H_2O$), *pyridine*, $(C_5H_5N)H[As(O_2C_6H_3{\cdot}OH)_3],H_2O$, *cinchonine*, and *strychnine* ($2H_2O$) have been prepared, and are analogous to the tripyrocatecholarsenates (*mercury* salt). H. F. Gillbe.

Active form of oxygen. F. R. Bichowsky and L. C. Copeland (Nature, 1927, **120**, 729).—An active form of oxygen, presumably monatomic, is produced when oxygen, saturated with water vapour, is passed through a discharge tube. A. A. Eldridge.

Stable and unstable molybdenum blues. Analytical applications to the determination of phosphoric and arsenic ions. G. Denigès (Compt. rend., 1927, **185**, 777—779).—True molybdenum blue ($MoO_2,4MoO_3$) is stable towards heat and dilution, and is precipitated by ether. Other types may be stable but ether-soluble (this vol., 433) or unstable and ether-insoluble, and of unknown structure. Various methods of preparation of each type are described. The true molybdenum blue may be used as follows for the rapid determination of phosphate and arsenate ions. The reagent, which is stable for a week, is a solution of sulphomolybdic acid (a 10% solution of ammonium molybdate with an equal volume of concentrated sulphuric acid) diluted fourfold, and reduced for 1 hr. by means of copper turnings. Five c.c. of the solution under investigation are boiled with 0·2 c.c. of reagent for 5 sec., allowed to cool, and after 10 min. the blue colour is compared with that of a standard generated under the same conditions. An appreciable colour is produced with 0·15 mg. of the ions per litre. J. Grant.

Systematic doctrine of affinity. XLV. Increase in reactivity through lattice distension, and ammines of the fluorides. W. Biltz and E. Rahlfs (Z. anorg. Chem., 1927, 166, 351—376; cf. this vol., 1143).—By tensimetric measurements, evidence has been obtained of the addition of the following numbers of molecules of ammonia to anhydrous fluorides: antimonious fluoride, 6, 4, 3, 1; mercuric fluoride, 5, 4, 2; cupric fluoride (dihydrate), 5; beryllium fluoride, 1; silver fluoride, 1 (an amine ?). Certain other fluorides do not react in the anhydrous state, but their hydrates may be reactive, part of the water being replaced by ammonia. In these cases, it is probable that the reduction in lattice energy consequent on the distension of the lattice produced by the water molecules is responsible for the reactivity. The existence of the following compounds obtained in this way has been detected; silver fluoride monohydrate with 2 mols. of ammonia; zinc fluoride dihydrate with ½, 3, and 4 mols. of ammonia; monohydrates of manganous, ferrous, cobaltous, and nickel fluorides, each with ½, 1, and 5 mols. of ammonia; aluminium fluoride dihydrate with 2 mols. of ammonia. The volume of the fluorine atoms in the pure anhydrous fluorides is, in general, much less than the zero volume, but is very variable, whilst in the hydrated salts the volume of the water molecules is nearly equal to the zero volume. In the ammines, the volume of the ammonia molecules approximates to the zero volume. R. Cuthill.

Formation of aquopentacyano-iron salts in aqueous solutions of hexacyano-iron complexes and the successive dissociation of the latter. S. Iimori (Z. anorg. Chem., 1927, 167, 145—172).—Aqueous solutions of ferro- and ferri-cyanides are gradually converted by light, heat, or excess of hydrogen ions into the corresponding aquopentacyano-compounds. The first stage in the dissociation of the ferro- and ferri-cyanide ions results in the formation of pentacyano-iron ions. The reputed existence of the isomeric β-ferro- and ferri-cyanides is ascribed to the influence of aquopentacyano-iron compounds, formed by dissociation, on the crystal form of the salt. H. F. Gillbe.

Univalent iron, cobalt, and nickel. II. W. Manchot and F. Kaess (Ber., 1927, 60, [*B*], 2175—2180; cf. this vol., 33).—The *compound* Ni(NO)·SEt may be prepared by adding an aqueous solution of potassium hydroxide to aqueous nickel acetate in an atmosphere of nitric oxide followed by introduction of ethyl mercaptan and agitation of the mixture with nitric oxide until the gas is no longer absorbed or, preferably, by passing nitric oxide over nickelous mercaptide at the ordinary temperature. Under the latter conditions, nitrosylethylmercaptide (cf. Lecher and Siefken, A., 1926, 819) is also readily isolated; this can also be obtained according to the first procedure if methyl alcohol and potassium methoxide are substituted for water and potassium hydroxide. Reduction of bivalent to univalent nickel proceeds therefore according to the scheme: $Ni(SEt)_2+2NO=NO·Ni·SEt+SEt·NO$.

[With H. Schmid.]—These observations suggest that the action between potassium thiosulphate, nitric oxide, and nickel chloride (this vol., 34) may be represented by the equations: $NiCl_2+3K_2S_2O_3+2NO=2KCl+NO·S·SO_3K+Ni(NO)·S·SO_3K,K_2S_2O_3$ and $2NO·S·SO_3K=2NO+K_2S_4O_6$. This view is supported by the detection of potassium tetrathionate in 45—50% yield in the mother-liquors from the precipitate of the nickel salt. H. Wren.

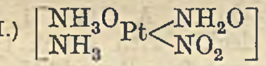
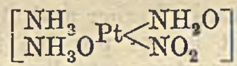
Cobaltic fluoride hydrate. E. Birk (Z. anorg. Chem., 1927, 166, 284—289).—Cobaltic fluoride prepared by Barbieri and Calzolari's method (A., 1905, ii, 393) is not the anhydrous salt, but a *hydrate*, $Co_2F_6,7H_2O$. It takes up ammonia at 70—80° with loss of water, luteo- and purpureo-fluorides probably being formed. The *X*-ray diagram closely resembles those of the bimolecular types of chromic fluoride hydrates (Werner and Costachescu, A., 1909, ii, 51), but it is not possible to decide with which type the structure actually corresponds. By addition of alcohol to a very concentrated solution of chromic fluoride, a *pentahydrate*, $CrF_3,5H_2O$, may be prepared. R. Cuthill.

Ruthenium. X. "Isomeric" chlorides. J. L. Howe (J. Amer. Chem. Soc., 1927, 49, 2381—2393).—The reduction of potassium hexachlororuthenate and of Claus' potassium pentachlororuthenite with stannous chloride yields in each case "aquo"-pentachlororuthenite, K_2RuCl_5, showing that the valency of ruthenium in each of the compounds is four. Claus' compound is now proved to be K_2RuCl_5OH, as originally suggested by Charonnat (A., 1925, ii, 586). The hydrated oxide usually considered to be Ru_2O_3,xH_2O is thus, in all probability, really RuO_2,xH_2O, since its solution always yields H_2RuCl_5OH. The "aquo" salts are the ordinary series M_2RuCl_5,H_2O. In all these salts the co-ordination number of ruthenium is six. Claus' view that the blue solution of reduced ruthenium contains bivalent metal is confirmed. S. K. Tweedy.

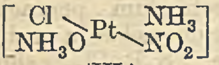
Complex salts of iridium containing hydrazine. L. A. Tschugaev (Ann. inst. platine, 1926, No. 4, 52—54).—When heated in aqueous solution, hydrazine hydrochloride and potassium chloroiridate yield the *compound* $[Ir(N_2H_5)Cl_5]H$, which, with tetramminoplatinous chloride or cæsium chloride yields, respectively, the *compounds* $[Ir(N_2H_5)Cl_5]_2[Pt4NH_3]$ and $[Ir(N_2H_5)Cl_5]Cs$. Chemical Abstracts.

Pentammine compounds of quadrivalent platinum. L. A. Tschugaev (Ann. inst. platine, 1926, No. 4, 1—36).—Compounds of the type $[5NH_3PtX]Y_3$ have been obtained from ammonium chloroplatinate and anhydrous ammonia; interaction in aqueous solution takes place in the presence of ammonium carbonate or a soluble phosphate. Hydroxypentammine salts are formed by the interaction of alkali with chloropentammine salts. Evidence is adduced for the existence of the ion $[Pt,5NH_3,Cl]^{\cdots}$. The *compounds* $[5NH_3PtCl]ClSO_4$ and $[5NH_3PtCl]ClPtCl_6,2H_2O$ are described. Reduction with zinc and dilute hydrochloric acid yields salts of bivalent platinum with the loss of 1 mol. of ammonia. Soluble salts of the type $[5NH_3PtCl]X_3$ with potassium iodide form the *compound* $[4NH_3PtI_2]I_2$. *Bromopentammineplatinic* salts, $[5NH_3PtBr]X_3$, have been obtained. Chemical Abstracts.

Mononitrites of bivalent platinum. I. I. I. Tschernyaev (Ann. inst. platine, 1926, No. 4, 243—275).—The base $[Pt(NH_3O)_4](OH)_2$ gives with 10% hydrobromic acid the *trans*-compound $[PtBr_2(NH_3O)_2],2H_2O$, whereas boiling hydrobromic acid (*d* 1·52) yields the compound $(NH_3O)_2PtBr_5$. *cis*- and *trans*-Dihydroxylaminoplatinous nitrite, and the oxalate (yielding with water or sulphuric acid the compound $[Pt(NH_3O)_4][Pt(C_2O_4)_2]$ and with hydrochloric acid the compound $[Pt(NH_3O)_4][PtCl_4]$), together with the *compounds* I (from *cis*-dihydroxylaminoplatinous nitrite and ammonia) and II (from *trans*-dihydroxylaminoplatinous nitrite and ammonia), were obtained.

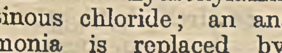
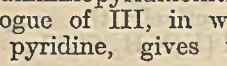
(I.)


(II.)

The compound II with hydrochloric acid gives *trans*-$[Pt(NH_3O)_2NO_2,NH_3]Cl$ (*chloroplatinite*). The compound I with hot hydrochloric acid gives III, which with water yields the compound $[Pt(NH_3O)(NH_3)(NO_2)(OH)]$, and on crystallisation from pyridine gives IV, which is undecomposed by acids :—

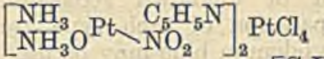

(III.)

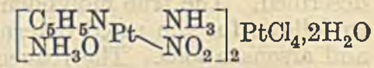

(IV.)

In I, II, and IV, the acid properties of hydroxylamine are increased by proximity of the nitrite group. *trans*-Diamminoplatinous nitrite with hydroxylamine hydrochloride gives nitrogen and *trans*-diamminoplatinous chloronitrite, a general method for obtaining *trans*-salts of the form (A=amine): $PtAA'ClNO_2$. *trans*-Diamminohydroxylaminonitritoplatinous nitrite gives a red chloroplatinite, the free base being soluble in water; the *cis*-compound gives a dark red chloroplatinite ($+4H_2O$), the free base being slightly soluble in water. The *trans*-compound $[Pt(C_5H_5N)NH_3(NO_2)_2]$, with hydroxylamine, yields compound V. The compound VI, with hydroxylamine,

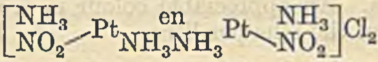
(V.)


(VI.)

affords hydroxylamineamminopyridinonitritoplatinous chloride; an analogue of III, in which ammonia is replaced by pyridine, gives with ammonia a yellow gel (*chloroplatinite* VII), whereas III with pyridine and potassium chloroplatinite


(VII.)

(VIII.)


yield VIII; hence the four co-ordinated groups are uniplanar. Complex *compounds* are produced by interaction of hydrazine sulphate with *trans*-diamminoplatinous nitrite and *trans*-hydroxylaminoamminoplatinous nitrite. The formation of the compounds en $Pt(NO_2)_2$ and $[en\ Pt(NH_3)(NO_2)]OH$ from $Pt(NH_3)_2(NO_2)_2$ is recorded; the *trans*-compound $[Pt(NH_3)_2Cl(NO_2)]$, however, yields the compound IX.


(IX.)

The ethylenediamine–platinum ring is not formed instantaneously. An analogous dihydroxylamino-derivative was prepared.

The following *compounds* are mentioned: *cis*-$[Pt(NH_3)_2(C_5H_5N)NO_2]NO_2$ (chloroplatinite), *trans*-$[Pt(NO_2)_2(C_5H_5N)(NH_3O)]$, *trans*-$[PtCl(NO_2)_2(NH_3)(NH_3O)]$, *trans*-$[Pt(NH_3)_2(C_5H_5N)(NO_2)]Cl$ (chloroplatinite); $[enPt(NH_3)(NO_2)]PtCl_4$. The author has thus obtained the first instances of isomerides with 3 and 4 substituents linked to platinum; Werner's assumptions are confirmed, the stability of the nitro-groups and the mobility of chlorine are established, the similarity of complexes to metals is instanced, and cases are disclosed in which cycles are not formed with ethylenediamine or oxalate groups. Chemical Abstracts.

Complex sulpho-acids of platinum. L. A. Tschugaev and S. E. Krasikov (Ann. inst. platine, 1926, No. 4, 44—47).—By passing sulphur dioxide into a hot solution of the compound $[Pt4NH_3]Cl$, the *compound* $[Pt,2NH_3,Cl,SO_3]_2[Pt4NH_3]$ is produced, with transient formation of the *compound* $[Pt4NH_3][Pt2NH_3(SO_3)_2]$. Both are *trans*-compounds. Chemical Abstracts.

Quantitative spectral analysis. J. Šebor (Chem. Listy, 1927, 21, 415—421).—The points of maximum and minimum absorption of light in the visible spectrum by solutions of a number of dyes vary according to the concentration of the dye. This is proposed to be used for the determination of such dyes. R. Truszkowski.

Calculation of gas analyses. Brutzkus (Compt. rend., 1927, 185, 861—863).—In a gas mixture which undergoes a chemical reaction in which the quantities of the constituents are increased or decreased, determinations of the percentage composition before and after the reaction will not give the amounts of the changes. If, however, one of the constituents takes no part in the reaction, any change in the proportion of it present in the mixture is due only to the change in volume of the latter. Hence, by reducing the quantity of each gas present to the same volume as that of the inert gas, the quantity remaining after the operation, and hence the gain or loss, may be determined in each case. If necessary an inert gas may be added to the mixture. J. Grant.

Electrolytic analysis with a dropping mercury cathode. J. Heyrovský (Bull. Soc. chim., 1927, [iv], **41**, 1224—1241).—A general account, with bibliography, of the above analytical method as developed by the author, his co-workers, and others (cf. A., 1926, 590, 1184, etc.) S. K. Tweedy.

Spot analysis. N. A. Tananaev (Z. anal. Chem., 1927, 72, 155—157).—Polemical, and a claim for partial priority. F. S. Hawkins.

Microchemical volumetric analysis. I. II. Separation of small quantities of barium and calcium. W. Geilmann and R. Höltje (Z. anorg. Chem., 1927, **167**, 113—127, 128—136).—I. The relative merits of various types of burettes and other apparatus for micro-analysis are discussed. The accuracy of titration of chromate solutions with sodium thiosulphate, of permanganate with sodium oxalate, and of potassium hydroxide with hydrochloric acid has been determined at concentrations between $0{\cdot}1N$ and $0{\cdot}001N$.

II. Quantities of calcium less than 5 mg. may be determined by precipitation with sodium oxalate solution, addition of a slight excess of $0{\cdot}02N$-potassium permanganate to the centrifuged solution, and titration with $0{\cdot}02N$-sodium thiosulphate. The direct determination, made by dissolving the washed calcium oxalate in dilute sulphuric acid, adding a slight excess of permanganate, and titrating with $0{\cdot}02N$-sodium thiosulphate, gives more accurate results, the error when about 5 mg. of calcium is present being ±0·015 mg. Barium, in quantities of the order of 5 mg., may be determined with accuracy by precipitation with an excess of standard potassium chromate solution and titration of the excess with $0{\cdot}01N$-sodium thiosulphate. Direct determination of the barium chromate gives inaccurate results. If, however, a known portion (as much as possible) of the centrifuged solution is withdrawn, the remaining solution together with the precipitate may be treated with hydrochloric acid and potassium iodide and titrated with $0{\cdot}02N$-thiosulphate solution, whereby 5 mg. of barium may be determined with an error of ±0·01 mg. In the portion of solution withdrawn calcium may be determined by either of the methods given above. H. F. Gillbe.

Vacuum flask for conductivity determination and for conductometric analysis. I. Remesov (Biochem. Z., 1927, **189**, 33—38).—A new vacuum flask is described and used for the determination of conductivity at constant temperatures without the use of a thermostat and for carrying out conductometric titrations. P. W. Clutterbuck.

Use of mixed indicators in acidimetry and alkalimetry. I. M. Kolthoff (Biochem. Z., 1927, **189**, 26—32).—A series of 25 mixed indicators is given showing change of colour at p_{H} ranging from 3·25 to 10·8 and their use is discussed.

P. W. Clutterbuck.

Further buffer solutions for the alkaline range. I. M. Kolthoff and J. J. Vleeschhouwer (Biochem. Z., 1927, **189**, 191—193, and Chem. Weekblad, 1927, **24**, 526).—Tables indicate the composition of solutions of p_{H} 9·2—11·0 obtained with mixtures of $0{\cdot}05M$-sodium hydroxide with $0{\cdot}05M$-borax, of p_{H} 11·0—12·0 with mixtures of $0{\cdot}1M$-disodium hydrogen phosphate and $0{\cdot}1N$-sodium hydroxide, and of p_{H} 6—9·2 with mixtures of $0{\cdot}1M$-potassium dihydrogen phosphate with $0{\cdot}05M$-borax. P. W. Clutterbuck.

Water analysis. W. R. Atkin and D. Burton.—See B., 1927, 830.

Determination of water in mixtures of benzene and alcohol. D. Peters.—See B., 1927, 858.

Adsorption method of titration. R. H. Burschtein (J. Russ. Phys. Chem. Soc., 1927, **59**, 521—536).—The adsorption method of titrating silver and halogen ions in the presence of organic dyes according to Fajans is discussed, and the mechanism explained on the theory of electrical adsorption. The colloidal particles of silver halide when once the equivalent point is passed adsorb silver or halogen ions, depending on which is in excess, and form with acid or basic dyes highly-coloured complexes, markedly different from the original dye. To give a sharp colour change, the silver halide–dye complex must be more soluble than the silver halide itself. Mixtures of halides can be titrated by choosing a mixture of dyes of suitable solubility. Thus potassium chloride and potassium iodide can be determined with sodium fluorescein, which gives a change from greenish-yellow to orange-red with the chloride, and rose-Bengal, which changes from bright red to purple with the iodide. The accuracy of the method is diminished by the coagulation of the silver halide sol near the end-point, and the action of such protective colloids as gelatin and egg-albumin was consequently investigated. No marked improvement results, but the concentration of the protective colloid does not affect the accuracy, so that the method can be employed in biochemical analysis, where small concentrations of halogen ions often exist in the presence of large amounts of colloidal proteins. The dyes employed belonged to the fluorescein group (acid) and to the rhodamine and triphenylmethane groups (basic).

The method can be extended to the determination of lead salts by means of potassium ferrocyanide, if mordant dyes, such as sodium alizarinsulphonate, which form brilliantly coloured "lakes" with the colloidal lead complex, are used.

Salts of weak acids cannot be determined, as the hydroxyl ions set free through hydrolysis destroy the colour reaction.

The method, which compares favourably with all other existing methods, is being extended to zinc, mercury, and copper. M. Zvegintzov.

Colorimetric determination of perchlorate in the presence of chlorate. O. S. Fedorova (J. Russ. Phys. Chem. Soc., 1927, **59**, 509—520).—A criticism and an extension of Hahn's method (B., 1926, 404) of determining perchlorates directly in the presence of chlorates by means of methylene-blue.

Solutions of perchlorates (more concentrated than 0·01%) give a green, bluish-violet, or deep purple precipitate, depending on the concentration. With solutions containing from 0·0008% to 0·01% pale blue to bright reddish-violet colorations are obtained in the presence of a concentrated solution of zinc sulphate, which greatly increases the sensitiveness of the methylene-blue. Chlorates also give a colour reaction with the dye, and their action must be neutralised by the addition of sodium nitrate solution.

A colorimetric table for varying concentrations of perchlorate is provided, and the amounts of zinc sulphate and sodium nitrate necessary to obtain the desired effect in the presence of different amounts of chlorates are determined. The influence of chlorides on the reaction is also investigated. M. Zvegintzov.

Determination of small quantities of iodine. P. A. Meerburg (Z. physikal. Chem., 1927, **130**, 105—108).—There is no satisfactory method of determining separately the organic and inorganic iodine in water, Fellenberg's method (this vol., 692) giving low results for the inorganic and high for the organic iodine. Total iodine is determined as follows: 3—6 litres of water together with a few c.c. of concentrated potassium carbonate solution are evaporated to dryness in a platinum basin and extracted with alcohol; the residue is heated to redness, moistened with potassium carbonate solution, and extracted with alcohol. The united extracts are evaporated, cautiously heated, extracted three times with alcohol, and the combined extracts evaporated to dryness, the residue being taken up in 1 c.c. of water. The iodine is then determined colorimetrically. S. J. Gregg.

Determination of iodide in mixtures of halides. H. Baines.—See B., 1927, 813.

Determination of sulphide, thiosulphate, and sulphur in insoluble carbonates. H. Brintzinger and F. Rodis.—See B., 1927, 841.

Determination of sulphate in solutions of tervalent chromium. M. N. Pavlov (Ukraine Chem. J., 1926, 2, 353—354).—Precipitation of sulphate in the usual way as barium sulphate is inaccurate in presence of tervalent chromium. Chromium is therefore removed as hydroxide by addition of magnesium oxide or carbonate at the ordinary temperature, the precipitate is filtered off, washed, and the filtrate used for the determination. A. Ratcliffe.

Examination of naturally occurring gases. V. F. Henrich and W. Herold (Ber., 1927, **60**, [*B*], 2047—2053; cf. A., 1920, ii, 767).—Improvements in the apparatus described previously are effected by placing the mixture of calcium and sodium used for the absorption of nitrogen in an iron (instead of glass) tube placed in a protecting tube of quartz or porcelain heated in an electric furnace. The open pneumatic trough is replaced by a eudiometer and levelling tube connected directly to the delivery tube of the mercury pump. Analyses of several naturally occurring gases are recorded and also of gases obtained by heating tectites at about 1000°. H. Wren.

Improved micro-Dumas determination of nitrogen. S. Ogawa (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 667—670).—The apparatus for the micro-determination of nitrogen by the methods of Pregl and Dubsky has been slightly modified in order to facilitate the removal of oxygen from the apparatus before the combustion is commenced. R. Cuthill.

Detection of nitric acid with ferrous sulphate. P. G. Popov (Ukraine Chem. J., 1926, 2, 391—394.)—The sensitivity of the brown ring test, and the difficulties arising when nitrites present are destroyed by the addition of carbamide, are discussed. A. Ratcliffe.

Reactions of nitrous acid. J. V. Dubský and A. Okáč (Publ. Fac. Sci. Univ. Masaryk, 1927, No. 83, 1—84).—The changes in colour produced in dyes by further diazotisation and coupling with a large number of reagents under specified conditions have been studied, and exhaustive tables have been drawn up to show the colour changes and the sensitiveness of the various reactions. Changes of colour from yellows and reds to reds and blues are more readily observed and measured than the development of the original yellow or red coloration, whilst the stability of the colours during treatment makes the tests more definite. The possibility of two colour changes in some cases, one on diazotisation and another on coupling, is a further advantage of this method of testing. Some 600 substances have been examined for this purpose, and those suitable for detection of nitrites are enumerated. S. I. Levy.

Colorimetric determination of minute quantities of dissolved phosphorus in oil. C. Stich.—See B., 1927, 851.

Use of amalgams in volumetric analysis. VII. Determination of phosphoric acid. S. Hakomori (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 719—722; cf. A., 1922, ii, 721).—Ammonium phosphomolybdate, precipitated by Woy's method, is dissolved in 2*N*-ammonia solution, reduced with 200 g. of zinc amalgam or cadmium amalgam and an amount of 1 : 1-sulphuric acid equal to 0·1 of the volume of the solution, and finally titrated with permanganate. The results are about 1% higher than those of the magnesium pyrophosphate method. R. Cuthill.

Simple mercury cathode for arsenic determinations. F. S. Aumonier.—See B., 1927, 813.

Volumetric determination of antimony and arsenic. P. E. Winkler (Bull. Soc. chim. Belg., 1927, **36**, 491—501).—Although the equilibrium $M^{\cdot\cdot\cdot\cdot\cdot}+2I' \rightleftharpoons M^{\cdot\cdot\cdot}+I_2$, where M represents antimony or arsenic, is completely displaced to the right in media which are sufficiently acid, direct titration of the liberated iodine is not possible because of oxidation of hydriodic acid by the air. Accurate results are, however, obtained by passing a stream of carbon dioxide through the boiling solution until all the iodine is expelled and after neutralisation and addition of sodium hydrogen carbonate, titrating with a solution of iodine.

For antimony the precipitated sulphide is dissolved in a mixture of 10 c.c. of 20% tartaric acid solution with 20 c.c. of 20% sodium hydroxide solution and 20 c.c. of hydrogen peroxide (20 vol.). The resulting solution is boiled for about 20 min., neutralised with hydrochloric acid, and diluted to 100 c.c. After addition of hydrochloric acid and potassium iodide, and starch, the iodine is removed. The cooled solution is neutralised (methyl-orange) with sodium carbonate and titrated, after addition of sodium hydrogen carbonate, with a standard solution of iodine.

Arsenic sulphide is dissolved in a mixture of 20 c.c. of 20% sodium hydroxide solution and 20 c.c. of hydrogen peroxide (20 vol.) and subsequent neutralisation is effected by sulphuric acid. Reduction to the arsenious state is effected with sulphuric acid, hydrochloric acid, and potassium iodide.

J. S. Carter.

Determination of small quantities of carbon monoxide. D. Stavorinus.—See B., 1927, 834.

Determination of carbon monoxide, hydrogen, and methane in air containing ethylene. J. Thorburn.—See B., 1927, 803.

Determination of carbonic acid by precipitation as barium carbonate and titration of the excess of alkali. J. Lindner (Z. anal. Chem., 1927, 72, 135—154).—Consistently high results obtained by this method are not due to the precipitation of basic carbonates, but chiefly to the presence of silica dissolved out of the glass. It exists as a colloidal solution which slowly reacts with the baryta and precipitates barium silicate from the solution. The presence of magnesium salts also causes a considerable positive error, and calcium salts act similarly if present in large quantities. In all cases, owing to the adsorption of alkali by the precipitate, a more accurate titre is obtained by warming the solution at the end of the titration. The determination of a mixture of carbonate and hydroxide by Winkler's method is also affected by the presence of silica.

F. S. Hawkins.

Electrolytic alkali determination in Drossbach's apparatus. H. Ginsberg (Z. anorg. Chem., 1927, 167, 183—184).—Accurate results may be obtained by employing the correct current and voltage, pure mercury, and polished nickel wire. The distance between the anode and the mercury surface should not exceed 1—2 cm. H. F. Gillbe.

Determination of lithium in scleron and similar aluminium alloys. E. Schürmann and W. Böhm.—See B., 1927, 818.

Micro-chemical determination of rubidium. E. S. Burkser and S. G. Rublev (Ukraine Chem. J., 1926, 2, 355—364).—Rubidium (up to $0{\cdot}01\ \gamma$) is detected by precipitation with a specially prepared solution of silver iodide, aurous iodide, and auric iodide in hydriodic acid. The black crystals so formed consist of the compound $3AuI,AuI_3,3RbI,2AgI$ or $3AuI,AuI_3,4RbI,AgI$, and their formation is neither hindered nor masked by the presence of even fairly large quantities of sodium, potassium, or ammonium salts. A. Ratcliffe.

Gravimetric determination of calcium. A. Franke and R. Dworzak (Z. anal. Chem., 1927, 72, 129—134).—If calcium is determined by precipitating as oxalate and igniting the precipitate, the mass gains in weight when kept in the desiccator. The increase is very marked when the drying agent is calcium chloride mixed with soda-lime, or calcium chloride alone, but is smaller when phosphorus pentoxide or well-burnt lime is used, and is therefore due to the absorption of moisture from the drying agent. The easiest and most accurate method of determination is to precipitate the calcium as oxalate, and weigh it as this salt after drying for 5 hrs. at 100—105°. Otherwise the oxalate, contained in a sintered porcelain crucible, should be ignited at 1000° in an electric furnace and cooled in a desiccator over well-burnt lime. F. S. Hawkins.

Detection of magnesium, especially in rocks, by means of diphenylcarbazide. F. Feigl (Z. anal. Chem., 1927, 72, 113—119).—Magnesium ammonium phosphate or carbonate and all magnesium salts which can be decomposed by treatment with alkali hydroxide are coloured rose-violet when treated with an alcoholic solution of diphenylcarbazide. Magnesite is coloured immediately by the reagent, whereas dolomite is not, suggesting that dolomite is a calcium magnesocarbonate. To detect magnesia in a carbonate rock the powdered substance is boiled for 2—3 min. with a 5% alcoholic solution of the reagent, the liquid decanted, and the substance boiled repeatedly with water until the latter ceases to become coloured; if the residue is coloured magnesia is present. In the case of a negative result a second portion of the rock is heated to redness, cooled, and subjected to the test; if a positive result is obtained the rock contains dolomite. A. R. Powell.

Detection of lead by the spot method. N. A. Tananaev (Z. anorg. Chem., 1927, 167, 81—86).—The reagent is prepared by adding to a concentrated stannous chloride solution sufficient potassium iodide solution to cause the liquid to set to a semi-solid on shaking; a concentrated solution of cadmium nitrate is then added drop by drop until a clear solution is obtained. Either hydrochloric acid or potassium thiocyanate may be used in place of cadmium nitrate but the reagent is less sensitive. The solution oxidises rapidly in the air, and should therefore be freshly prepared for the test. On addition of a solution containing lead ions an orange or a red precipitate is produced, which contains lead, tin, and iodine. If a drop of the solution to be tested is placed on filter-paper and treated with a drop of dilute sulphuric acid, lead, if present, is converted into sulphate, and on washing the spot with a little sulphuric acid from a capillary tube other metals present are carried to the outer edge of the spot. Addition of a drop of the reagent to the centre of the spot produces an orange stain, whilst if both lead and bismuth are present the stain is brown. H. F. Gillbe.

Reaction of aluminium with the ammonium salt of aurintricarboxylic acid [" aluminon "] under different experimental conditions, and its application to the colorimetric determination of aluminium in water. J. H. Yoe and W. L. Hill (J. Amer. Chem. Soc., 1927, 49, 2395—2407).—The use of aluminon as an analytical reagent for aluminium is investigated, including the effect of ageing (decrease of colour intensity with time), the quantities and concentrations of the reagents, the conditions of lake formation, and the influence of foreign ions. The effect of ageing is practically the same in both the light and the dark; the colour intensity passes through a maximum with increasing concentration of hydrochloric acid. In colorimetric analysis iron

must previously be separated from the aluminium. The lower limit of the test is 0·002 mg. By stabilising the lake with a protective colloid (*e.g.*, starch) up to 3 mg. of aluminium may be determined. A standard colorimetric method is developed and applied to the determination of aluminium in potable water.
S. K. TWEEDY.

" Potassium chlorate method " of determining manganese. M. MARQUEYROL and L. TOQUET (Ann. Chim. analyt., 1927, [ii], 9, 289—295).—Errors arising in the determination of manganese by oxidation in concentrated nitric acid solution with potassium chlorate are attributed to the solubility of the resulting manganese dioxide in nitric acid. The presence of potassium chlorate diminishes this solubility considerably; less chlorate is required for concentrated than for more dilute nitric acid, although the solubility of manganese dioxide in nitric acid alone increases with the concentration. The procedure should therefore involve operation at a temperature sufficiently low to prevent the disappearance of the chlorate from solution, and the use of a small amount of potassium chlorate and of highly concentrated nitric acid. G. A. ELLIOTT.

Determination of cobalt and other alloyed elements in cobalt, cobalt steel, and high-speed tool steels. E. SCHIFFER.—See B., 1927, 845.

Volumetric determination of tin. B. S. EVANS (Analyst, 1927, 52, 590—591).—The solution of tin in about 250 c.c. of dilute hydrochloric acid and a strip of sheet lead (about 20×2 cm. bent into a coil) are placed in a conical flask carrying a tube bent twice at right angles capable of being moved vertically in the stopper, another tube connected to a Kipp apparatus, and a separating funnel. Before inserting the stopper the doubly bent tube is drawn up and the funnel tap closed. A steady stream of carbon dioxide is then passed through the solution, which is boiled for 1 hr.; the outlet tube is then closed and the flask cooled under pressure from the Kipp apparatus. The outlet tube is pushed down into the solution and its free end placed in a flask containing 20 g. of sodium oxalate and a measured excess of 0·1*N*-iodine solution. The liquid is then blown over under the carbon dioxide pressure and 50 c.c. of rinsing water are passed through. The unreduced iodine is titrated with sodium thiosulphate.
D. G. HEWER.

Analysis of niobium and tungsten groups. I. WADA and S. KATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 227—263).—The original solid is dissolved by heating with nitric acid, followed by similar treatment with hydrofluoric acid. The latter solution contains the niobium and tungsten groups, and is acidified with sulphuric acid and treated with hydrogen sulphide to remove arsenic, antimony, selenium, tellurium, and part of the molybdenum. Ammonia and ammonium sulphide are added to the residual solution, thereby precipitating the niobium group, together with titanium, zirconium, and iron, and leaving the tungsten group in solution. The precipitate is boiled with sodium salicylate, when any titanium, iron, and vanadium present dissolves, leaving a residue of niobium, zirconium and tantalum; this is dissolved in hydrofluoric acid and tantalum, together with part of the zirconium, is precipitated as the potassium double fluoride. The tantalum is then separated from zirconium by hydrolysis of a sulphuric acid solution, and any zirconium left in solution with the niobium is removed by precipitation as its basic phosphate. To effect the separation of tungsten, the solution left after treatment with alkaline ammonium sulphide is acidified with hydrochloric acid, and the precipitate is evaporated with nitric acid. In the presence of tin or tungsten a residue insoluble in water is obtained. The residue is dissolved again in ammonium sulphide solution; on addition of excess of hydrochloric acid, tungsten alone is precipitated. F. S. HAWKINS.

Separation of platinum and iridium. B. G. KARPOV (Ann. inst. platine, 1926, No. 4, 360—363).—When a mixture of ammonium chloroplatinate and chloroiridate in aqueous solution is reduced at 100° with mercury, the precipitate on ignition yields platinum containing 0·04—0·11% of iridium; the iridium is obtained as oxide from the liquid and washings by evaporation with nitric acid and conversion into the tartrate. CHEMICAL ABSTRACTS.

Determination of platinum, palladium, and rhodium. V. N. IVANOV (Ann. inst. platine, 1926, No. 4, 331—338).—Thiocyanates precipitate the *compound* $Pd_3S_2(CSNH_2)_2$ from solutions (1% or less) of palladium salts; platinum salts and sodium thiocyanate yield *platinous thiocyanate*, hydrolysed by boiling water to the *compound* $Pt_4(OH)_4S(CSNH_2)_2$, whereby platinum may be rapidly determined; the presence of copper or iron produces slightly high results. Osmium and ruthenium do not give similar compounds, iridium gives an unsuitable precipitate, but palladium and rhodium behave similarly to platinum. When heated, the compounds yield the respective metals. CHEMICAL ABSTRACTS.

Rapid determination of palladium in platinum. O. E. ZVJAGINSTSEV (Ann. inst. platine, 1926, 364—366).—Solutions (1%) of palladium and platinum salts, respectively, give reddish-brown and dark brown colorations with potassium iodide. The solutions, which must be slightly acid, can, however, be compared colorimetrically 30—40 min. after preparation. The method is accurate to 0·0002 g. of palladium in 1 g. of platinum when 1 c.c. of potassium iodide solution (1 in 10^3) is used with 10 c.c. of the platinum solution. CHEMICAL ABSTRACTS.

Detection of iridium, and colorimetric determination of small quantities of iridium in platinum. V. G. CHLOPIN (Ann. inst. platine, 1926, No. 4, 324—330).—Quadrivalent iridium in aqueous solution (0·001%) gives with benzidine a sky-blue coloration; other ions react as follows: $Pt^{\cdot\cdot}$ none, concentrated $Pt^{\cdot\cdot\cdot\cdot}$ rose precipitate, $Ir^{\cdot\cdot\cdot}$ green, $Rh^{\cdot\cdot\cdot}$ rose-yellow precipitate, $Pd^{\cdot\cdot}$ none, $Os^{\cdot\cdot\cdot\cdot}$ yellow precipitate. Osmic acid gives a blue colour.
CHEMICAL ABSTRACTS.

Ruthenium. XI. Volumetric determination of ruthenium. J. L. HOWE (J. Amer. Chem. Soc., 1927, 49, 2393—2395).—Volatile ruthenium tetroxide is condensed in concentrated hydrochloric acid, the solution is boiled and then standard stannous chloride solution is added, the excess being determined by titration with iodine solution. The amount of stannous chloride required is always somewhat less than that required theoretically for reducing the ruthenium to the tervalent state, so that the method is applicable only when small amounts of ruthenium are present or when only an approximate result is required. S. K. Tweedy.

Light source for continuous spectrum. V. D. Snyder (J. Amer. Chem. Soc., 1927, 49, 2510—2511).—A lamp is described and figured in which a Tesla spark is maintained under water. S. K. Tweedy.

Nickel electrical resistance thermometers. W. Del Regno (Rend. Accad. Sci. fis. mat. Napoli, 1926, [iii], 32, 194—201).—Platinum can be replaced by nickel in electrical resistance thermometers for measuring temperature differences below 500°, and for measuring temperatures directly below 360°, with a notable increase in sensitivity, nickel having a high thermal coefficient of electrical resistance. The latter may be expressed by $R_t=R_0+at+bt^2+ct^3$, where a, b, and c are constants characteristic of the threads employed, and have the respective values in a sample examined of $3{\cdot}085\times10^{-3}$, $7{\cdot}7\times10^{-7}$, and $1{\cdot}06\times10^{-8}$. The oxidation of nickel is negligible below 500°, the tensile strength is higher than that of platinum, the change of resistance with temperature shows no hysteresis, and the influence of traces of impurities is, in contrast with platinum, very slight. E. W. Wignall.

Copper–constantan thermocouples and the hydrogen thermometer compared from 15° to 283° Abs. W. F. Giauque, R. M. Buffington, and W. A. Schulze (J. Amer. Chem. Soc., 1927, 49, 2343—2354).—The construction of a sensitive copper–constantan thermocouple is described and a method of testing for inhomogeneities in metallic wires intended for use in such low-temperature couples is outlined. A hydrogen thermometer is also described which can be maintained at any temperature between the b. p. of hydrogen and 290° Abs. to within 0·01°; it is designed for the calibration of thermocouples. Calibrations below 25° Abs. are in error, presumably because of adsorption of hydrogen by the glass thermometer bulb (cf. following abstract). The calibrated thermocouple gives 234·18° Abs. for the m. p. of mercury, and the vapour pressure of hydrogen chloride, measured with reference to such a thermocouple as a temperature standard, is stated to agree with the precision measurements of Henning and Stock to 0·01—0·02° (Z. Physik, 1921, 4, 226). S. K. Tweedy.

Hydrogen gas thermometer compared with the oxygen and hydrogen vapour-pressure thermometers by means of a copper–constantan thermocouple. W. F. Giauque, H. L. Johnston, and K. K. Kelley (J. Amer. Chem. Soc., 1927, 49, 2367—2372).—A copper–constantan thermocouple, calibrated as previously described (cf. preceding abstract), was compared with the Leiden temperature scales of the oxygen and the hydrogen vapour-pressure thermometers. Complete agreement was found with the former scale; a discrepancy below 25° Abs. with the latter scale indicated adsorption of gas at these temperatures in the hydrogen thermometer used for calibrating the couple. The triple point pressure of hydrogen is 5·370 international cm. of mercury, and the temperature is 13·92° Abs. The equation $\log p(\text{cm.})=-39{\cdot}2/T+2{\cdot}70\log T+0{\cdot}4584$ is derived for the vapour pressure of solid hydrogen. S. K. Tweedy.

Adiabatic microcalorimeter for radiological researches. W. Swientoslawski and (Mlle.) A. Dorabialska (Compt. rend., 1927, 185, 763—765).—The apparatus consists of a thick copper container, in which the calorimeter proper is suspended, immersed in a controlled thermostat. The alteration in temperature of the inner vessel, owing to the evolution of heat by the substance under investigation, is registered by means of a galvanometer connected with a thermocouple, and is balanced by raising the temperature of the thermostat so that the needle of the galvanometer is always at the zero point. The apparatus has a degree of accuracy of 0·7 for radiological work, and may be used to measure any continuous thermal effect. J. Grant.

Determination of specific gravity of small amounts of liquids and solids. P. L. du Noüy (J. Biol. Chem., 1927, 74, 443—448).—By means of a modified form of the author's torsion balance for the determination of surface tension the specific gravity of 1 c.c. of a liquid or of 0·1 g. of a solid can be determined to the third place of decimals. C. R. Harington.

Thermo-hydrometer. A. S. Webb (J. S. African Chem. Inst., 1927, 10, 14—15).—An ordinary hydrometer is modified by filling the large bulb with a mixture of alcohol and water coloured with methyl-red. This solution, rising or falling in the stem according to the temperature of the liquid in which it is floating, indicates changes of concentration of liquids regardless of temperature changes. The mixture having the correct coefficient of expansion is found by trial. In practice, a constant concentration at varying temperatures may be secured by maintaining the surface of the filling liquid level with that of the solution being prepared. R. A. Pratt.

Vacuum distillation technique. M. Demontvignier (Bull. Soc. chim., 1927, [iv], 41, 1244—1251).—A simple mercury-vapour "ejector" which is not fragile and is capable of producing a stable vacuum down to 1 mm. (? 0·1 mm.) with a water backing-pump is described. The degree of evacuation is controlled by the rate of heating of the mercury. A mercury-vapour pump of similar design is figured. An accurate, compact form of the McLeod gauge, capable of measuring pressures between 0·1 and 20 mm., is also described. S. K. Tweedy.

Burette for the accurate measurement of gas volumes without gas connexion to a compensator. E. R. Weaver and M. Shepherd (U.S. Bur. Stand., Sci. Papers No. 559, 1927, 22, 375—382).—A gas burette embodying a novel compensator to eliminate errors due to diffusion of gas into the manometer is described and illustrated. The burette proper consists of five 20 c.c. pear-shaped bulbs forming the main stem and a graduated side tube for measuring fractional parts of the bulbs. The lower end of the side tube is connected with a second parallel tube which acts as a mercury seal to the manometer proper and as a balancing intermediate manometer. All the mercury levels are read by means of vernier scales, so that an accuracy of 0·01 c.c. is readily obtained. A. R. Powell.

Colorimeter for precise matching of solutions in Nessler tubes. J. H. Yoe (Ind. Eng. Chem., 1927, **19**, 1131).—Light reflected by a mirror passes upwards through the two tubes for comparison and impinges on two mirrors set at 45°, one of which is half the width of the other. The light from each tube thus occupies half the field as seen through an observation tube with eyepiece and diaphragm. By proportioning these correctly the interference of light reflected from the sides of the Nessler tubes is eliminated. C. Irwin.

Trace of an ancient theory in a modern principle. C. M. van Deventer (Z. physikal. Chem., 1927, **130**, 33—38).—The basic principle underlying the principles of Le Chatelier and van 't Hoff was recognised by Aristotle and Theophrastes. S. J. Gregg.

History of witherite. G. Fowles (Chem. News, 1927, **135**, 309—310).—Witherite, discovered by Withering and described by him (Phil. Trans., 1784, 74, 293) as a compound of " terra ponderosa " (barium oxide) and " fixed air " (carbon dioxide), was obtained from a lead mine at Alston Moor, Cumberland, whereas the origin of the specimen is variously described in the literature as Scotland and Lancashire. Withering's investigations on this " terra ponderosa aërata " are briefly described. R. A. Pratt.

Mineralogical Chemistry.

Variations in the ozone content of the atmosphere. J. Cabannes and J. Dufay (J. Phys. Radium, 1927, [vi], **8**, 353—364).—Seasonal changes in the thickness of the stratum of ozone in the upper atmosphere were observed at stations at Mount Wilson and at Calama (Chile). The history of the variations in the quantity of ozone in the atmosphere is partly recounted for the period 1908—1920 through a consideration of the monthly means of the factors of transparency of the atmosphere for chosen wavelengths. The results obtained at Mount Wilson are compared with the work of Dobson and Harrison at Oxford. An attempt is made to correlate the results with solar activity, but no relationship is found to exist between the monthly values of the thickness of ozone and the number of sunspots seen during the same months, or between these values and the solar constant, thus confirming the records of Dobson and Harrison. The thickness of the ozone stratum is subject to seasonal variations and is to a certain extent associated with local climatic conditions. R. A. Pratt.

Gases of the Mt. Pelée lavas of 1902. E. S. Shepherd and H. E. Merwin (J. Geol., 1927, **35**, 97—116).—Detailed analyses are given of five specimens of hypersthene-andesite and of the gases evolved when chips are heated in a vacuum. The volatile matter includes carbon dioxide, carbon monoxide, hydrogen, nitrogen, argon, sulphur, chlorine, fluorine, and water, and the amount ranges from 4·3 to 26·5 c.c. (at 1200° and 760 mm.) per g. of rock, being higher in the glassy varieties. On the average, 80% consists of water, and 9% of carbon dioxide. Analysis of the finely-powdered rock may show as much as ten times as much water as the rock actually contains. The formation of pumice and the glassy surface of " bread-crust " bombs is discussed.

L. J. Spencer.

Yellow incrustation of the Vesuvian lava of [the eruption of] 1631. F. Zambonini and G. Carobbi (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **32**, 124).—The " vesbium " thought by Scacchi to be present in lava from the Vesuvian eruption of 1631 is vanadium. Vesbina has the composition $(Cu,Pb)_3(VO_4)_3,Cu(OH)_2,5H_2O$, in which lead is also partly replaced by rare-earth metals, including lanthanum, cerium, neodymium, yttrium, and erbium. Vesbina was formed by the action of water on the cooling lava. E. W. Wignall.

Pyromorphite from Leadhills, Lanarkshire, Scotland, and mimetite from Santa Eulalia Chihuahua, Mexico. G. Carobbi (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], **32**, 54—69).—The presence of chromium partly, at least, as lead chromate in pyromorphite from Leadhills, Lanarkshire, has been proved and also of manganese, calcium, strontium, barium, as well as cerium, lanthanum, neodymium, yttrium, europium, gadolinium, dysprosium, and erbium. The spectrograph indicates the presence of traces of ytterbium and holmium.

In mimetite from Santa Eulalia, chromium, manganese, zinc, calcium, barium, and strontium have been found. Spectroscopic examination indicates the complete absence of the rare earths. M. Carlton.

Composition and properties of rodonites. P. Aloisi (Atti R. Accad. Lincei, 1927, [vi], **5**, 1017—1021).—Crystallographic and optical characteristics of three samples of rodonite of different origin and composition are discussed with reference to the relationship between these properties and the composition of the mineral. R. W. Lunt.

Metaxite [serpentine] from Liubotina, Banat. M. Savul (Bull. Sci. Acad. Roumaine, 1927, **10**, No. 8—9, 32—35).—The dark-green serpentine, derived from gabbro, readily breaks up into columns and grinds to fine fibres. On account of the columnar structure it is referred to the variety metaxite: d 2·618, H 3—4, n 1·565, $\gamma-\alpha$ <0·008. The fibres give straight extinction with positive elongation. Analysis gave: SiO_2 41·69, TiO_2 nil, Al_2O_3 2·08,

Fe_2O_3 1·48, Cr_2O_3 0·006, FeO 4·31, MnO trace, MgO 37·40, CaO nil, H_2O (−110°) 0·48, H_2O (+110°) 12·34, total 99·786. The serpentine is veined with aragonite. The frequent presence of aragonite, rather than calcite, in serpentines is attributed to the presence of magnesia in the solutions. L. J. SPENCER.

"Blythite" and the manganese garnet from Amelia, Virginia. E. V. SHANNON (J. Wash. Acad. Sci., 1927, 17, 444—452).—To explain the composition of some manganese garnets Fermor (Rec. Geol. Surv. India, 1926, 59, 191) has assumed the presence of the molecule $3MnO,Mn_2O_3,3SiO_2$, which he termed "blythite." A new analysis of the reddish amber-coloured garnet (*d* 4·153, *n* 1·794) from Amelia, Virginia, gave: SiO_2 35·76, TiO_2 trace, Al_2O_3 17·38, Fe_2O_3 0·92, FeO 4·90, MnO 37·98, MgO 0·22, CaO 1·66, H_2O 0·58, total 99·40. Agreement with the garnet formula is obtained if the manganese is reckoned as MnO 34·86 and Mn_2O_3 3·47%. The composition then corresponds with spessartine 70·41, "blythite" 12·13, almandine 11·47, andradite 3·05, grossular 1·81, pyrope 0·81%. The existence of the "blythite" molecule could, however, only be established if a trustworthy method were available for the determination of manganic manganese in garnet. The low alumina and high manganese oxide shown in an earlier analysis of the Amelia garnet is evidently due to the faulty precipitation of alumina as acetate. L. J. SPENCER.

Structure of the orthoclase molecule. O. K. BOTWINKIN (Z. anorg. Chem., 1927, **167**, 190—192).—The orthoclase molecule is very stable towards water and aqueous solutions of carbon dioxide, although with rise of temperature some decomposition occurs. Increase of pressure up to 120 atm. has but little influence on the amount of decomposition. H. F. GILLBE.

Analyses of three Australian rocks. M. AUROUSSEAU (Proc. Linnean Soc. N.S. Wales, 1926, 51, 614—626).—Detailed analyses are given of nepheline-basanite (previously described as fayalite-basalt and melilite-basalt) from Tasmania, a micrographic granite from New South Wales, and an amphibolite from Western Australia. The chemical composition of the granite as deduced by micrometric analysis of thin sections is discussed. L. J. SPENCER.

Organic Chemistry.

Catalytic hydrogenations in liquid media by platinum and palladium. G. VAVON (Bull. Soc. chim., 1927, [iv], 41, 1253—1290).—A lecture.

Catalytic oxidation of methane to formaldehyde. I. S. S. MEDVEDEV (Trans. Karpov Inst. Chem., 1924, No. 3, 54—65; cf. A., 1926, 1012).—Using gold, platinum, manganese sesquioxide (most active), copper oxide (least active), silver oxide, lead oxide, or cerium dioxide on asbestos, and 1 litre per 20 min. at 250—350°, only carbon dioxide is obtained; with 1 litre per min. at 500°, copper oxide yields traces of formaldehyde and carbon monoxide. Glass at 600° gives a large yield of formaldehyde owing to the smaller chemical activity of the surface in not forming peroxides. With methane containing 3—7% of hydrogen, lead catalysts at 500—700° give the highest yields of formaldehyde. The presence of lead chloride or hydrogen chloride (0·13%) raises the relative yield of formaldehyde. With a mixture of methane (13·8%) and oxygen (17·98%) at 0·23 litre per min., at 600°, the yield of formaldehyde was 5·02% of the methane taken. CHEMICAL ABSTRACTS.

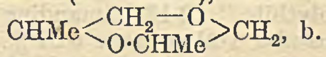
Rearrangement of *iso*propylethylene to trimethylethylene and the pyrogenic decomposition of Δ^{β}-pentene and trimethylethylene. J. F. NORRIS and R. REUTER (J. Amer. Chem. Soc., 1927, 49, 2624—2640; cf. this vol., 440).—When γ-methyl-Δ^{α}-butene is passed over alumina at 450°, the time of contact being 15 sec., 10% of the hydrocarbon is converted into β-methyl-Δ^{β}-butene. This proportion is increased if phosphoric acid is used as catalyst, whilst with aluminium sulphate 47% of the hydrocarbon undergoes this rearrangement. When *iso*amyl alcohol is passed over alumina at a similar rate at 375°, 48% of the alcohol is decomposed, but rearrangement of the resulting hydrocarbon is not observed. With aluminium sulphate, 90% of the alcohol is decomposed, and 70% of the hydrocarbon is rearranged. With phosphoric acid, a higher temperature (405°) is necessary to effect dehydration, and the proportion of the hydrocarbon rearranged is less. Treatment of γ-methyl-Δ^{α}-butene with 84% sulphuric acid at 35° for 10 min. affords a *polymeride*, b. p. about 150°. With 60—69% sulphuric acid, a small amount of *tert.*-amyl alcohol is produced, indicating rearrangement of the hydrocarbon as above. When Δ^{β}-pentene is passed through a carbon-coated silica tube at 600°, it yields, per 100 pts.: hydrocarbons of higher mol. wt., apparently saturated, 15 pts.; methane, 7·8 pts.; butadiene, 8 pts.; butene, 8 pts.; propylene, 4 pts.; ethylene, 2 pts., and unchanged hydrocarbon, 33 pts. At 650°, trimethylethylene is decomposed as above to about the same extent as is the Δ^{β}-pentene at 600°. Rearrangement to γ-methyl-Δ^{α}-butene was not observed, and the products again contained 33% of higher hydrocarbons. The pyrogenic decomposition of both hydrocarbons appears to proceed by removal of the terminal methyl group, with subsequent hydrogenation of the two radicals thus formed, the hydrogen being derived from the total breakdown of a portion of the hydrocarbon, as indicated by the deposition of carbon. Δ^{β}-Pentene has m. p. −138±2°, b. p. 36·39±0·04°/760 mm., d_4^{15} 0·65551, n_D^{15} 1·3839. γ-Methyl-Δ^{α}-butene is viscous at −180°, and has b. p. 20·10±0·05°/760 mm., d_4^{15} 0·63197, n_D^{15} 1·3675. Trimethylethylene has m. p. −123±2°, b. p. 38·42±0·04°/760 mm., d_4^{15} 0·66708, n_D^{15} 1·3906. *tert.*-Amyl alcohol has m. p. −11·9±0·5°, b. p. 101·76±0·04°/760 mm., d_4^{15} 0·81382, n_D^{15} 1·4078. F. G. WILLSON.

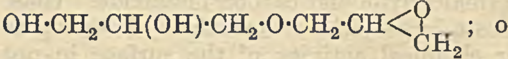
Preparation of tetraiodomethane. J. F. Durand (Bull. Soc. chim., 1927, [iv], 41, 1251—1252).—Tetraiodomethane is prepared in 75% yield by the action of a potassium hydroxide solution of iodine on iodoform at 90° (cf. Dehn, A., 1909, i, 867).
G. A. C. Gough.

Action of ultra-violet rays on chloropicrin. A. Piutti and F. P. Mazza (Gazzetta, 1927, 57, 610—614).—When chloropicrin is exposed to ultra-violet light it decomposes slowly to give nitrosyl chloride and carbonyl chloride, which itself decomposes to the extent of 5%. The proportions of the products are determined by absorbing carbon monoxide in ammoniacal cuprous chloride, after other substances have been condensed by liquid air; the latter are transferred to a pipette containing mercury and amalgamated copper, which absorbs chlorine and decomposes nitrosyl chloride, liberating nitric oxide. Finally the carbonyl chloride is absorbed in alcohol, and the nitric oxide is determined.
E. W. Wignall.

Reactivity of atoms and groups in organic compounds. II. Relative reactivities of the hydroxyl hydrogen atoms in certain alcohols. J. F. Norris and F. Cortese (J. Amer. Chem. Soc., 1927, 49, 2640—2650; cf. A., 1925, i, 626).—The values of the (second order) reaction constants for the reaction between *p*-nitrobenzoyl chloride and 18 alcohols, under the conditions previously laid down, have been determined. From the results obtained, together with those previously reported, the following conclusions are reached: (1) in normal primary alcohols, the reactivity of the hydroxyl hydrogen decreases progressively in the first three members, increases progressively for the next three, and then decreases again; the same applies to secondary alcohols with the hydroxyl group in the β-position; (2) the introduction, into a primary alcohol, of a methyl group as a side-chain is of greater effect than a corresponding increase in the length of the carbon chain; this effect is greatest in the α-position, decreases progressively in the β- and γ-positions, and then begins to increase again; (3) the percentage reduction in reaction constant effected by the introduction of a methyl group as a side-chain is of the same order of magnitude whatever the length of the chain, for the same position of substitution; the relative effect is less in the β- than in the α-position; (4) the values of the constants of the secondary alcohols containing 3, 4, 5, and 6 carbon atoms are, respectively, 15·8, 10·0, 7·5, and 7·6% of those of the primary alcohols containing the same number of carbon atoms, the effect in this case increasing with increasing mol. wt. in the first three members of the series; (5) the constants of tertiary alcohols containing four and five carbon atoms are, respectively, 3·7 and 3·2% of those of the corresponding primary alcohols; (6) the reactivity is markedly dependent on the position of the hydroxyl group in a straight chain, the constants of α-, β-, and γ-hydroxy-*n*-pentanes being in the ratio 1 : 0·075 : 0·045; (7) with aromatic alcohols, there is an alternation in the value of the constant as the phenyl radical is removed from the hydroxyl group, but the phenyl group depresses the reactivity in all cases examined. With all the alcohols so far examined, the value of the reaction constant decreases slowly after a certain proportion of the alcohol has been esterified. With primary alcohols, this drift sets in after 20—35%, with secondary alcohols after 4—7%, and with tertiary alcohols after still smaller percentage conversions.
F. G. Willson.

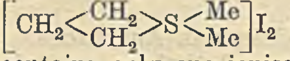
Decomposition of pentaerythrityl tetraformate by heat. P. van Romburgh (Z. physikal. Chem., 1927, 130, 334—336).—Pentaerythrityl tetraformate, m. p. 57°, formed by heating 1 mol. of pentaerythritol with 8 mols. of concentrated formic acid, decomposes quantitatively when heated at 220° : $C_5H_8(CO_2H)_4 \longrightarrow C_5H_8(OH)_4 + 4CO$. The formates of other αγ-glycols undergo a partial decomposition at considerably higher temperatures. L. L. Bircumshaw.

Polymerisation products of propylene oxide and of glycidol. P. A. Levene and A. Walti (J. Biol. Chem., 1927, 75, 325—336).—On distillation of propylene glycol with sulphuric acid, or on distillation of dihydroxypropyl ether (see below), there was obtained the *substance*  $CHMe{<}{\substack{CH_2{-}O\\O{\cdot}CHMe}}{>}CH_2$, b. p. 117—125°; this compound was also obtained by heating propylene oxide for 4 weeks at 165—170°. Propylene oxide, $[\alpha]_D^{20}$ +10·3°, on prolonged heating with potassium hydroxide, gave a termolecular condensation *product*, $C_9H_{20}O_4$, b. p. 128—130°/2·4 mm., $[\alpha]_D^{20}$ −43·0°, and a quadrimolecular *product*, $C_{12}H_{26}O_5$, b. p. 130—140°/2·4 mm., $[\alpha]_D^{20}$ −49·19°; these products, together with dihydroxypropyl ether, were formed on prolonged heating of propylene oxide with propylene glycol, the reaction proceeding at a lower temperature and more rapidly in presence of sulphuric acid; thus propylene oxide, $[\alpha]_D^{20}$ −10·3°, with optically active propylene glycol gave *dihydroxypropyl ether*, b. p. 129—132°/30 mm., $[\alpha]_D^{20}$ −36·4°. Glycidol, on heating at 100° for 42 hrs., gave a compound which, on hydrolysis with sulphuric acid, yielded diglyceryl ether and, on treatment with ammonia, took up less than one amino-group; it is regarded as



$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH{<}{\substack{O\\|\\CH_2}}$; on stronger and more prolonged heating a compound with the same empirical formula and mol. wt. 444 was obtained. C. R. Harington.

The supposed dimethiodide of trimethylene sulphide. G. M. Bennett and A. L. Hock (J.C.S., 1927, 2496—2499).—This substance, hitherto regarded as possessing the unique structure



$\left[CH_2{<}{\substack{CH_2\\CH_2}}{>}S{<}{\substack{Me\\Me}}\right]I_2$ (A., 1917, i, 153), actually contains only one ionised iodine atom and yields a *chloroaurate* and a *chloroplatinate* both containing iodine. It is really dimethyl-γ-iodopropylsulphonium iodide. The trimethylene sulphide ring of the intermediate monomethiodide ruptures to give methyl γ-iodopropyl sulphide, which then reacts with methyl iodide to give the sulphonium iodide. This view is confirmed by synthesis: γ-hydroxypropyl mercaptan, on methylation with methyl sulphate, yields *methyl γ-hydroxypropyl sulphide*, b. p. 102°/24 mm., d_4^{20} (vac.) 1·030, which in turn is converted into impure *dimethyl-γ-hydroxypropylsulphonium iodide* by methyl iodide.

Treatment of the last-named substance with hydrogen iodide in xylene yields *dimethyl-γ-iodopropylsulphonium iodide*, m. p. 97·5°, identical with the supposed dimethiodide. G. A. C. Gough.

Refractivity and dispersivity of normal monobasic aliphatic acids. H. I. Waterman and S. H. Bertram (Rec. trav. chim., 1927, 46, 699—702).—The refractivity and dispersivity of the normal aliphatic acids of 2 to 18 carbon atoms (with the exception of the C_6 acid, for which *iso*butylacetic acid was used) have been determined at 70° for the sodium line and the *C*, *F*, and *G′* lines of the hydrogen spectrum. The lower acids were fractionally distilled, and the middle acids also, in a cathodic vacuum; the higher acids were crystallised from acetone. The following are the respective values for n_D^{70}: C_2, 1·3531; C_3, 1·3662; C_4, 1·3775; C_5, 1·3877; C_6, 1·3967; C_7, 1·4029; C_8, 1·4085; C_9, 1·4130; C_{10}, 1·4170; C_{11}, 1·4203; C_{12}, 1·4225; C_{13}, 1·4249; C_{14}, 1·4268; C_{15}, 1·4287; C_{16}, 1·4303; C_{17}, 1·4319; C_{18}, 1·4332.

The increments in $n_D.M$ in passing from one acid to the next higher form two series, and are at first greater when passing to an acid with an odd number of carbon atoms, but after undecoic acid are greater for the reverse direction. E. W. Wignall.

Determination of mixtures of isomeric unsaturated compounds. II. Iodometric methods. R. P. Linstead and C. J. May (J.C.S., 1927, 2565—2579; cf. this vol., 445).—A solution of iodine in aqueous potassium iodide reacts with Δ^1-*cyclo*hexenylacetic acid in aqueous sodium carbonate to afford the *γ-lactone* of 1-*iodo*-2-*hydroxy*cyclo*hexylacetic acid*, m. p. 58°. The amounts of the components in a mixture of the above acid with *cyclo*hexylideneacetic acid may be determined to within 5% (see also Bougault, A., 1908, i, 537) by the preferential addition of iodine to the βγ-unsaturated acid under standard conditions. A new explanation for the mechanism of the addition is suggested. The method is applied to acids which cannot be separated from their isomerides (dialkylacrylic acids). Measurements are made of the addition of bromine to mixtures of the isomeric ethyl*cyclo*hexenones and of iodine chloride to the ethyl esters of *cyclo*hexylideneacetic, Δ^1-*cyclo*hexenylacetic, and styrylacetic acids and the results used to determine the composition of equilibrium mixtures of these substances.

G. A. C. Gough.

Three-carbon system. XIV. Effect of conditions on isomeric change in unsaturated acids. R. P. Linstead (J.C.S., 1927, 2579—2585).—The iodine addition method (preceding abstract) shows that an equilibrium mixture of Δ^1-*cyclo*hexenylacetic acid and *cyclo*hexylideneacetic acid contains 88% of the former acid and that this value is independent of temperature, pressure, and concentration of either the acid or the catalytic alkali. The velocity of interconversion is diminished by dilution and especially by decrease of the concentration of the alkali. The results indicate the optimum conditions for hydrolysis of an ester of an unstable, unsaturated acid without movement of the double linking. G. A. C. Gough.

Action of formates on silver acetate. G. Gurevitsch and E. Pokrovskaya (Ukraine Chem. J., 1926, 2, 414—429).—The action of silver acetate on various salts of formic acid, given by the equation, $2AgOAc+H\cdot CO_2M \longrightarrow 2Ag+CO_2+MOAc+AcOH$, has been studied with the view of determining the effect of various cations on the velocity coefficient, *K*, the latter being calculated from the usual equation for a termolecular reaction. The reaction was carried out at 80°, the concentrations of the silver acetate and the formate being 0·04 and 0·02 g.-mol./litre, respectively. Halving the concentration doubled *K*. The velocity coefficient increases somewhat with the duration of the reaction, but its average value remains constant for the cations, $Na^{\cdot}$, $K^{\cdot}$, $H^{\cdot}$, $Sr^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot}$. When the concentration of the formate was increased to 100 times that of the silver acetate, and the temperature lowered to 45°, *K* remained constant throughout the reaction, but was greater for a univalent than for a bivalent ion. For ions of the same valency, increase of atomic weight led to an increase of *K*. In the case of formic acid itself, the velocity coefficient was one thirtieth of that for potassium formate. E. Rothstein.

Metallic derivatives of the enolic forms of monocarbonyl compounds. IX. Condensations of ethyl acetate. X. Preparation and properties of ketenacetals. H. Scheibler and E. Marhenkel (Annalen, 1927, 458, 1—39).—The mixture (I) obtained by treating ethyl acetate with sodium, sodamide, or sodium ethoxide at a low temperature contains the "primary reaction product" (II), ethyl sodioacetoacetate, and the additive product $CMe(ONa)(OEt)_2$. The proportion of each (*e.g.*, 13·1%, 34·6%, and 52·3%, respectively) may be determined by comparing the amounts of acetic acid formed when the mixture is treated with water at 60° and with 20% sulphuric acid (cf. A., 1922, i, 426). The behaviour of (II) towards benzaldehyde shows that it cannot have the constitution $COMe\cdot CH_2\cdot C(OEt)_2\cdot ONa$ (A., 1925, i, 1417), and it is now regarded as a quinhydrone-like sodio-derivative of ethyl acetate, $\left[\begin{matrix}CH_3\cdot C(OEt){:}O\cdots\\ CH_2{:}C(OEt)\cdot O—\end{matrix}\right]Na$. When (I) is heated alone or in ethyl acetate (II) evolves ethyl alcohol, forming ethyl sodioacetate. Neither this product nor that obtained by refluxing the latter compound with alcohol yields ketenacetal when decomposed by water. Acetone, ethyl alcohol, and sodium carbonate, as well as ketenacetal, are obtained by treating (I) with water at 80°. The new formula explains simply these and other characteristic reactions of the substance (II). In general, the following steps are postulated in the condensation of two carbonyl compounds, at least one of which forms an enol (Claisen, acetoacetic, aldol, and cinnamic ester condensations): (*a*) formation of a metallic ketyl (with sodium) or of an additive compound (with sodamide or sodium ethoxide), (*b*) conversion into a sodio-enolate with loss of hydrogen or alcohol, (*c*) formation with a further mol. of ketone of a complex of type (II), (*d*) condensation within the complex. The statement of Adickes (A., 1925, i, 1378) that only esters containing adjacent carbonyl groups form alkali alkoxide additive products is shown to be incorrect. Reasons are given for preferring the new mechanism for the acetoacetic condensation to the older (cf. Swarts, this vol., 132) and newer (A., 1905, i, 258) mechanisms of Claisen.

[With R. Nikolić.]—When the primary reaction product from sodium propoxide and propyl acetate is treated with water and the propyl alcohol removed from the product as the phenylurethane, *keten dipropylacetal*, b. p. 104—106°, d_4^{22} 0·7999, n_D^{22} 1·3769, is obtained. Similarly, using the appropriate ester and alkali alkoxide, *keten di*iso*butylacetal*, b. p. 110—112°, d_4^{20} 0·8145, n_D^{20} 1·3966; *keten di*iso*amylacetal*, b. p. 131—133°, d_4^{19} 0·8104, n_D^{19} 1·4021; *ethoxyketen diethylacetal* (*triethoxyethylene*), b. p. 163—165°, d_4^{22} 0·9047, n_D^{22} 1·4038, and *methylketen diethylacetal*, b. p. 78—81°, d_4^{18} 0·8002, n_D^{18} 1·3673, are prepared in 5—10% yield. Ketenacetals are also obtained in slightly smaller yield by treating the primary reaction products successively with phosphoryl chloride and sodium alkoxide. The reaction, which affords evidence in favour of formulæ of the type (II), is represented thus: $(II) \longrightarrow [CH_2{:}C(OEt){\cdot}O{\cdot}]_3PO \longrightarrow CH_2{:}CCl{\cdot}OEt) \longrightarrow CH_2{:}C(OEt)_2$ (cf. Scheibler, this vol., 338). Unlike those containing negative groups (cf. Reitter and Weindel, A., 1907, i, 748; Staudinger, A., 1922, i, 1015), the above ketenacetals are fairly stable towards water and alkalis. Keten diethylacetal is rapidly oxidised by alkaline permanganate, probably to ethyl hydrogen oxalate, since oxalic acid is formed on hydrolysis. With bromine it yields ethyl bromide and ethyl bromoacetate, and with sodamide in ethereal solution, ammonia, sodium ethoxide, and *sodium ethoxyacetylide*, $CNa{:}C{\cdot}OEt$. The white *silver ethoxyacetylide* decomposes in presence of water, giving metallic silver. Similarly phenylketen diethylacetal and sodamide in benzene give a product, b. p. 100—120°/15 mm., containing ethoxyphenylacetylene, which is converted by water into phenylacetic acid.

H. E. F. Notton.

Interaction of bromine with acetic anhydride. II. K. J. P. Orton, H. B. Watson, and H. I. Hughes (J.C.S., 1927, 2458—2465).—Contrary to previous observations (*ibid.*, 1912, **101**, 1722; 1923, **123**, 3081), it is found that pure acetic anhydride is attacked by bromine at the ordinary temperature in the absence of light. Measurements of the velocity of the reaction indicate that hydrogen bromide, formed in minute amount by direct bromination, reacts with the anhydride to give acetic anhydride and acetyl bromide. The latter is rapidly brominated and then reacts with further acetic anhydride to give bromoacetic anhydride and to regenerate acetyl bromide. Hydrogen, acetyl, propionyl, or benzoyl bromides accelerate the reaction as do ferric chloride, stannic chloride, iodine, iodine chloride, and sulphuric acid; the latter class of substance probably induce enolisation and direct bromination of the anhydride. The reaction is completely inhibited by traces of quinoline (probably contained in the samples used in previous work) and partly by other basic substances and alkali bromides. Nitric acid and acetyl nitrate have powerful inhibitory action. G. A. C. Gough.

Action of acetic anhydride containing sulphoacetic acid on aliphatic double linkings. F. Ebel and M. W. Goldberg (Helv. Chim. Acta, 1927, **10**, 677—680).—When treated with acetic anhydride containing 2% of sulphuric acid, *cyclo*hexene undergoes a condensation of the Friedel and Crafts type, giving Δ^1-*cyclo*hexenyl methyl ketone (cf. A., 1922, i, 1033). An intermediate compound cannot be isolated. The reagent has no action on ethylene, methyl cinnamate, or safrole. *d*-Pinene affords, on gentle treatment at 100°, a mixture from which (*a*) a fraction, b. p. 156—158°/720 mm., d_4^{20} 0·853, n_D^{23} 1·4683, containing hydrocarbons, $C_{10}H_{16}$ and $C_{10}H_{18}$, probably pinene and a monocyclic terpene with one double linking, respectively, and (*b*) a triply unsaturated *diterpene*, b. p. 170°/12 mm., d_4^{20} 0·923, n_D^{20} 1·5143, are obtained. Vigorous treatment at 120° gives a *substance*, $C_{10}H_{16}O$, b. p. 215°/727 mm., d_4^{20} 0·956, n_D^{23} 1·4853, probably a monocyclic unsaturated ketone.

H. E. F. Notton.

Halogeno-acylato-compounds of quadrivalent titanium. M. Giua and E. Monath (Z. anorg. Chem., 1927, **166**, 306—310).—By the action of titanium tetrachloride on formic, propionic, butyric, and *iso*valeric acids, respectively, mixtures of substances have been obtained, similar to the compound previously described in the case of acetic acid (A., 1925, i, 531). An analogous bromine *compound*, $Ti_2Br_4(OAc)_4$, is formed by interaction between titanium tetrabromide and a mixture of acetic acid and acetic anhydride. Titanium chloroacetate reacts with alizarin to form a substance which is probably a type of lake. R. Cuthill.

Derivatives of petroselic and petroselidic acids. A. Steger and J. van Loon (Rec. trav. chim., 1927, **46**, 703—708).—By heating pure petroselic acid (van Loon, this vol., 853) with glycerol and zinc dust (2%), pure tripetroselin, m. p. 26·2°, iodine value 85·9, saponification value 189·8 (cf. Vongerichten and Köhler, A., 1909, i, 454), is obtained; the same product is prepared by crystallisation of the natural glyceride of parsley-seed oil from an ether–alcohol mixture. The product of the action of nitrogen peroxide on petroselic acid, m. p. 52·7° (cf. Hilditch and Jones, this vol., 540), is, by analogy with elaidic acid, named "petroselidic acid"; it yields similarly *tripetroselidin*, m. p. 50·1°. Oxidation by alkaline potassium permanganate yields dihydroxy-acids, m. p. 122·2° from petroselic acid, 117·2° from petroselidic acid. Methyl petroselate is oxidised by perbenzoic acid in chloroform to an εζ-oxidostearic acid, m. p. 59·2°, converted by sulphuric acid into a water-soluble derivative, which on warming in water yields the dihydroxy-acid of m. p. 117·0° (obtained by oxidising petroselidic acid). Methyl petroselidate, m. p. 20·0°, yields similarly an εζ-oxidostearic acid of m. p. 65·4°, converted into the dihydroxy-acid, m. p. 122·0°, obtained from petroselic acid. E. W. Wignall.

Salts of α-linolic tetrabromide from Philippine Lumbang oil. C. M. Jovellanos and A. P. West (Philippine J. Sci., 1927, **33**, 349—356).—Metallic salts of α-linolic tetrabromide, obtained as previously described (this vol., 304), have been prepared by a general method of conversion into the potassium salt, which then interacts, in alcoholic solution, with the solution of the inorganic salt. The following salts are described: *cadmium*, m. p. 135·7—137·8°; *cobalt*,

m. p. 156·5° to opaque drops stable at 190°; *copper*, m. p. 145·4°; *magnesium*, m. p. 150·1—151·7°; and *manganese*, m. p. 144·9—147·5°. A table of solubilities is given for seventeen organic liquids.

E. Holmes.

α-Elæostearic acid from tung oil. J. Böeseken [with W. C. Smit, J. J. Hoogland, and A. G. van den Broek] (Rec. trav. chim., 1927, 46, 619—634).—In continuation of earlier work (A., 1925, i, 507, 1129), and to confirm the theory that α-elæostearic acid contains three conjugated double linkings between the θ and ν carbon atoms, the action of "peracetic" acid (a mixture of glacial acetic acid and 60% hydrogen peroxide) and of catalytic hydrogenation under pressure on α-elæostearic acid and its partly brominated derivatives has been examined mainly along the line of determining the times necessary for saturation of the various double linkings. All the observed facts are accounted for if the acid has the structure indicated, and if addition occurs according to Thiele's hypothesis. When acted on by Wijs' solution two of the three linkings are saturated, under given conditions, in less than ½ hr., whilst the third requires 6 days, this being in accordance with the behaviour of known conjugated systems. In the case of bromine, two molecules are introduced rapidly, but the third is added only under the influence of ultra-violet light. When tetrabromo-α-elæostearic acid is treated with "peracetic" acid 90% of the theoretical amount of oxygen is absorbed after 8 days. From the reaction product is isolated *tetrabromodihydroxymonoacetylstearic acid*, m. p. 106°. When free α-elæostearic acid is treated with one, two, and three mols. of "peracetic" acid the results are complicated by the fact that it is found impossible to control the reaction so that only one, or only two double linkings are completely saturated before further addition begins, that the hydroxyl groups inserted are so situated that ring closure by loss of water is possible to give a variety of anhydrides, and further that acetylation may also proceed at one or more of the free hydroxyl groups. It is probable that the final substance is a saturated acid having three pairs of carbon atoms bridged through single atoms of oxygen. Catalytic hydrogenation under pressure allows the reaction to proceed at comparatively low temperatures. As before, progressive saturation of the double linkings follows Thiele's hypothesis, and the introduction of two molecules of hydrogen gives an oleic acid having the double linking between the κ and λ carbon atoms.

E. Holmes.

Dehydrogenation of succinic acid. A. Hahn and W. Haarmann (Z. Biol., 1927, 86, 523—524; cf. Bach and Michlin, this vol., 591; Thunberg, A., 1918, i, 140, ii, 87; 1920, i, 784).—A preliminary account of experiments on the action of muscle on succinic acid in presence of methylene-blue and in absence of oxygen, in which malic acid and a smaller quantity of fumaric acid were isolated. The evidence favours the view that the succinic acid provides the hydrogen necessary for the reduction of the dye, being itself oxidised to fumaric acid, which rapidly adds water under the influence of a special ferment to form malic acid.

W. J. Powell.

Stereochemical studies. XIV. Hydrolysis of esters. XV. Alkaline decomposition of monochlorosuccinic acid. XVI. Hydrolysis of the monohalogenosuccinic acids. B. Holmberg (Ber., 1927, 60, [*B*], 2185—2194, 2194—2198, 2198—2211).—XIV. It appears generally valid to consider that during hydrolysis of a carboxylic ester by water without hydrogen-ion catalysis the alkyl group of the ester unites with the hydroxyl from the water: $\mathrm{R'O{\cdot}CO{\cdot}R+HO{\cdot}H=R'{\cdot}OH+HO{\cdot}CO{\cdot}R}$. Hence in those esters which are hydrolysed only in the presence of hydrogen ions it is probable that the union between the carbinol carbon and the oxygen atom is so firm that hydrolysis takes place according to the scheme:

$$\mathrm{R'O{\cdot}CO{\cdot}R}+\overset{+}{\mathrm{H}}(\mathrm{H_2O})_x=\mathrm{R'{\cdot}OH+HO{\cdot}CO{\cdot}R}+\overset{+}{\mathrm{H}}(\mathrm{H_2O})_{x-1}.$$

The cause of the change lies in the tendency of the alkoxy-radical to unite with hydrogen to form an electrically slightly dissociated compound and the ability of the ion, owing to its hydration, to bring all the elements required for the completion of the change. It is therefore to be expected that other ions containing atoms prone to complex formation with alkoxy-groups will be catalytically active in ester hydrolysis or, more generally expressed, that hydrogen-ion catalysis is only a special instance of a more general complex catalysis. The existence of this new type of catalysis is established by measurement of the rate of hydrolysis of sodium acetoxyacetate in aqueous solution alone and in the presence of copper sulphate (catalyst $\overset{+}{\mathrm{Cu}}\mathrm{OH}$), barium acetoxyacetate and copper sulphate, sodium acetoxyacetate, sodium acetate, or sodium glycollate and copper sulphate, acetoxyacetic acid and copper sulphate, sodium *dl*-acetylmalate or sodium monohalogenosuccinates and copper sulphate.

XV. The decomposition of monochlorosuccinic acid by alkalis consists of two changes, the first unimolecular, in which the hydroxyl ion reacts with the ion of monochlorosuccinic acid with the production of the ion of fumaric acid and bromine, and the second a bimolecular reaction in which the chlorosuccinic ion forms first the ion of propiolactonecarboxylic acid and the bromine ion and ultimately malic acid. The expressions $C_2=0{\cdot}444\times[\mathrm{Na}^{\cdot}]^{\frac{1}{2}}=0{\cdot}80\times[\mathrm{Ba}]^{1/3}$ are valid for the bimolecular reaction between sodium chlorosuccinate and sodium hydroxide or barium chlorosuccinate and barium hydroxide, whereas according to Johansson (A., 1913, ii, 126) the corresponding expressions for bromosuccinic acid are $C_2=5{\cdot}7\times[\mathrm{Na}^{\cdot}]^{\frac{1}{2}}=11{\cdot}8\times[\mathrm{Ba}]^{1/3}$.

XVI. The isolation of (+)-propiolactonecarboxylic acid permits its conversion by ammonia into *d*(+)-β-malamic acid and hence establishes its position in the *d*-series. Since it is transformed by alkalis into *d*(+)-malic acid the change occurs without inversion under the influence of hydroxyl ions. Analogously, the addition of other anions must be supposed to occur without inversion and the lævorotatory halogeno- and sulphur-substituted succinic acids must be regarded as *d*(−)-forms. Conversely, the transformation of an active halogenosuccinic acid into propiolactonecarboxylic acid of the opposite sign occurs without inversion. Hydrolysis of *d*(+)-propiolactonecarboxylic acid in more or less acidic solution gives lævorotatory malic acid and is thus accompanied by inversion. Related to this is the observation that the small quantities of malic acid obtained by the alkaline decomposition of *d*(—)-halogenosuccinic acids are invariably dextrorotatory, whereas decomposition in acid solution generally gives lævorotatory malic acid as shown by Walden's classical experiments and a new series. Inversion during the hydrolysis of propiolactonecarboxylic acid is at first sight surprising, since it is not observed during the hydrolysis of carboxylic esters, acetylmandelic acid, or acetylmalic acid. The reactions do not, however, proceed in the same manner, since, in the first case, hydrogen ions are not generally involved to an appreciable extent. The steric relationships involved in the conversion of a *d*(—)-halogenosuccinic acid into malic acid are expressed by the schemes:

$$d(-)\text{-}\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CHX\cdot CH_2\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2}=d(+)\text{-}\overset{-}{\mathrm{C}}\mathrm{O_2\cdot}\underline{\mathrm{CH\cdot CH_2\cdot CO\cdot O}}+\overset{-}{\mathrm{X}};\ d(+)\text{-}\overset{-}{\mathrm{C}}\mathrm{O_2\cdot}\underline{\mathrm{CH\cdot CH_2\cdot CO\cdot O}}+\overset{-}{\mathrm{O}}\mathrm{H}=$$

$$d(+)\text{-}\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CH(OH)\cdot CH_2\cdot CO_2};\ d(+)\text{-}\overset{-}{\mathrm{C}}\mathrm{O_2\cdot}\underline{\mathrm{CH\cdot CH_2\cdot CO\cdot O}}+\mathrm{H_2O}=l(-)\text{-}\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CH(OH)\cdot CH_2\cdot CO_2H};$$

$$d(+)\text{-}\underline{\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CH\cdot CH_2}}\mathrm{\cdot CO\cdot O}+\overset{+}{\mathrm{H}}\mathrm{(H_2O)}_x=$$

$d(+)\text{-}\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CH(OH)\cdot CH_2\cdot CO_2H}+\overset{+}{\mathrm{H}}\mathrm{(H_2O)}_{x-1}$. Further possibilities are expressed by the schemes:

$\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CHX\cdot CH_2\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2}+\overset{-}{\mathrm{O}}\mathrm{H}=\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CH(OH)\cdot CH_2\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2}+\overset{-}{\mathrm{X}}$ and $\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CHX\cdot CH_2\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2}+\mathrm{H_2O}=\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CH(OH)\cdot CH_2\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2}+\overset{+}{\mathrm{H}}+\overset{-}{\mathrm{X}}$, but since the yields of fumaric acid are greater and of malic acid smaller as the acidity or alkalinity of the solution increases it appears that in these cases the reactions $\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CHX\cdot CH_2\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2}+\overset{-}{\mathrm{O}}\mathrm{H}=\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CH{:}CH\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2}+\mathrm{H_2O}+\overset{-}{\mathrm{X}}$ and $\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CHX\cdot CH_2\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2}=\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CH{:}CH\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2}+\overset{+}{\mathrm{H}}+\overset{-}{\mathrm{X}}$ almost completely dominate. Complication due to the formation of compounds of the type $\overset{-}{\mathrm{C}}\mathrm{O_2\cdot CH(CH_2\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2)\cdot O\cdot CO\cdot CHX\cdot CH_2\cdot}\overset{-}{\mathrm{C}}\mathrm{O_2}$ do not appear to occur in dilute solution (cf. Senter, A., 1912, i, 828). The above deductions do not appear to be in harmony with Walden's observations as far as experiments with the hydroxides of tin, lead, cadmium, and copper are concerned. The nature of the metals indicates that hydrolysis in these cases is not due to hydrogen or hydroxyl ions, but to metallic ions as a consequence of complex catalysis. This view is confirmed by a lengthy series of experiments in which it is shown that the cupric ion favours the production of *d*(+)-malic acid so pronouncedly that the action is appreciable in acid solution. A similar effect is produced by beryllium and aluminium ions which have a marked tendency to form complexes with hydroxy-acids, whereas the magnesium ion does not differ appreciably from the calcium ion. In agreement with the influence of the cupric ion on the hydrolysis of propiolactonecarboxylic acid, inversion is not observed when copper hydroxide acts on *l*(—)-acetylmalic acid.

H. WREN.

Methylpolymethylenedicarboxylic acids connected with the investigation of muscone. L. RUZICKA. I. [with R. STEIGER] **Syntheses from citronellal.** II. [with M. STOLL] **Synthesis of β-methyltridecane-αν-dicarboxylic acid** (Helv. Chim. Acta, 1927, 10, 680—694).—Citronellideneacetic acid is readily prepared in quantity by the method of Rupe and Lotz (A., 1903, i, 841). The ethyl ester, obtained almost pure by using 1% alcoholic sulphuric acid, is reduced by sodium and alcohol, first to *citronellylacetic acid* (*δθ-dimethyl-*Δ^{η}*-decenoic acid*) (I), b. p. 168—169°/12 mm., d_4^{18} 0·9211, n_D^{18} 1·4595 (*ethyl* ester, b. p. 145—155°/12 mm., $[\alpha]_D$ —2·0°); then to *ει-dimethyl-*Δ^{θ}*-decen-α-ol*, b. p. 140—150°/12 mm., d_4^{15} 0·865, $[\alpha]_D$ —1·25°. This is converted by dry hydrogen bromide into *α-bromo-ει-dimethyl-*Δ^{θ}*-decene*, b. p. 145—150°/15 mm., d_4^{15} 1·06, which condenses with ethyl malonate giving ethyl *ζκ-dimethyl-*Δ^{ι}*-undecene-αα-dicarboxylate*, b. p. 160—165°/0·5 mm., $[\alpha]_D$ —2·0°, converted by hydrolysis and distillation into *ζκ-dimethyl-*Δ^{ι}*-dodecenoic acid*, b. p. 178—180°/12 mm., $[\alpha]_D$ —1·6° (*ethyl* ester, b. p. 155—165°/12 mm., $[\alpha]_D$ —1·6°). By repeating these operations the following series of compounds is prepared: *ηλ-dimethyl-*Δ^{κ}*-dodecen-α-ol*, b. p. 160—165°/13 mm., $[\alpha]_D$ —1·0°; *α-bromo-ηλ-dimethyl-*Δ^{κ}*-dodecene*, b. p. 155—160°/12 mm., *ethyl θμ-dimethyl-*Δ^{λ}*-tridecene-αα-dicarboxylate*, b. p. 180—185°/1 mm., $[\alpha]_D$ —1·0°; *θμ-dimethyl-*Δ^{λ}*-tetradecenoic acid* (II), b. p. 160—165°/1 mm. (*ethyl* ester, b. p. 185—190°/12 mm., $[\alpha]_D$ —1·0°); *ιν-dimethyl-*Δ^{μ}*-tetradecen-α-ol*, b. p. 178—182°/12 mm., $[\alpha]_D$ —0·85°; *α-bromo-ιν-dimethyl-*Δ^{μ}*-tetradecene*, b. p. 170—175°/12 mm., which is converted through the nitrile into *ιν-dimethyl-*Δ^{μ}*-pentadecenoic acid* (III), b. p. 170°/0·5 mm.; *ethyl κξ-dimethyl-*Δ^{ν}*-pentadecene-αα-dicarboxylate*, b. p. 175—180°/0·5 mm., $[\alpha]_D$ —0·6°; *κξ-dimethyl-*Δ^{ν}*-hexadecenoic acid* (IV), b. p. 175—180°/1 mm. (*ethyl* ester, b. p. 200°/11 mm.); *λο-dimethyl-*Δ^{ξ}*-hexadecen-α-ol*, b. p. 195—200°/13 mm.; *α-bromo-λο-dimethyl-*Δ^{ξ}*-hexadecene*, b. p. 190—200°/10 mm., which is converted through the nitrile into *λο-dimethyl-*Δ^{ξ}*-heptadecenoic acid* (V), b. p. 190°/0·5 mm. The new acids are oxidised by ozone and chromic acid to methylated dicarboxylic acids, from which the second higher homologues may be prepared by standard methods (cf. A., 1926, 499). Thus, from (I) is obtained *γ-methylhexane-αζ-dicarboxylic acid*, m. p. 81°, b. p. 190—210°/12 mm. (*ethyl* ester, b. p. 150—160°/13 mm.); from (II), *γ-methyldecane-ακ-dicarboxylic acid*, m. p. 71° (*ethyl* ester, b. p. 140°/0·5 mm.), and *δ-methyldodecane-αμ-dicarboxylic acid*, m. p. 74—75°; from (III), *γ-methylundecane-αλ-dicarboxylic acid*, b. p. 190—200°/0·5 mm., m. p. 47°, and *δ-methyltridecane-αν-dicarboxylic acid*, m. p. 54—55°; from (IV), *γ-methyldodecane-αμ-dicarboxylic acid*, m. p. 76—77°; *δ-methyltetradecane-αξ-diol*, b. p. 200°/0·4 mm.; *αξ-dibromo-δ-methyltetradecane*, b. p. 165—170°/0·5 mm., and *δ-methyltetradecane-αξ-dicarboxylic acid*, m. p. 75—76°, and from (V), γ-methyltridecane-αν-dicarboxylic acid, b. p. 200°/0·5 mm., m. p. 62—63° (cf. Chuit, Boelsing, and Malet, this vol., 446). All the dicarboxylic acids prepared in this way, except γ-methylhexane-αζ-dicarboxylic acid, are optically inactive, the γ-methyl derivatives, unlike the corresponding β-methyl derivatives (this vol., 57), being racemised by alkali. Many of these acids when apparently pure exhibit variations in m. p. which are attributed to the presence of allotropic forms.

Regulated hydrolysis of ethyl undecane-αλ-dicarboxylate affords the monoethyl ester, converted by thionyl chloride at the ordinary temperature into *ethyl* λ-*chlorocarbonyldodecoate*, b. p. 185—188°/5 mm., which yields with ammonia *ethyl* λ-*carbamidododecoate*, m. p. 91—92°. The acid chloride reacts with zinc methyl iodide (cf. Blaise, A., 1914, i, 141) forming *ethyl* μ-*ketotetradecoate* (I), b. p. 164—166°/1 mm. (*semicarbazone*, m. p. 105—106°). In the same way ethyl azelate yields *ethyl* η-*chlorocarbonyloctoate*, b. p. 155—158°/15 mm., and *ethyl* θ-*ketodecoate*, b. p. 151—153°/11 mm. (*semicarbazone*, m. p. 102—103°), and ethyl sebacate yields ethyl θ-*chlorocarbonylnonoate*, b. p. 168—170°/15 mm., and *ethyl* ι-*ketoundecoate*, b. p. 161—163°/12 mm. The keto-ester (I) with zinc and ethyl bromoacetate gives a mixture of *ethyl* β-*hydroxy*-β-*methyltridecane*-αν-*dicarboxylate* and *ethyl* β-*methyl*-Δ^{α}-*tridecene*-αν-*dicarboxylate*, from which the latter, b. p. 186—187°/2 mm., is obtained by treatment with phosphorus tribromide, hydrolysis with alkali, and re-esterification. It is hydrogenated in presence of platinum-black to *ethyl* β-*methyltridecane*-αν-*dicarboxylate*, b. p. 186—187°/2 mm., from which β-methyltridecane-αν-dicarboxylic acid (this vol., 57, 446) (*dihydrazide*, m. p. 148—152°; *diamide*, m. p. 145—150°; *dianilide*, m. p. 131—133°) is obtained.

H. E. F. NOTTON.

Condensation products of *d*-tartaric and of malic acid with chloral. F. H. YORSTON (Rec. trav. chim., 1927, 46, 711—714).—*d*-Tartaric acid and chloral hydrate condense in presence of concentrated sulphuric acid to give the *chloralides* I, m. p. 160°, $[\alpha]_D$ +42° to 48°, according to solvent; and II, m. p. 173°, $[\alpha]_{5780}$ −54·6° in benzene, +32·4° in acetone. One form only of *malic acid chloralide* was obtained, of rotation varying with the solvent.

E. W. WIGNALL.

Effect of ionisation on optical rotation. III. The βε-anhydro-sugar acids. P. A. LEVENE and L. W. BASS (J. Biol. Chem., 1927, 74, 727—737).—In the βε-anhydro-sugar acids, the difference in optical rotatory power between the undissociated acid and the acid ion is less than in the case of the sugar acids themselves (cf. A., 1924, i, 615); in the βε-anhydrodicarboxylic acids the change in rotation on passing from one molecular species to another is roughly proportional to the distance traversed by the ionisable groups.

C. R. HARINGTON.

Lactone formation of galactoarabonic and melibionic acids and its bearing on the structure of lactose and of melibiose. P. A. LEVENE and O. WINTERSTEINER (J. Biol. Chem., 1927, 75, 315—324).—Galactoarabinose was oxidised with barium hypoiodite to give *galactoarabonic acid* (*calcium* salt, $[\alpha]_D$ +33·6°); the free acid, $[\alpha]_D^{21}$ +31·9° at first, showed a diphasic mutarotation, indicating that the galactose is linked to the γ-carbon atom of the arabinose, and therefore, in lactose, to the δ-carbon atom of the dextrose (cf. Levene and Sobotka, this vol., 340). Melibionic acid, $[\alpha]_D^{20}$ +108·8° at first, showed a monophasic mutarotation similar to that of lactobionic acid (*loc. cit.*); in melibiose therefore the linking appears to be on the δ-carbon atom of the dextrose, which is in disagreement with the conclusions of Haworth and Leitch (J.C.S., 1918, **113**, 189) and of Zemplén (this vol., 545).

C. R. HARINGTON.

Walden inversion. X. Oxidation of α-thiolcarboxylic acids to sulphonic acids; Walden inversion in the series of α-hydroxycarboxylic acids. P. A. LEVENE, T. MORI, and L. A. MIKESKA (J. Biol. Chem., 1927, 75, 337—365).—In every sulphonic acid investigated the difference of rotation between the free acid and its salts is in the same sense as in the corresponding thiol acid; the change in polarity from $\cdot SH$ to $\cdot SO_3H$ involves therefore no change in configuration. Tables are given summarising the numerical values of the molecular rotations of α-substituted fatty acids and the occurrence or non-occurrence of Walden inversion in the interconversion of these derivatives. α-Bromo-*n*-butyric acid, $[\alpha]_D^{20}$ +12·9° in water (sodium salt, $[\alpha]_D^{20}$ +1·67°), gave l-α-*thiol*-n-*butyric acid*, b. p. 103—107°/15 mm., $[\alpha]_D^{20}$ −17·66° in ether (*monosodium* salt, $[\alpha]_D^{20}$ +1·38°; *dipotassium* salt, $[\alpha]_D^{20}$ +0·31°), which yielded l-α-*sulpho*-n-*butyric acid*, $[\alpha]_D^{20}$ −3·97° in water (*monopotassium* salt, $[\alpha]_D^{20}$ −2·09°). α-Bromo-*n*-valeric acid, on resolution through the quinine salt, gave d-α-*bromo*-n-*valeric acid*, b. p. 123—124°/15 mm., $[\alpha]_D^{20}$ +20·3° in water (*sodium* salt, $[\alpha]_D^{20}$ +7·28°), which was converted into *l*-α-*xantho*-n-*valeric acid*, $[\alpha]_D^{20}$ −18·1° in ether; this yielded l-α-*thiol*-n-*valeric acid*, b. p. 122—124°/13 mm., $[\alpha]_D^{20}$ −17·1° in ether (*monosodium* salt, $[\alpha]_D^{20}$ +0·44°, *disodium* salt, $[\alpha]_D^{20}$ +3·55°), which was oxidised to d-α-*sulpho*-n-*valeric acid*, $[\alpha]_D^{20}$ +0·96° (*disodium* salt, $[\alpha]_D^{20}$ +8·81°; *monosodium* salt, $[\alpha]_D^{20}$ +0·42°). α-Bromo*iso*valeric acid was best resolved by means of cinchonidine in acetone; the *l*-acid, $[\alpha]_D^{20}$ −7·7° in ether, gave d-α-*thiol*iso*valeric acid*, b. p. 114—115°/13 mm., $[\alpha]_D^{20}$ +13·3° in ether (*monosodium* salt, $[\alpha]_D^{20}$ +2·24°; *disodium* salt, $[\alpha]_D^{20}$ −4·03°), which was also obtained by direct resolution of α-thiol*iso*valeric acid with cinchonidine, and yielded d-α-*sulpho*iso*valeric acid*, $[\alpha]_D^{20}$ +1·80° (*monosodium* salt, $[\alpha]_D^{20}$ +0·98°; *disodium* salt, $[\alpha]_D^{20}$ −3·57°). α-Bromo-*n*-hexoic acid, resolved with strychnine, gave l-α-*bromo*-n-*hexoic acid*, b. p. 129—130°/14 mm., $[\alpha]_D^{20}$ −22·6° (*sodium* salt, $[\alpha]_D^{20}$ −7·22°), which yielded d-α-*thiol*-n-*hexoic acid*, b. p. 112—115°/1·8 mm., $[\alpha]_D^{20}$ +29·29° in ether (*monosodium* salt, $[\alpha]_D^{20}$ +0·76°; *disodium* salt, $[\alpha]_D^{20}$ −6·05°); this gave l-α-*sulpho*-n-*hexoic acid*, $[\alpha]_D^{20}$ −3·08° (*monosodium* salt, $[\alpha]_D^{20}$ −2·77°; *disodium* salt, $[\alpha]_D^{20}$ −14·43°). d-α-*Bromo*iso*hexoic acid*, $[\alpha]_D^{20}$ +29·8° in ether (*sodium* salt, $[\alpha]_D^{20}$ +10·37°), gave l-α-*thiol*iso*hexoic acid*, b. p. 126—126·5°/15 mm., $[\alpha]_D^{20}$ −15·6° in ether; d-α-*thiol*iso*hexoic acid*, $[\alpha]_D^{20}$ +19·4° in ether (*monosodium* salt, $[\alpha]_D^{21}$ −0·87°; *disodium* salt, $[\alpha]_D^{20}$ −11·68°), was obtained by resolution of α-thiol*iso*hexoic acid with quinine, and yielded l-α-*sulpho*iso*hexoic acid*, $[\alpha]_D^{20}$ −4·22° (*monosodium* salt, $[\alpha]_D^{20}$ −3·38°; *disodium* salt, $[\alpha]_D^{20}$ −16·9°). l-α-*Bromophenylacetic acid*, $[\alpha]_D^{20}$ −106·4°, gave d-α-*thiolphenylacetic acid*, m. p.

80—87°, $[\alpha]_D^{20}$ +114·5° in ether (*monosodium* salt, $[\alpha]_D^{20}$ +78·9°; *disodium* salt, $[\alpha]_D^{20}$ +33·2°), which yielded d-α-*sulphophenylacetic acid*, $[\alpha]_D^{20}$ +1·43° (*monosodium* salt, $[\alpha]_D^{20}$ +1·83°; *disodium* salt, $[\alpha]_D^{20}$ +5·6°). d-α-Bromo-*n*-valeric acid gave, with sodium carbonate, l-α-*hydroxy*-n-*valeric acid*, $[\alpha]_D^{20}$ −1·40° (*sodium* salt, $[\alpha]_D^{20}$ +2·65°); d-α-*hydroxy*-n-*hexoic acid* (from l-α-bromo-*n*-hexoic acid) had $[\alpha]_D^{20}$ +0·72° (*sodium* salt, $[\alpha]_D^{20}$ −4·02°); l-α-*hydroxy*-n-*hexoic acid*, by resolution of the inactive acid with cinchonidine in chloroform, had m. p. 60—61°, $[\alpha]_D^{20}$ −3·75° (sodium salt, $[\alpha]_D^{20}$ +14·77°); α-*bromo*iso*hexoic acid*, $[\alpha]_D^{20}$ 12·1°, gave l-α-*hydroxy*iso*hexoic acid*, $[\alpha]_D^{20}$ −0·53° (*sodium* salt, $[\alpha]_D^{20}$ −2·81°). C. R. HARINGTON.

Identification and determination of aldehydes and ketones. S. VEIBEL (Bull. Soc. chim., 1927, [iv], **41**, 1410—1416).—The m. p. of semicarbazones are appreciably lower when taken slowly than when determined quickly. For the determination of mol. wt. of semicarbazones, 0·1—0·2 g. is heated under reflux during 30 min. with water (100 c.c.) and concentrated sulphuric acid (10 c.c.) to effect complete dissolution. Potassium iodate (0·4—0·5 g.) is then added, and the mixture boiled until the colour of the iodine disappears. Ammonia is then determined by the usual method. For ten examples quoted the method is accurate to 0·6%, except for *o*-nitrobenzaldehydesemicarbazone. Application of the method to crude semicarbazones gives results which are usually high. H. BURTON.

Affinity, reactivity, and structure in acetal formation. II. W. H. GARTUNG and H. ADKINS (J. Amer. Chem. Soc., 1927, **49**, 2517—2524; cf. A., 1925, i, 784).—Equilibrium constants have been determined for the reactions between ethyl alcohol and amino-, bromo-, cyano-, and imino-acetaldehyde, β-chloropropaldehyde, glycollaldehyde, acraldehyde, crotonaldehyde, heptaldehyde, propaldehyde, acetaldehyde, butaldehyde, and cinnamaldehyde. The values of $-RT \log K$ indicate that the effect of a given substituent on affinity in the acetal reaction is not constant, either qualitatively or quantitatively. The same substituent may increase or decrease the affinity in different cases. Aminoacetal has b. p. 52—53°/2 mm., d^{25} 0·9161, n^{25} 1·4120; diacetalamine has b. p. 127—130°/3 mm., d^{25} 0·9541, n^{25} 1·4210 (cf. Wohl, A., 1888, 443; Wolff, *ibid.*, 809). F. G. WILLSON.

Action of formaldehyde on sodium hydroxide. P. MALVEZIN (Bull. Assoc. Chim. Sucr., 1927, **44**, 441—442).—The reactions described by Mestre (this vol., 960) were studied previously by the author. J. H. LANE.

Effect of dextrose on condensation of formaldehyde. I. Determination of urinary sugar. F. B. KINGSBURY (J. Biol. Chem., 1927, **75**, 241—245).—Polymerisation of formaldehyde to reducing sugars, on heating in alkaline solution, is accelerated by the presence of dextrose or other reducing sugar. The colour developed on heating an alkaline solution of 2 : 4-dinitro-α-naphthol-7-sulphonic acid with sodium sulphite, formaldehyde, and a solution containing reducing sugars, is proportional to the amount of the latter present; on the basis of this observation a colorimetric method for the determination of urinary sugar is described. C. R. HARINGTON.

γ-Chloropropaldehyde dimethyl acetal. R. VOET (Bull. Soc. chim., 1927, [iv], **41**, 1308—1314).—Acraldehyde (1 mol.) and methyl alcohol (1 mol.) in presence of 1% of dry hydrogen chloride react, forming acraldehyde methyl semiacetal, which decomposes on attempted distillation. Similar results are obtained using 2 mols. of the alcohol, but if 1 mol. of hydrogen chloride is employed a good yield of γ-chloropropaldehyde dimethyl acetal is obtained. Excess of hydrogen chloride must be avoided as the chloroacetal is converted by the acid partly into methyl αγ-dichloropropyl ether. Water does not affect the pure acetal, but if a trace of acid is present it decomposes rapidly. With 3 mols. of the alcohol there is obtained ααγ-*trimethoxypropane*, b. p. 148°, d^{20} 0·941, also converted by hydrogen chloride into methyl αγ-dichloropropyl ether. H. BURTON.

***dl*-Glyceraldehyde.** H. G. REEVES (J.C.S., 1927, 2477—2485).—*dl*-Glyceraldehyde, prepared by a modification of Wohl's method (A., 1899, i, 11; cf. Witzemann, A., 1914, i, 1124), is shown to exist in three modifications. The crystalline form, m. p. 138·5°, d_{18}^{18} 1·455, is bimolecular in freshly-prepared aqueous solutions, but on keeping passes to a unimolecular form. The syrup from which the crystalline form is deposited is unimolecular. Titrations of alcoholic solutions of each of these preparations with bromine show that they contain 0·54 and 5·7% respectively of an enolic form, the existence of which in alkaline solutions of glyceraldehyde is demonstrated by colorimetric and refractometric measurements. G. A. C. GOUGH.

Supposed dimeric crotonaldehyde. M. V. IONESCU (Bull. Soc. chim., 1927, [iv], **41**, 1314—1318).—Condensation of the dimeric crotonaldehyde (Delépine, A., 1909, i, 84; 1910, i, 219) with dimethyldihydroresorcinol in presence of piperidine affords a *compound*, $C_{24}H_{34}O_5$, m. p. 190° (*sodium* derivative). In boiling alcohol in presence of piperidine, in boiling acetic acid, or in cold acetic–sulphuric acids this substance loses 1 mol. of water, yielding a *hydroxanthene*, $C_{24}H_{32}O_4$, m. p. 176°, and condenses with 1 : 3-diketohydrindene in alcohol–piperidine solution to give a bisdi-indone derivative. H. BURTON.

Preparation of methyl *n*-alkyl ketones. S. TSURUMI (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 677—685).—The best conditions for the ketonic decomposition of *n*-alkylacetoacetic esters have been studied. From results obtained in the preparation of the ketones from methyl *n*-butyl to methyl *n*-octyl ketone, it is evident that a 15—20% solution of sodium hydroxide gives the optimum yields. E. HOLMES.

Catalytic condensation of acetone at high temperatures and pressures. II. V. N. IPATIEV and A. D. PETROV (J. Russ. Phys. Chem. Soc., 1927, **59**, 427—430; cf. A., 1926, 1130).—The products of condensation of acetone at constant temperatures (350—400°) and time of heating (10—12 hrs.) at a maximum pressure of 100 atm. in the presence of aluminium oxide were investigated. Among the products separated by fractionation were identified mesitylene, a sesquiterpene, b. p. 122—127°/10 mm., n_D^{17} 1·527, mesityl oxide, *iso*phorone, and *iso*xylitone, b. p. 126—128°. On nitration of the fraction of b. p. 122—127°, a yellow, amorphous *compound* which decomposes with incandescence on heating is obtained.

M. Zvegintzov.

Preparation of α-diketones from αβ-unsaturated ketones. C. Dufraisse and H. Moureu (Bull. Soc. chim., 1927, [iv], **41**, 1370—1378).—A more detailed account of work already abstracted (this vol., 246; cf. *ibid.*, 884).

H. Burton.

Action of hydrochloric and hydrobromic acids on carbohydrates. H. Colin and E. Ruppol (Bull. Soc. Chim. biol., 1927, **9**, 928—931).—Ketoses and most of their derivatives give a rich purple colour when treated with hydrogen bromide in presence of moisture. Hydrogen chloride gives a similar colour with the free ketoses but not, apart from certain exceptions, with their derivatives (cf. Fenton and Gostling, J.C.S., 1898, **73**, 554; 1901, **79**, 361).

W. O. Kermack.

Cryoscopy of carbohydrate acetates. M. Bergmann, E. Knehe, and E. von Lippmann (Annalen, 1927, **458**, 93—101).—The mol. wt. of amylose triacetate (this vol., 342) from potato starch, and of the *triacetate*, $[\alpha]_D^{17}$ +175·1° in chloroform, of a new carbohydrate (to be described later) from potato amylopectin have been determined by cryoscopic measurements at concentrations of 0·1—0·3%, in glacial acetic acid in absence of air, and in phenol. The values in each case approach that required for a hexose anhydride triacetate, and remain sensibly unchanged for periods of up to 27 days. The same results are obtained using lichenin triacetate, $[\alpha]_D^{20}$ +35·2°, prepared by the pyridine method (this vol., 341), and inulin triacetate (cf. A., 1926, 1230). The initial decrease in mol. wt. and subsequent gradual increase to infinity described by Hess (A., 1926, 715; this vol., 753) are not observed. The work of Hess is criticised and it is suggested that cryoscopic results are of value for the determination of constitution only when supported by independent evidence of the homogeneity of the solute particles.

H. E. F. Notton.

1 : 3 : 4 : 6-Tetramethyl-γ-fructose and 2 : 3 : 5-trimethyl-γ-arabinose. Oxidation of *d*- and *l*-trimethyl-γ-arabonolactone. W. N. Haworth, E. L. Hirst, and A. Learner (J.C.S., 1927, 2432—2436; cf. A., 1926, 273, 1025; this vol., 1057).—*l*-Trimethyl-γ-arabonolactone, m. p. 30—32°, $[\alpha]_D$ −44° to 25° (in water; period 20 days), yields a mixture of methyl *d*-dimethoxysuccinate (identified by means of the amide and the methylamide) with the original substance on oxidation with nitric acid followed by esterification of the product. *d*-Trimethyl-γ-arabonolactone yields similarly the corresponding derivatives of *l*-dimethoxysuccinic acid. In neither case was any trimethoxyglutaric acid derivative detected and hence these results support the butylene-oxide formula for *d*-tetramethyl-γ-fructose and *l*-trimethyl-γ-arabinose.

G. A. C. Gough.

Structure of the normal and γ-forms of tetramethylglucose. Oxidation of tetramethyl-δ- and -γ-gluconolactones. W. N. Haworth, E. L. Hirst, and E. J. Miller (J.C.S., 1927, 2436—2443).—Oxidation of tetramethyl-δ-gluconolactone affords finally methyl *d*-dimethoxysuccinate and methyl *i*-xylotrimethoxyglutarate alone. The γ-lactone affords similarly methyl *d*-dimethoxysuccinate only. These results confirm the structure assigned to the lactones and to the two forms of glucose (A., 1926, 273).

[With A. Learner.]—2 : 3 : 4-Trimethyl-β-methylglucoside, identical with that prepared from gentiobiose, may be obtained from triphenylmethylglucose by methylation followed by alcoholysis of the product with methyl-alcoholic hydrogen chloride.

G. A. C. Gough.

Condensation products of ethyl acetoacetate. III. Compounds of dextrose. Antiketogenesis. E. S. West (J. Biol. Chem., 1927, **74**, 561—589).—On heating dextrose and ethyl acetoacetate in alcoholic solution in presence of zinc chloride there was obtained a compound, $C_{12}H_{18}O_7$, $[\alpha]_D^{26}$ −19° in methyl alcohol. The substance did not reduce Fehling's solution, but acquired this property when boiled for a short time with dilute acid; on prolonged boiling with acid it lost 1 mol. of carbon dioxide, and with alkali it yielded an *acid*, $C_{10}H_{14}O_7$, m. p. 160—161°, $[\alpha]_D^{26}$ −21·54° in methyl alcohol, −17·08° in water (*sodium* salt, $[\alpha]_D^{25}$ −14·86°); it is regarded as ethyl dextrose*cyclo*acetoacetate. On acetylation it gave a *tetra-acetyl* compound, m. p. 84°, $[\alpha]_D^{26}$ −36·85° in chloroform. Dextrose*cyclo*acetoacetic acid when boiled with water gave the *anhydro-acid*, $C_{10}H_{12}O_6$, m. p. 140°, $[\alpha]_D^{25}$ −111·7° in methyl alcohol, −120·1° in chloroform (*sodium* salt, $[\alpha]_D^{25}$ −126·6°); on acetylation it yielded a *tetra-acetyl* compound, m. p. 94°, $[\alpha]_D^{25}$ −38·4° in chloroform, and, on methylation, a *tetramethyl* derivative, $[\alpha]_D^{25}$ −42·2° in chloroform. In the latter preparation evidence was obtained of the formation of a compound with powerful reducing properties, probably tetramethylglucoseacetoacetic acid. Ethyl dextrose*cyclo*acetoacetate, on treatment with cold hydrochloric acid, gave *ethyl anhydroglucose*cyclo*acetoacetate*, b. p. 208°/0·8 mm., $[\alpha]_D^{25}$ −89·9° in methyl alcohol (*diacetyl* derivative, b. p. 175°/0·6 mm., $[\alpha]_D^{25}$ −67° in chloroform); with hydrochloric acid at 30° it gave *ethyl dianhydroglucose*cyclo*acetoacetate*, b. p. 200°/0·8 mm., $[\alpha]_D^{26}$ −30·6° in methyl alcohol (*diacetyl* derivative, b. p. 220°/0·8 mm., $[\alpha]_D^{25}$ −59·5° in chloroform); finally, on more prolonged treatment with hydrochloric acid it yielded *ethyl trianhydroglucose*cyclo*acetoacetate*, m. p. 137°, which gave, with phenylhydrazine, a *substance*, $C_{17}H_{20}O_3N_2$, m. p. 177—180° (decomp.).

The fact that certain of the above series of compounds are powerful reducing agents, being more readily oxidised, *in vitro*, than dextrose itself, is discussed in its possible relationship to the mechanism of antiketogenesis in the organism.

C. R. Harington.

Ring structure in normal galactose. Oxidation of tetramethyl-δ-galactonolactone. W. N. Haworth, E. L. Hirst, and D. I. Jones (J.C.S., 1927, 2428—2432).—The amylene-oxide structure of tetramethyl-δ-galactonolactone and hence of normal galactose is confirmed by oxidation of the lactone with nitric acid followed by esterification of the product with methyl alcohol, whereby methyl *l*-arabotrimethoxyglutarate, b. p. 95°/0·08 mm., is obtained, identified by preparation of the amide and the methylamide. The *phenylhydrazide* of tetramethylgalactonic acid, m. p. 135—137°, is incidentally described.

G. A. C. GOUGH.

Pentamethyl-*d*-mannose, pentamethyl-*d*-galactose, and their dimethylacetals. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1927, 74, 695—699).—Diethylmercaptomannose was converted into *pentamethyldiethylmercaptomannose*, b. p. 155—160°/0·2 mm., $[\alpha]^{20}_{D}$ +39·4° in methyl alcohol, which, with mercuric chloride, gave *pentamethylmannose*, b. p. 98—100°/0·1 mm., $[\alpha]^{20}_{D}$ +9·1° in *s*-tetrachloroethane, $[\alpha]^{5}_{D}$ +8·0° to $[\alpha]^{20}_{D}$ +17·8° in methyl alcohol (*dimethylacetal*, b. p. 112—114°/0·1 mm., $[\alpha]^{20}_{D}$ +21·2° in methyl alcohol, +19·3° in *s*-tetrachloroethane). *Pentamethyldiethylmercaptogalactose*, b. p. 155—160°/0·2 mm., optically inactive in methyl alcohol, gave *pentamethylgalactose*, $[\alpha]^{20}_{D}$ −4·8° in *s*-tetrachloroethane, and 0° to −10° in methyl alcohol (*dimethylacetal*, b. p. 118—120°/0·6 mm., $[\alpha]_{D}$ 0° in *s*-tetrachloroethane). The above two pentamethylhexoses had similar properties to the pentamethylglucose previously prepared (A., 1926, 1026).

C. R. HARINGTON.

Sucrose. W. D. HELDERMAN (Z. physikal. Chem., 1927, 130, 396—404).—The densities and heats of dissolution of different preparations of sucrose have been determined, and values ranging from d^{30}_{4} 1·5860 to 1·5715 and −1095 to −813 g.-cal. (1 mol. in 400 mols. of water) have been obtained. Sugars with different physical properties are prepared by precipitating sucrose with ethyl and methyl alcohol, respectively. In general, the ethyl alcohol preparations have the greater densities and the greater negative heats of dissolution. By treating sucrose of low density with ethyl alcohol or saturated sugar solution at the ordinary temperature, a rise takes place both in the density and the heat of dissolution. These facts are explained by assuming the existence of at least two allotropic modifications of sucrose, of which that prepared by precipitation with ethyl alcohol is the stable form at the ordinary temperature. It is suggested that the deviating values found by different investigators for many of the physical constants of sucrose are to be ascribed to the fact that the measurements were made with undefined mixtures of two or more modifications of the sugar.

L. L. BIRCUMSHAW.

Action of iodine on starch. S. V. GORBATSCHEV and E. N. VINOGRADOVA (J. Russ. Phys. Chem. Soc., 1927, 59, 433—458).—The adsorption of iodine from aqueous solutions in the absence of iodides at first rapidly increases with the time, then slows down. The final amount adsorbed depends both on the concentration of the solution and on the "history" of the process. The adsorption curve does not obey the equation of adsorption for gases. If potassium iodide is present in excess (up to saturation), the adsorption process is completely reversible, and the adsorption increases with increase of concentration of the iodide. Sodium chloride has a similar effect. Free sulphuric acid up to 1·5*N* had no appreciable effect. Other anions in concentrations from 0·19*N* to 0·2*N* vary in their activity according to the series: $OAc' > I' > Br' > NO_3' > Cl' > SO_4''$, which is similar to that of their facility for adsorption.

The difference in the activity of the various cations is less marked, the series being $Ca^{\cdot\cdot} > K^{\cdot\cdot} > Sr^{\cdot\cdot} > Mg^{\cdot\cdot} > Na^{\cdot} > Zn^{\cdot\cdot} > Ba^{\cdot\cdot} > NH_4^{\cdot} > H^{\cdot}$.

Rise of temperature (below 40°, when the starch molecule breaks down), contrary to expectation, favours adsorption, according to a linear function. This cannot be due to the formation of iodide (which acts as a promoter) by reduction, since the effect is unaltered by the presence of an oxidising agent. If a saturated solution of sodium chloride is used, the relation is no longer linear. The property of adsorbing iodine vapour is also shown by perfectly dry starch.

The suggested mechanism of the process is one of electrical adsorption. Starch is negatively charged in colloidal solutions, and it is assumed that the iodine molecule is positive, since it can form the complex ion I_3'. When all the negative charge is neutralised, adsorption ceases, any residual positive charge being due to adsorbed hydrogen ions, as is shown by the removal by starch of hydroxyl ions from alkaline solutions. The addition of easily adsorbed anions to the solution removes the inhibiting hydrogen ions from the starch. The positive temperature coefficient is due to the decrease of adsorption of hydrogen ions with rise of temperature. If these are removed, the coefficient becomes negative, the process being, thus, one of true adsorption.

M. ZVEGINTZOV.

Acyl wandering in partly acylated methylglucosides. B. HELFERICH, H. BREDERECK, and A. SCHNEIDMÜLLER (Annalen, 1927, 458, 111—116).—2 : 3 : 4-Triacetyl-6-triphenylmethyl-α-methylglucoside (A., 1926, 274) is hydrolysed by acetic and hydrobromic acids to 2 : 3 : 4-*triacetyl-α-methylglucoside*, m. p. 111° (corr.), $[\alpha]^{20\cdot5}_{D}$ +148·8° in chloroform, which mutarotates in 0·001*N*-sodium hydroxide to an end value of $[\alpha]^{20}_{D}$ +107·8°. 2 : 3 : 4-Triacetyl-β-methylglucoside (cf. Oldham, A., 1926, 151) (6-p-*toluenesulphonyl* derivative, m. p. 171°, $[\alpha]^{19}_{D}$ +33·1°), prepared similarly from 2 : 3 : 4-triacetyl-6-triphenylmethyl-β-methylglucoside, also changes in presence of alkali to (?)2 : 3 : 6-*triacetyl*-β-*methylglucoside*, m. p. 114—115°, [α] −64·9° in chloroform [(?)4-p-*toluenesulphonyl* derivative, m. p. 118°, $[\alpha]^{15}_{D}$ −29·7°]. The view that the 1-substituent does not take part in the isomeric change is thus confirmed (cf. this vol., 858).

H. E. F. NOTTON.

Di*iso*propylideneglucose. IV. α- and β-Isomerides of γεζ-trimethylmethylglucoside and of βγεζ-tetramethylmethylglucoside. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1927, 74, 701—711).—Fractional distillation of larger amounts of γεζ-trimethylmethylglucoside (cf. A., 1926, 1228) gave a *d*-fraction, b. p. 105—109°/0·4 mm., $[\alpha]^{20}_{D}$ +93° in methyl alcohol, and an *l*-fraction, b. p. 145—150°/0·2 mm., $[\alpha]^{20}_{D}$ −87° in methyl alcohol. In 0·2% methyl-alcoholic hydrochloric acid the *d*-form mutarotated to $[\alpha]^{24\cdot2}_{D}$ −13·0° and the *l*-form to $[\alpha]^{24\cdot2}_{D}$ −12·5° at similar rates. On hydrolysis, the *d*-form yielded a product with $[\alpha]^{20}_{D}$ −12·3° in methyl alcohol, and the *l*-form one with $[\alpha]^{20}_{D}$ −10°; the two trimethylglucoses thus obtained gave, with bromine, acids of which the sodium salts had $[\alpha]_D^{20}$ $+31{\cdot}0°$ and $+31{\cdot}3°$. Further methylation of the trimethylmethylglucosides gave βγεζ-tetramethylmethylglucosides with $[\alpha]_D^{20}$ $+104°$ and $-63°$; these mutarotated to $[\alpha]_D^{24{\cdot}8}$ $-22{\cdot}5°$ and $-17{\cdot}7°$; the tetramethylglucoses obtained on hydrolysis had b. p. 122°/0·4 mm., $[\alpha]_D^{20}$ $-20{\cdot}5°$ in methyl alcohol, and b. p. 122°/0·05 mm., $[\alpha]_D^{20}$ $-13{\cdot}5°$. The *d*- and *l*-forms of the above tri- and tetra-methylmethylglucosides are therefore to be regarded as α- and β-isomerides.

C. R. Harington.

Bitter principle of Makabuhay, *Tinospora Rumphii*, Boerlage. J. Marañon (Philippine J. Sci., 1927, 33, 357—361).—The bitter principle of *Tinospora Rumphii*, Boerlage, has been isolated from the dried plant stems by extraction with water, followed by evaporation and extraction of the residue with alcohol, tannin being removed by means of a lead salt. The *principle*, m. p. 154—155°, is obtained as white flakes from chloroform solution, the yield being 0·95% calculated on the dry sample. It is freely soluble in alcohol, slightly soluble in other organic solvents and in water, and is probably a glucoside.

E. Holmes.

Halogenated tertiary amines. C. S. Marvel and W. H. Zartman.—See this vol., 1064.

Determination of tetrapropylammonium ions as tetrapropylammonium diamminochromithiocyanate, $NPr_4[(SCN)_4Cr(NH_3)_2]$. F. Hein and F. A. Segitz (Z. anal. Chem., 1927, 72, 119—121).—The ice-cold solution (30 c.c.) of tetrapropylammonium salt is treated drop by drop with 20 c.c. of a 0·05*N*-solution in 10% alcohol of Reinecke's salt (ammonium diamminochromithiocyanate), 10—15 c.c. of a 15% solution of sodium chloride are added, and, after 24 hrs., the light rose-coloured, crystalline precipitate is collected on a porous glass filter, washed free from chlorides with ice-cold water, dried at the ordinary temperature in a vacuum over calcium chloride, and weighed.

A. R. Powell.

Neutral salt additive compounds of alkaline-earth glutamates and aspartates. W. K. Anslow and H. King (Biochem. J., 1927, 21, 1168—1178).—The following double *salts*, each containing 1 mol. of the organic salt and 1 mol. of the halide, are described: calcium glutamate with calcium chloride ($2H_2O$), calcium bromide ($2H_2O$), calcium iodide ($2{\cdot}5H_2O$); barium glutarate with barium chloride ($6H_2O$), barium bromide (anhyd. and $4H_2O$), barium iodide ($6H_2O$); strontium glutamate with strontium chloride ($12H_2O$), strontium bromide ($11H_2O$), strontium iodide ($7H_2O$); strontium aspartate with strontium chloride ($2H_2O$). Barium aspartate and barium chloride apparently form a series of mixed crystals. No additive compounds could be obtained from lithium glutamate and lithium halides, calcium chloride and glutamic acid hydrochloride, calcium chloride and glutamic acid, and calcium aspartate and calcium chloride. Calcium, strontium, barium, lithium, and sodium glutamates were also prepared. The specific rotations of the above compounds over a wide range of concentrations were determined. At high concentrations these compounds are dextrorotatory but become lævorotatory in the region of low concentration, the curves showing a tendency to flatten out at 1—2% dilutions; the ionic value for the negative glutamate ion at this region of concentration is about of the same order for all the compounds. Glutamic acid was prepared by hydrolysis of gluten flour with hydrochloric acid and by decomposing the resulting hydrochloride with aniline and alcohol. The constitution of the additive compounds is discussed from the point of view of electron sharing.

S. S. Zilva.

Separation of arginine and histidine. III. Preparation of arginine. H. B. Vickery and C. S. Leavenworth (J. Biol. Chem., 1927, 75, 115—122; cf. this vol., 546).—The purified protein is hydrolysed with hydrochloric acid and most of the latter is removed by evaporation; the solution of the residue is treated with silver oxide and sulphuric acid in excess and then with barium hydroxide to p_H 7·0; the filtrate, after further addition of excess of silver oxide and sulphuric acid, is treated with barium hydroxide until alkaline to phenolphthalein; arginine is recovered from the precipitate by decomposition with hydrogen sulphide and isolated as the picrate. The yield of arginine from edestin was 14·45%. A method of recovering silver from the residues in the above preparation is described.

C. R. Harington.

Mercury compound of allantoic acid suitable for the identification of this ureide in the green vegetable of *Phaseolus vulgaris*. R. Fosse and A. Hieulle (Compt. rend., 1927, 185, 800—802; cf. this vol., 1116; Fosse, A., 1926, 548).—Allantoic acid may be conveniently identified by means of its mercury compound, which is formed by the union of 2 mols. of the ureide with 1 mol. of mercuric oxide and is therefore hydrated *mercury allantoate*, ($+H_2O$). Since products of variable composition may be obtained under certain conditions, the method of preparation is given in detail. From crude dixanthylallantoic acid, which is obtained by treating extracts of *Phaseolus* with xanthhydrol, mercury allantoate may be prepared by treatment with ether and alcoholic hydrogen chloride, the residue after washing with ether being dissolved in water and treated with mercuric nitrate in slightly acid solution.

W. J. Powell.

Photosynthesis of carbamide from ammonium carbonate. W. R. Fearon and C. B. M'Kenna (Biochem. J., 1927, 21, 1087—1090).—Carbamide has been produced by exposure of ammonium carbonate to ultra-violet irradiation (200—250 μμ). The effect of accessory reagents such as dextrose, hydroxylamine, formaldehyde, methylene-blue, ammonium nitrate, hydrogen peroxide, copper, iron, uranium, methyl-orange, eosin, and malachite-green was examined. The last reagent had the most definite effect in increasing the yield of carbamide.

S. S. Zilva.

Preparation of methylguanidine according to Werner and Bell. E. Philippi and K. Morsch (Ber., 1927, 60, [*B*], 2120—2122; cf. Werner and Bell, J.C.S., 1922, **121**, 1790; Kapeller, A., 1926, 943).—The action of dicyanodiamide on methylamine hydrochloride gives methylguanidine in 80—90% yield. It may be isolated through the chloroplatinate or picrate. In the former case, methylamine chloroplatinate must first be removed and the other by-products (methyldiguanide and guanidine) remain in the final mother-liquors, whereas in the latter case methyldiguanide and guanidine are removed as picrates and methylamine is left in the final liquors. Werner and Bell's picrate, decomp. 285°, is derived from methyldiguanide and guanidine; methylguanidine picrate has m. p. 198·5—199·5°.

H. Wren.

Reactions of thiosemicarbazones. III. W. Baird, R. Burns, and F. J. Wilson (J.C.S., 1927, 2527—2534).—Alkyl halides react with the sodium derivative of acetonethiosemicarbazone in alcoholic solution to give *S*-alkyl compounds, which are hydrolysed to *S*-alkylthiosemicarbazides by 0·5*N*-hydrochloric acid. In this way the following compounds are prepared: *acetone*-S-*ethylthiosemicarbazone*, m. p. 55°; S-*ethylthiosemicarbazide dihydrochloride*, m. p. (indef.) 60°; *benzaldehyde*-S-*ethylthiosemicarbazone*, m. p. 66° (*hydrochloride*, m. p. 195°); *acetone*-S-*propylthiosemicarbazone*, b. p. 121°/7 mm., m. p. 26—27°; S-*propylthiosemicarbazide dihydrochloride* (syrup); *benzaldehyde*-S-*propylthiosemicarbazone*, m. p. 54° (*hydrochloride*, m. p. 209°); *acetone*-S-*allylthiosemicarbazone*, m. p. 51°; S-*allylthiosemicarbazide dihydrochloride*, m. p. 75°; *benzaldehyde*-S-*allylthiosemicarbazone*, m. p. 42° (*hydrochloride*, m. p. 190°); *acetone*-S-n-*butylthiosemicarbazone*, b. p. 146°/16 mm.; S-n-*butylthiosemicarbazide dihydrochloride*, m. p. 100—101° (decomp.); *benzaldehyde*-S-n-*butylthiosemicarbazone*, m. p. 50°; *acetone*-S-o-*carbethoxybenzylthiosemicarbazone*, m. p. 66° (from ethyl ω-bromo-*o*-toluate); S-o-*carbethoxybenzylthiosemicarbazide dihydrochloride*, m. p. 125—130° (decomp.); *benzaldehyde*-S-o-*carbethoxybenzylthiosemicarbazone*, m. p. 74° (*hydrochloride* $+H_2O$, m. p. 115°). Acetonethiosemicarbazone reacts with primary amines in boiling toluene solution to give ammonia and the following δ-substituted thiosemicarbazones: with benzylamine, *acetone-δ-benzylthiosemicarbazone*, m. p. 147—148°; *δ-benzylthiosemicarbazide*, m. p. 130° [*hydrochloride*, m. p. 189°; *benzylidene* derivative, m. p. 133—134° (also prepared from hydrazine hydrate and benzylthiocarbamide)]; with α-phenylethylamine, *acetone-δ-α-phenylethylthiosemicarbazone*, m. p. 89—90°; *δ-α-phenylethylthiosemicarbazide*, m. p. 84° (*hydrochloride*, m. p. 157—158°; *benzylidene* derivative, m. p. 128—129°); with *n*-heptylamine, *acetone-δ-*n-*heptylthiosemicarbazone*, m. p. 75°; *δ-*n-*heptylthiosemicarbazide*, m. p. 54—55° (*hydrochloride*, m. p. 135—136°; *benzylidene* derivative, m. p. 73°); with aniline, a small amount of an unidentified *substance*, m. p. 245°. With β-naphthylamine, hydrogen sulphide and ammonia were evolved and a *substance*, m. p. 275° (possibly di-β-naphthyliminotetrahydrothiodiazole), and *acetone-δ-β-naphthylthiosemicarbazone*, m. p. 150—151° (when crystallised from alcohol; separates from benzene as an amorphous powder, m. p. 137—138°), are produced. The last-named compound, when hydrolysed with dilute hydrochloric acid, gives a *substance*, m. p. 252°, which may be hydrazinedithiocarbo-β-naphthylamide, formed by the decomposition of δ-β-naphthylthiosemicarbazide hydrochloride. *Acetophenone-δ-benzylthiosemicarbazide*, m. p. 160—161°, gives acetophenone and δ-benzylthiosemicarbazide hydrochloride, besides hydrazine hydrochloride and benzylthiocarbimide, on hydrolysis.

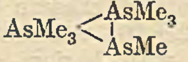
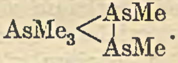
G. A. C. Gough.

Constitution of ordinary hydrocyanic acid. C. J. Enklaar (Rec. trav. chim., 1927, 46, 709—710).—Speculative. E. W. Wignall.

Pentenonitriles. A. Castille and J. Gueurden (Bull. Soc. chim. Belg., 1927, 36, 509—516).—See this vol., 961.

Nitrile of thiodipropionic acid. V. Nekrassov (J. pr. Chem., 1927, [ii], **117**, 211—213; cf. Bennett and Hock, A., 1926, 146).—β-Chloropropionitrile (Chapman and Stephen, A., 1925, i, 669) and anhydrous sodium sulphide in ether–methyl alcohol afford *ββ′-dicyanodiethyl sulphide*, m. p. 24—25°, which is hydrolysed by boiling concentrated hydrochloric acid to ββ′-thiodipropionic acid (Lovén, A., 1896, i, 412). H. E. F. Notton.

Cadet's oil. I. Preparation of cacodylic acid from trimethylarsine. A. Valeur and P. Gailliot (Bull. Soc. chim., 1927, [iv], **41**, 1318—1323).—Trimethylarsine (1 mol.) combines with 1 mol. of arsenious chloride, methylarsenious chloride, or phenylarsenious chloride in benzene solution, yielding crystalline additive *compounds*. The additive compounds from arsenious chloride and methylarsenious chloride decompose when heated at 200° for 10 hrs., yielding, in each case, arsenious chloride, tetramethylarsonium chloride, and arsenic. Trimethylarsine is chlorinated in benzene solution, yielding the *dichloride*, which decomposes when heated at 180°, giving methyl chloride and cacodyl chloride (87%). The latter is oxidised by hydrogen peroxide to cacodylic acid (99%). H. Burton.

High-boiling products of Cadet's oil. A. Valeur and P. Gailliot (Compt. rend., 1927, **185**, 779—781).—Fractional distillation of crude Cadet's oil (obtained by heating potassium acetate with arsenious acid) yields trimethylarsine, a mixture of cacodyl and cacodyl oxide, and 1—2% of a blue liquid, b. p. 115—120°/5 mm., d^{15} 1·647, which is not spontaneously inflammable in air and does not crystallise at −80°. It consists of a mixture, inseparable by distillation, of two methylated *derivatives*,  $AsMe_3{<}\begin{matrix}AsMe_3\\ |\\ AsMe\end{matrix}$ and  $AsMe_3{<}\begin{matrix}AsMe\\ |\\ AsMe\end{matrix}$. The former with 2 mols. of methyl iodide yields a colourless crystalline *product*, $Me_4As{\cdot}AsMeI_2{\cdot}AsMe_4$, the latter with 1 mol. forms a light yellow, viscous *oil*, $Me_4As{\cdot}AsMe{\cdot}AsMeI$. With ethyl iodide two similar *products*, $Me_3EtAs{\cdot}AsMeI_2{\cdot}AsMe_3Et$ and $Me_3EtAs{\cdot}AsMe{\cdot}AsMeI$, are obtained. The blue colour of the liquid mentioned above is readily discharged on exposure to air, and is probably due to the presence of minute particles in suspension. The colour does not fade, however, if the sample is kept in a sealed vessel even when exposed to light. Pure cacodyl has b. p. 163°, m. p. −5°, d^{15} 1·447. W. J. Powell.

Constitution of Grignard's organo-magnesium derivatives. I. Action of water and hydrogen sulphide on asymmetric organo-magnesium

derivatives. L. Kierzek (Bull. Soc. chim., 1927, [iv], **41**, 1299—1308; cf. Ivanov, this vol., 961; Grignard, *ibid.*, 962).—Decomposition of magnesium methyl iodide with water or dry hydrogen sulphide (cf. Mingoia, A., 1926, 388; this vol., 147), followed by extraction with ether, and analysis of the ethereal extract, shows that magnesium iodide is dissolved. The results confirm Jolibois' formula, $R_2Mg,MgHal_2$ (A., 1912, i, 753), for the constitution of Grignard reagents.
H. Burton.

Barium phenyl iodide. H. Gilman and F. Schulze (Bull. Soc. chim., 1927, [iv], **41**, 1333—1336).—Iodobenzene reacts slowly with electrolytic barium, in presence of ether and a trace of iodine, yielding *barium phenyl iodide* (not isolated), since the reaction mixture reacts with carbon dioxide giving benzoic acid, with α-naphthylcarbimide affording benz-α-naphthalide, and with ethyl benzoate forming triphenylcarbinol. Ethyl iodide gives practically no metallic derivative. These barium compounds are more difficult to prepare than the corresponding calcium compounds (A., 1926, 1130).
H. Burton.

Differential cleavage of the carbon-to-carbon linking by alkali metals. J. B. Conant and B. S. Garvey (J. Amer. Chem. Soc., 1927, **49**, 2599—2603).—Compounds containing a reactive carbon-to-carbon linking can be differentiated by the relative rates of their reactions, in ether or benzene, with the liquid sodium–potassium alloy, 40% sodium amalgam, and 1% sodium amalgam. Thus, when 0·00025 mol. in 5 c.c. of solvent is shaken for 5 min. with 1 c.c. of the liquid metal, hexaphenylethane develops the red colour of the metallic derivative of triphenylmethyl in all cases (cf. Schlenk and Marcus, A., 1914, i, 823; Ziegler and Thielmann, A., 1923, i, 921); dibenzyldixanthyl, di-*n*-butyldixanthyl, diethyldixanthyl, and dimethyldixanthyl are unattacked only by the 1% sodium amalgam; dixanthyl is attacked by the sodium–potassium alloy in either solvent, and by the 40% sodium amalgam in ether only (cf. Conant and Garvey, this vol., 975); tetraphenylethane is attacked only by the sodium–potassium alloy, and dibenzyl is not attacked by either reagent. The rate of cleavage of a number of substituted dixanthyls, and dixanthyl itself, by the sodium–potassium alloy is essentially the same, indicating that this is controlled by a physical process. The following acids, prepared by treating the appropriate metallic derivatives with carbon dioxide (cf. Conant and Garvey, *loc. cit.*), are described: *methylxanthanoic acid*, m. p. 205—206° (*methyl* ester, m. p. 96—97°); *ethylxanthanoic acid*, m. p. 173—174°; n-*butylxanthanoic acid*, m. p. 144—145° (*methyl* ester, m. p. 73—74°); *benzylxanthanoic acid*, m. p. 232° (*methyl* ester, m. p. 103—104°).
F. G. Willson.

Transformation of phenols into hydrocarbons by hydrogen under pressure in presence of catalysts. A. Kling and D. Florentin (Bull. Soc. chim., 1927, [iv], **41**, 1341—1350).—A more detailed account of work already published (this vol., 452).
H. Burton.

Use of nitrogen tetroxide in place of nitric acid in organic nitrations. L. A. Pinck (J. Amer. Chem. Soc., 1927, **49**, 2536—2539).—Nitrobenzene is obtained in 94·4% yield by adding benzene (1 mol.) to a solution of nitrogen tetroxide (1·05 mols.) in 95% sulphuric acid (1·75 mols.) at 55—60°. Dinitrobenzene is obtained in 93·4% yield by adding nitrobenzene (1 mol.) to a solution of nitrogen tetroxide (1·10 mols.) in fuming sulphuric acid (2·8 mols.; 104·3% H_2SO_4) at 60—75°. Nitrotoluene and α-nitronaphthalene are obtained similarly to nitrobenzene in 87·5% and 88·4% yields, respectively.
F. G. Willson.

Electropyrogenic decompositions. II. Benzene; turpentine. F. G. Müller and A. Bänninger (Helv. Chim. Acta, 1927, **10**, 763—770).—When an electric arc is maintained below the surface of benzene (cf. A., 1926, 43, 44), the products are amorphous carbon (25%), phenylacetylene (0·1%), diphenyl (0·33%), anthracene, diacetylene (0·03%), traces of higher acetylenes, and a gaseous mixture of acetylene 8·9—9·75%, ethylene 0·0—0·7%, benzene 0·9—1·5%, methane 0·5—3·6%, hydrogen 86·2—88·7%, and carbon monoxide trace. It is suggested that the primary decomposition products are free phenyl and acetylenyl radicals. The polymerisation of diacetylene is hastened by exposure to ultra-violet light. Oil of turpentine is decomposed by the electric arc, yielding carbon (29%), isoprene (3·9%), products condensed at −40° to −80°, from which a mixture (0·03%) containing diacetylene (60%), propinene (25%), and pentinene (15%) is isolated, and a gaseous mixture containing acetylene 8·2—8·9%, ethylene 9·3—11·4%, benzene 0·8—1·1%, methane 17·2—19·8%, and hydrogen 59·7—64·2%.
H. E. F. Notton.

Condensation of nitrobenzyl chlorides with benzene by the Friedel and Crafts reaction, in relation to the theory of induced alternate polarities. S. C. J. Olivier and G. Berger (Rec. trav. chim., 1927, **46**, 605—608).—The views of van Duin (this vol., 662) are criticised. Although the effect of an *ortho* substituent is unknown *a priori*, it is found experimentally that the *o*>*p*>*m* rule (cf. Shoesmith and Taylor, this vol., 50), and the parallelism between ease of substitution in a certain position in an aromatic nucleus and ease of hydrolysis of halogen in a side-chain attached in that position, hold good. Comparative velocity coefficients are given for the effects of substituents on the hydrolysis of substituted benzyl chlorides, and on the reaction of substituted benzenesulphonyl chlorides with benzene in presence of aluminium chloride. The accelerating effect of the *p*-methyl group is much less in the latter reaction than in the former, and the retarding effect of the *m*-nitro-group also less in the latter than the former. It may be considered that the aluminium chloride attached to the nitro-group renders it more negative, and thus decreases its alternate polar effect.
E. W. Wignall.

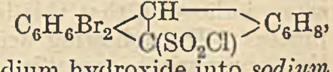
Formation of additive compounds as prelude to chemical changes. F. Ebel (Ber., 1927, **60**, [*B*], 2079—2088).—The action between *p*-toluenesulphonyl chloride and aniline in dry ether has been examined by determination of the amine hydrochloride produced. In the presence of a large excess of aniline, the rate of reaction is directly and the half period inversely proportional to the fourth power of the concentration of the amine, whilst, if the latter is maintained constant, the half period is independent of the concentration of the sulphonyl chloride. The change appears to consist in the primary formation of an additive compound, $C_7H_7\cdot SO_2Cl,3NH_2Ph$, which, under the influence of a fourth molecule of the base, loses hydrogen chloride, the latter reaction determining the velocity of change. The presence of the additive compound cannot be demonstrated at any period of the change. The fourth molecule of aniline may be replaced by a tertiary base such as dimethylaniline and the acceleration produced is proportional to the concentration of the latter substance. The reaction therefore presents an instance of negative autocatalysis in which the catalyst, aniline, is also initial material and disappears during the reaction. It is the converse of the Landolt reaction. The action of the catalyst is not necessarily restricted to the facilitation of a single phase of the reaction, but extends to several such phases.

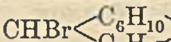
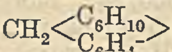
An explanation is afforded of the favourable action of pyridine in organic acylations, but the use of the cyclic base in the present instance is rendered impossible by the formation of by-products.

Evidence is also adduced in favour of the view that there are no actual processes of substitution but that all reactions occur by the production of additive compounds followed by simple fission. H. WREN.

Preparation of crystalline xylenesulphonic acids and their technical importance. E. ORLOV (Ukraine Chem. J., 1926, 2, 365—369).—Equal volumes of technical xylene (containing the three isomerides with a small amount of ethylbenzene) and sulphuric acid (*d* 1·84) are shaken together until no more heat is evolved, a temperature of 65—70° being reached. On cooling, water equal in volume to half the sulphuric acid is added, and the mixture separates into three layers, the middle one containing the xylenesulphonic acids, which after keeping for 2 days crystallise as a feathery mass, m. p. 70°. On adding water and distilling, almost pure *m*-xylene comes over with the water between 125° and 155°, the yield being 60% of the total xylene originally taken. At 155—200°, a mixture of the *meta* and *para* isomerides distils over. This method for the formation of the sulphonic acids is not suitable for benzene, toluene, or ethylbenzene. E. ROTHSTEIN.

Hydrogenation of naphthalene at high temperature and pressure without catalysts. HUGEL and J. FRIESS (Bull. Soc. chim., 1927, [iv], 41, 1185—1186).—A reply to Kling and Florentin (this vol., 452). Naphthalene is not hydrogenated in the absence of catalysts at 520° and 250 kg./cm.^{2} by hydrogen containing a trace of oxygen. G. A. C. GOUGH.

Hydrogenation of anthracene. II. Transformations of octhracenesulphonic acid [*s*-octahydroanthracene-9-sulphonic acid]. G. SCHROETER [with S. GÖTZKY] (Ber., 1927, 60, [*B*], 2035—2045; cf. A., 1925, i, 125, 127, 130).—*s*-Octahydroanthracene is converted by short treatment with concentrated sulphuric acid at a temperature not exceeding 70° into the sparingly soluble *s*-octahydroanthracene-9-sulphonic acid; if the reaction is prolonged or the temperature further raised, the sulphonic acid passes into solution from which *s*-octahydrophenanthrene-9-sulphonic acid can be isolated in yield which is quantitative except for losses caused by oxidation. The transformation is irreversible and takes place only in sulphuric acid solution. If sodium *s*-octahydroanthracene-9-sulphonate is heated under diminished presence, *s*-octahydroanthracene (80—85%), sulphur dioxide, and sodium sulphate are produced. When mixtures of the two sulphonates are heated, the anthracene derivatives alone suffer change. Separation of the sulphonic acids from one another is effected by partial hydrolysis with boiling, fuming hydrochloric acid, the anthracene compound thereby yielding *s*-octahydroanthracene, whereas *s*-octahydrophenanthrene-9-sulphonic acid remains unchanged. The action of bromine water or bromine in glacial acetic acid on *s*-octahydroanthracene-9-sulphonic acid yields 9 : 10-*dibromo*-s-*octahydroanthracene*, m. p. 200—201°, which is also prepared from the hydrocarbon and bromine in chloroform. Nascent bromine and iodine, however, afford 9-*bromo*-s-*octahydroanthracene*, m. p. 74—75°, and 9-*iodo*-s-*octahydroanthracene*, m. p. 72—73°, in which the halogen atom is very firmly retained. Treatment of 9-bromo-*s*-octahydroanthracene with sulphuric acid at 50—60° yields 9 : 10-dibromo-*s*-octahydroanthracene and *s*-octahydroanthracene-9-sulphonic acid, whereas chlorosulphonic acid converts it smoothly into 9-*bromo*-s-*octahydroanthracene*-10-*sulphonyl chloride*, m. p. 146—147°, hydrolysed to *sodium* 9-*bromo*-s-*octahydroanthracene*-10-*sulphonate* (+5H_2O). The latter substance is transformed by nitric acid into 9-*bromo*-10-*nitro*-s-*octahydroanthracene*, m. p. 235° (decomp.), also obtained in poorer yield by the action of nitric acid on an emulsion of *s*-octahydroanthracene in chloroform and sulphuric acid; more energetic nitration of the hydrocarbon appears to yield 9 : 10-*dinitro*-s-*octahydroanthracene*. 9-*Bromo*-10-*amino*-s-*octahydroanthracene*, m. p. 157—162°, and its *hydrochloride*, m. p. 138—140°, are obtained from the mononitro-derivative by means of titanium trichloride. The attachment of the sulphur atom to the ring carbon atom is much firmer in *s*-octahydroanthracene-9-sulphonyl chloride than in the corresponding sulphonic acid; the compound reacts with bromine in carbon tetrachloride in sunlight to give a dibromo - derivative,  $C_6H_6Br_2<\begin{matrix}CH\text{——}\\ |\\ C(SO_2Cl)\end{matrix}>C_6H_8$, converted by alcoholic sodium hydroxide into *sodium* 1 : 2 : 3 : 4-*tetrahydroanthracene*-9-*sulphonate* (+2H_2O) [corresponding *barium* salt (+8H_2O)], characterised by conversion into 1 : 2 : 3 : 4-tetrahydroanthracene and 9 : 10-dibromotetrahydroanthracene, m. p. 166—168°.

Godchot's "dibromo-octahydroanthracene,"  $CHBr<\begin{matrix}C_6H_{10}\\ C_6H_4\end{matrix}>CHBr$, m. p. 194° (cf. A., 1907, i, 308, 836, 840, 841), is probably 9 : 10-dibromo-*s*-octahydroanthracene, m. p. 200—201°, and his liquid "monobromo-octahydroanthracene,"  $CH_2<\begin{matrix}C_6H_{10}\\ C_6H_4\end{matrix}>CHBr$, is probably a mixture of *s*-octahydroanthracene and its 9 : 10-dibromo-compound. The "dibromohexahydroanthracene,"  $CHBr<\begin{matrix}C_6H_8\\ C_6H_4\end{matrix}>CHBr$, m. p. 163°, is regarded as slightly impure 9 : 10-dibromo-1 : 2 : 3 : 4-tetrahydroanthracene, m. p. 166—168°. Godchot's chloro-derivatives are probably subject to similar interpretation. H. Wren.

Electrometric titration of aniline with bromine. A. V. Pamfilov and V. E. Kisseleva (Z. anal. Chem., 1927, 72, 100—112).—The end-point of the potentiometric titration of aniline with bromine in a neutral solution or with bromate in an acid solution is exceedingly sharp, being marked by a potential jump of 0·1—0·2 volt according to the strength of the solution. Bromine is most suitable for weak solutions (0·01N or weaker) and bromate for more concentrated solutions of aniline. In solutions as weak as 0·00002M the results with bromine are within 2% of the theoretical. A platinum wire is used as indicator electrode and the solution is stirred mechanically during titration. A. R. Powell.

Nitroaniline styphnates. N. N. Efremov (J. Russ. Phys. Chem. Soc., 1927, 59, 391—404).—The systems formed by styphnic acid with aniline and each of the three nitroanilines were investigated. When styphnic acid and aniline are fused together the mixture decomposes violently. When a solution of the components in a mixture of alcohol (75%) and ethyl acetate (25%) is boiled, a 62% yield of a crystalline *compound*, $NH_2Ph,C_6H(OH)_2(NO_2)_3$, is obtained, which decomposes on fusion. Styphnic acid and *o*-nitroaniline give a simple binary system, eutectic at 45·6° with 64·2% of *o*-nitroaniline. With *m*-nitroaniline two *compounds* are formed, $C_6H_4(NH_2){\cdot}NO_2,C_6H(OH)_2(NO_2)_3$, bright orange, m. p. 156·6° (calc. 156·2°), and $2C_6H_4(NH_2){\cdot}NO_2,C_6H(OH)_2(NO_2)_3$, lemon-yellow, decomp. 110—112° (m. p. calc. 105·0°). The two eutectics are at 140·2° and 98·6°, with 17·7% and 76·4% of *m*-nitroaniline. *p*-Nitroaniline forms a yellow *compound*, $C_6H_4(NH_2){\cdot}NO_2,C_6H(OH)_2(NO_2)_3$, m. p. 132·3° (calc. 129·8°). The eutectics are at 124·7° and 112·2° with 28·3% and 62·3% of *p*-nitroaniline, respectively. M. Zvegintzov.

Tenacity of organic radicals. VI. J. von Braun and L. Tauber (Annalen, 1927, 458, 102—111).—In continuation of previous work (A., 1924, i, 632; 1925, i, 1401) it is shown that the firmness of attachment to nitrogen of the propargyl radical is decreased by introduction of a hydrocarbon residue in the γ-position, and that the relative tenacity of the allyl and propargyl radicals is unchanged by γ-substitution. γ-Amylpropargyl alcohol (Moureu, A., 1901, i, 442) affords with phosphorus tribromide *γ-amylpropargyl bromide* [*α-bromo-Δ$^{\beta}$-octinene*], b. p. 95°/12 mm., together with its *hydrobromide*, b. p. 120—125°/14 mm. *γ-Phenylpropargyl bromide*, b. p. 135°/15 mm., is prepared similarly. By combination of aniline with the requisite alkyl bromide at a low temperature the following secondary bases are obtained: (*a*) β-*bromoallylaniline*, b. p. 147°/15 mm. (*hydrochloride*, m. p. 165°; *benzoyl* derivative, m. p. 79°; oily *picrate* and *nitroso*-derivative), which is converted by boiling aqueous alcoholic alkali into aniline and *propargylaniline*, b. p. 121°/15 mm. (*hydrochloride*, m. p. 141°; *phenylthiourethane*, m. p. 93°; *silver* derivative). The latter gives with cyanogen bromide *propargylaniline hydrobromide*, m. p. 118°, and *phenylpropargylcyanamide*, m. p. 48—49°, and with γ-amylpropargyl bromide, *propargyl-γ-amylpropargylaniline*, b. p. 163°/3 mm., which also yields phenylpropargylcyanamide (60% of theoretical) but no phenyl-γ-amylpropargylcyanamide when treated with cyanogen bromide; (*b*) *γ-phenylpropargylaniline*, m. p. 29°, b. p. 206°/15 mm. (*hydrochloride*, m. p. 166°; *picrate*, decomp. 200°); (*c*) *cinnamylaniline*, m. p. 21°, b. p. 200—202°/12 mm. (*hydrochloride*, m. p. 185°; *hydrobromide*, m. p. 156°; *picrate*, m. p. 137°; *nitroso*-derivative, m. p. 68—69°), from which *phenylcinnamylcyanamide*, m. p. 82—83°, is obtained. With phenylpropargyl bromide it forms the weakly basic *cinnamyl-γ-phenylpropargylaniline*, m. p. 60°, which is converted by cyanogen bromide into a mixture of cyanamide derivatives from which traces only of *phenyl-γ-phenylpropargylcyanamide*, m. p. 94°, can be isolated.

H. E. F. Notton.

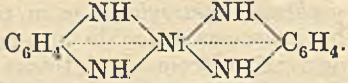
Organic compounds of tin tetrabromide. G. I. Costeanu (Ber., 1927, 60, [*B*], 2223—2225).—The following compounds are described: *aniline hexabromostannate*, $H_2SnBr_6,2NH_2Ph$; *diphenylamine hexabromostannate*; additive *compounds* of tin tetrabromide with salicylaldehyde, $SnBr_4,2C_7H_6O_2$, and cinnamaldehyde, $SnBr_4,2C_9H_8O$; *hexabromostannates* of pyridine and quinoline. The compounds are very stable and generally crystalline; in aqueous, alcoholic, and ethereal solution they exhibit the properties of their organic components. H. Wren.

Action of trimethylethylene oxide on benzylamine. G. Gabel (Ukraine Chem. J., 1926, 2, 382—386).—One part of trimethylethylene oxide reacts with four parts of benzylamine in a sealed tube at 160—180° in 6—8 hrs., yielding *γ-benzylamino*-β-*methyl*iso*butyl alcohol*, $OH{\cdot}CMe_2{\cdot}CHMe{\cdot}NH{\cdot}CH_2Ph$, b. p. 152—154°/20 mm., d_{15}^{15} 0·9437. The compound is not formed at 100°, but if 1 mol. of water is present in the reaction mixture, the reaction takes place at 90°. The following salts are described: *chloroaurate*, m. p. 140—142°, *picrate*; m. p. 163—164°; *hydrochloride*, m. p. 155—157°. The *chloroplatinate* could be obtained only as a thick syrup. Attempts to prepare dihydroxydi*iso*amylbenzylamine by the action of benzylamine on excess of trimethylethylene oxide were unsuccessful. E. Rothstein.

Action of chlorosulphonic acid on α- and β-naphthylamines. A. Corbellini (Giorn. Chim. Ind. Appl., 1927, 9, 355—357).—Chlorosulphonic acid exerts a sulphonating action on α- and β-naphthylamine sulphates, the principal products formed being those obtained by the use of other sulphonating agents. Thus, with the α-compound the main products are the 4- and 5-sulphonic acids, which result also from the action of oleum, whereas β-naphthylamine gives the 5- and 8-sulphonic acids in proportions similar to those formed by the action of either sulphuric acid or oleum.

T. H. Pope.

Compounds of nickel with *o*-phenylenediamine and tolylene-3 : 4-diamine. F. Feigl and M. Fürth (Monatsh., 1927, 48, 445—450).—Addition of an aqueous solution of *o*-phenylenediamine or tolylene-3 : 4-diamine to an ammoniacal solution of nickel chloride yields, on keeping, bluish-violet, amorphous precipitates of the nickel *compounds* of composition $Ni[C_6H_4(NH)_2]_2$ and $Ni[C_6H_3Me(NH)_2]_2$, respectively, which are stable, are unattacked by alkalis, and possess oxidising properties. They dissolve in dilute mineral acids to yield brown solutions which no longer liberate iodine from potassium iodide nor oxidise stannous chloride. Attempts to determine the valency of the nickel present by measurements of the iodine liberated from potassium iodide solution, or the oxidation of stannous chloride lead to somewhat inconclusive results, the balance of evidence supporting the view that the nickel is quadrivalent. It is suggested that co-ordination compounds of nickel hydroxide and the diamine are first formed which lose water giving compounds of the type



$C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}Ni{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}C_6H_4$.

J. W. BAKER.

Diphenyl and its derivatives. Interpretation of the phenomena of optical isomerism. L. MASCARELLI (Atti R. Accad. Lincei, 1927, [vi], 6, 60—65).—Unsuccessful attempts to resolve 2 : 2′-diaminodiphenyl, 2 : 2′-diamino-4 : 4′-dimethyldiphenyl, and 2 : 2′-diamino-5 : 5′-dimethyldiphenyl into optical isomerides are described. When treated with *d*-tartaric acid, 2 : 2′-diamino-6 : 6′-dimethyldiphenyl yields a less soluble salt, m. p. 159—160°, which, on treatment with ammonia, gives a product, m. p. 151°, which exhibits lævo-rotation in hydrochloric acid solution (cf. Meisenheimer and Höring, this vol., 766).

T. H. POPE.

Manufacture of *ar*-tetrahydronaphthylamines and derivatives thereof. SOC. CHEM. IND. IN BASLE.—See B., 1927, 808.

Manufacture of *cyclo*hexylamines. I. G. FARBENIND. A.-G.—See B., 1927, 809.

New azine dyes and intermediates [1 : 3-di-*p*-anisylaminonaphthalenesulphonic acids]. I. G. FARBENIND. A.-G.—See B., 1927, 808.

Formation of benzeneazoxy-*p*-phenols. D. BIGIAVI (Gazzetta, 1927, 57, 555—556).—The benzoylphenylhydrazone of benzoquinone, when heated with peracetic acid, gives *O*-benzoylbenzeneazophenol, which is immediately oxidised to a mixture of the α- and β-azoxy-compounds, m. p. 156° and 117°, respectively. Since acetic acid has no action on the phenylhydrazone, it is possible that " perhydrolysis " of the benzoyl group is the first stage. E. W. WIGNALL.

The two isomeric benzeneazoxy-*p*-toluenes. D. BIGIAVI and V. SABATELLI (Gazzetta, 1927, 57, 557—567).—When benzeneazo-*p*-toluene is treated with peracetic acid, two *benzeneazoxy*-p-*toluenes* are obtained. The α-isomeride, $NPhO{:}N{\cdot}C_6H_4Me$, (I), has m. p. 46°; the β-isomeride, $NPh{:}NO{\cdot}C_6H_4Me$, (II), obtained in smaller quantity, forms monoclinic crystals, $a:b:c=0{\cdot}7138:1:0{\cdot}7145$; $\beta=70°\ 55'$, m. p. 65°. The former does not react with bromine, but (II) gives a p-*bromo*-derivative, m. p. 112°, reduced by tin and hydrochloric acid to *p*-bromoaniline and *p*-toluidine, and by aluminium amalgam to a product containing the *hydrazo*-compound, which with mercuric oxide yields p-*bromobenzeneazo*-p-*toluene*, m. p. 153°, identical with that obtained from *p*-bromoaniline and *p*-nitrosotoluene. The β-compound gives a p-*nitro*-derivative, m. p. 163°, identical with the product of the action of peracetic acid on *p*-nitrobenzeneazo-*p*-toluene, obtained from *p*-nitroaniline and *p*-nitrosotoluene. The action of light on (I) yields a red *substance*, m. p. 112—114°, probably an *o*-hydroxy-compound; (II) very slowly turns yellow. Chromic acid oxidation converts (I) into *α-azoxybenzene*-p-*carboxylic acid*, m. p. 230—234°; (II) slowly gives the corresponding β-*acid*, m. p. 241°. Sulphuric acid converts (I) or (II) into a *substance*, $C_{13}H_{12}ON_2$, m. p. 150°, which is not *p*-hydroxy-*p*′-methylazobenzene, and a black substance, m. p. above 250°.

With ethyl nitrite and potassium ethoxide, (II) reacts in a similar manner to *p*-nitrotoluene (which yields the potassium salt of *p*-nitrobenzaldoxime), but no product is isolated. E. W. WIGNALL.

Sulphites of azo-compounds. A. T. KING (J.C.S., 1927, 2639—2647).—The reaction of hydroxyazo-compounds with sodium hydrogen sulphite has been investigated for varying amounts of sulphurous acid and sodium hydroxide. It proceeds at a maximum rate when more than one equivalent of alkali is present. Consequently it is considered that the compounds formed are sulphurous esters of the type $NPh{:}N{\cdot}C_{10}H_6{\cdot}O{\cdot}SO_2H$. The sulphite compounds are stable towards dilute mineral acids and towards acid iodine solution, but the original dye is regenerated with sodium hydroxide. Azo dyes derived from α-naphthol are less reactive towards sodium hydrogen sulphite than those from β-naphthol, whilst aminoazo-compounds do not give sulphite derivatives but may be decomposed completely. The following are described: *sodium* 4-*sulpho*-*α*-*naphthaleneazo*-β-*naphthyl sulphite*, *sodium* p-*sulphobenzeneazo*-β-*naphthyl sulphite*, *sodium benzeneazo*-6 : 8-*disulpho*-β-*naphthyl sulphite*, *sodium α*-*naphthaleneazo*-6 : 8-*disulpho*-β-*naphthyl sulphite*. M. CLARK.

Metallic complexes [co-ordination compounds] of arylazophenanthrols. G. B. CRIPPA [with G. VENTURINI] (Gazzetta, 1927, 57, 593—597).—The property of arylazo-β-naphthylamines and -β-naphthols of giving co-ordinated copper and other compounds is not shared by the corresponding benzene derivatives; 9-arylazo-10-phenanthrols, however, give such compounds, of the general formulæ M_2Cu, M_2Ni, M_2Co, where M is the organic molecule. The compounds are insoluble in water, insoluble or slightly soluble in alcohol or light petroleum, but more or less soluble in hot chloroform, benzene, or xylene. The majority do not melt below 320°. The cobalt compounds are all obtained with difficulty. 9-Benzeneazo-10-hydroxyphenanthrene in chloroform solution forms with ammoniacal copper sulphate the *copper* compound and, similarly, *nickel* and *cobalt* compounds. 9-*p*-Tolueneazo-10-phenanthrol gives a *copper* compound, m. p. 281—282°, *nickel* and *cobalt* compounds. 9-m-*Tolueneazo*-10-*phenanthrol*, m. p. 149°, obtained by condensing *m*-tolylhydrazine hydrochloride with phenanthraquinone, gives a *copper* compound, m. p. 259°, *nickel* and *cobalt* compounds; the corresponding *o*-tolueneazo-compound is not sufficiently soluble in alcohol or chloroform to give co-ordination compounds.

E. W. WIGNALL.

Diazo-sulphonates. W. L. Hall and H. D. Gibbs (J. Wash. Acad. Sci., 1927, 17, 433—444).—Success in the preparation of diazo-sulphonates by the action of sodium sulphite on diazo-compounds depends on the proper control of the p_H value of the reaction mixture. The following procedure gave successful results in all the cases investigated. The diazotised solution and an amount of sodium hydroxide solution sufficient to neutralise the excess of acid are added simultaneously to a cooled sodium sulphite solution, the p_H value of the reaction mixture being kept strictly within certain empirical limits (which vary slightly from case to case but are usually p_H 5·6—9·0) so that at no period is sulphur dioxide liberated; the reaction is completed by heating at 70°. High concentration of all solutions is advisable and salting out of the product is sometimes necessary. The compounds obtained are the very stable *anti* type and are all yellow or orange in colour. By this method ten diazo-sulphonates have been prepared from the appropriate amino-compounds of which the following have not previously been described: *sodium toluene*-o-*diazonium*-, *sodium* m-*xylene*-4-*diazonium*-, *sodium* p-*sulphotoluene*-o-*diazonium*-, *sodium* 2 : 6-*dichlorophenol*-4-*diazonium*-, and *sodium* 2 : 6-*dibromophenol*-4-*diazonium-sulphonates*. On reduction with zinc dust and acetic acid the corresponding hydrazinesulphonates are obtained. The following were prepared by reduction of the corresponding inner diazo-anhydride, but are not described: 3 : 5-*dichloro*-4-*hydroxy*-, 3 : 5-*dibromo*-4-*hydroxy*-, and 3 : 5-*dibromo*-4-*methoxy-phenylhydrazine hydrochlorides*. Diazotisation of 2 : 6-dibromo-4-anisidine in the presence of an insufficient excess of acid yields 3 : 5 : 3′ : 5′-*tetrabromo*-4 : 4′-*dimethoxydiazoaminobenzene*, m. p. 187·7°. J. W. Baker.

Oxidation of phenol with hydrogen peroxide in presence of iron salts. H. Goldhammer (Biochem. Z., 1927, 189, 81—87).—A considerable amount of pyrocatechol is always obtained by oxidation of phenol with hydrogen peroxide in presence of ferric sulphate, together with pyrogallol, purpurogallin, and traces of quinol. A method is described for the determination of each of these constituents in the mixture, and it was found that, according to the conditions of the experiment, the yield of pyrocatechol varied from 3 to 45%. The *o*-dihydroxy-derivative obtained by treating tyrosine in a similar way was produced transiently and in such small amount that its determination was impossible. The highest yield of melanin was 7·6%.

P. W. Clutterbuck.

Additive compounds of phenols and ammonia. II. Ammoniation of mononitrophenols; higher ammoniates. E. Briner and O. Agathon (Helv. Chim. Acta, 1927, 10, 770—781).—Vapour-pressure measurements of nitrophenol–ammonia systems (cf. A., 1926, 1241) have been extended to pressures above the atmospheric. Ammonium *o*-nitrophenoxide forms a *diammoniate*, with an energy change of the order of 60 g.-cal. per g.-mol. *Ammonium* m-*nitrophenoxide*, orange-red, m. p. 58°, does not appear to combine with ammonia, but the *p*-nitrophenoxide probably gives a *monoammoniate*. H. E. F. Notton.

Hydrolysis of organic compounds: [effect of] hydrogen-ion concentration. S. C. J. Olivier and G. Berger (Rec. trav. chim., 1927, 46, 609—618).—Hydrogen-ion concentration, which is without influence on the rate of hydrolysis of esters of strong acids (cf. A., 1925, ii, 802), is similarly ineffective in the hydrolysis of picryl acetate, 2 : 4 : 6-trinitrophenetole, acetic anhydride, benzoyl chloride, and benzenesulphonyl chloride, whilst it has a slight influence on that of benzoic anhydride.

Picryl acetate, m. p. 76°, obtained by the method of Hantzsch (A., 1906, i, 353) contains free picric acid; after washing with water and drying very rapidly the m. p. 96·5—97·5° is found. The ester is dissolved in 50% aqueous acetone and is shaken with benzene and a 2% aqueous potassium sulphate solution; the acid passing into solution in the aqueous layer is titrated. The velocity coefficient $k_{20}=0·032$ is unchanged in presence of 0·0215*N*-hydrochloric acid, rising slightly to 0·040(?) in presence of 0·1075*N*-acid. 2 : 4 : 6-Trinitrophenetole (ethyl picrate), which is decomposed by light and is investigated therefore in the dark, has $k_{30}=0·00012$, unchanged by the presence of hydrochloric acid. Acetic anhydride, which is determined by its reaction with aniline to give acetanilide and acetic acid, has $k_0=0·034$, unchanged by hydrochloric acid. Benzoic anhydride has $k_{40}=0·00079$, rising to 0·0015 as hydrochloric acid is added up to a concentration of 0·211*N*. Benzoyl chloride has $k_0=0·027$, unchanged by sulphuric acid; the velocity of hydrolysis of benzenesulphonyl chloride is not increased by adding sulphuric acid.

E. W. Wignall.

Trisuccinylpicramine. M. Covello and (Signa.) R. Gabrieli (Rend. Accad. Sci. fis. mat. Napoli, 1926, [iii], 32, 147—150).—2 : 4 : 6-Triaminophenol condenses with succinic anhydride to give 2 : 4 : 6-*trisuccinimidophenol*, m. p. 250°, which is hydrolysed by potassium hydroxide solution to *phenol*-2 : 4 : 6-*trisuccinamic acid*, $HO{\cdot}C_6H_2(NH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H)_3$, m. p. 265° (*silver* salt), and is oxidised by nitric acid to 2 : 6-*disuccinimidobenzoquinone*, decomp. 300° (*phenylhydrazide*, m. p. 260° decomp.), which is reduced to the corresponding *quinol*, m. p. 280°.

E. W. Wignall.

Relative directive powers of groups of the forms RO and RR′N in aromatic substitution. VII. Nitration of benzphenetidide and of *o*-, *m*-, and *p*-nitrobenzphenetidides. R. C. Fawcett and R. Robinson (J.C.S., 1927, 2414—2422).—The following compounds, obtained by benzoylation of the appropriate phenetoles, are described: 2- and 3-*nitro*-4-*benzamidophenetole* (I) and (II), m. p. 149—150° and 121·5—122°; 2- and 3-*nitro*-4-o-*nitrobenzamidophenetole* (III) and (IV), m. p. 165—166° and 131—131·5°; 2- and 3-*nitro*-4-m-*nitrobenzamidophenetole*, (V) and (VI), m. p. 202—203° and 157·5—158°; 2- and 3-*nitro*-4-p-*nitrobenzamidophenetole*, (VII) and (VIII), m. p. 208·5—209·5° and 183·5—184·5°. Nitration of benz-*p*-phenetidide in acetic acid, using 2·5 mols. of nitric acid, gives a quantitative yield made up of 7·5% of (I) and 92·5% of (II). Nitration with 12 mols. of nitric acid gives 13% of (I) and 87% of (II). Nitration of *o*-, *m*-, and *p*-nitrobenzphenetidides with 12 mols. of nitric acid gives 43·7% of (III) and 56·3%

of (IV), 30·6% of (V) and 69·4% of (VI), and 33·2% of (VII) and 66·8% of (VIII), respectively. The mixtures of nitro-derivative obtained were analysed thermally. The bearing of these results on the electronic theory of benzene substitution is discussed. M. Clark.

Bromophenols. XXVIII. Dibromo-*o*-anisidine and tribromo-*o*-anisidine. M. Kohn and H. Karlin (Monatsh., 1927, 48, 599—611).—Nitration of 3 : 5-dibromo-*o*-acetanisidide with a mixture of nitric acid (*d* 1·52) and concentrated sulphuric acid at 0° yields 3 : 5-*dibromo*-4 : 6-*dinitro*-o-*acetanisidide*, decomp. 200°. This on hydrolysis with concentrated sulphuric acid and subsequent treatment with pyridine yields an *N*-methylpyridinium salt which on treatment with dilute sulphuric acid yields 3 : 5-*dibromopicramic acid*, m. p. 150°. Treatment of 3 : 5-dibromoanisidine hydrobromide with either liquid bromine or bromine in acetic acid yields 3 : 5 : 6-*tribromo*-o-*anisidine*, m. p. 102°, which on treatment with nitrous acid yields 3 : 5 : 6-tribromoanisole, m. p. 82°, b. p. 305—312°, and this on demethylation yields 3 : 5 : 6-tribromophenol (Bamberger and Kraus, A., 1907, i, 161) (*benzoate*, m. p. 133°). Nitration of 3 : 5 : 6-tribromoanisole with nitric acid (*d* 1·52) at 0° yields 3 : 5 : 6-*tribromo*-2 : 4-*dinitroanisole*, m. p. 141—142°. Chlorination of 3 : 5 : 6-tribromophenol yields 2 : 4-*dichloro*-3 : 5 : 6-*tribromophenol*, m. p. 208—209°, which on methylation with methyl sulphate yields 2 : 4-dichloro-3 : 5 : 6-tribromoanisole (this vol., 51). Iodination of the tribromophenol yields 3 : 5 : 6-*tribromo*-2 : 4-*di-iodophenol*, m. p. 196—197°, which on methylation yields 3 : 5 : 6 - *tribromo*-2 : 4-*di-iodoanisole*, m. p. 176—177°. Nitration of 3 : 5 : 6-tribromo-*o*-acetanisidide with a mixture of nitric acid (*d* 1·52) and concentrated sulphuric acid yields 3 : 5 : 6-*tribromo*-4-*nitro*-o-*acetanisidide*, decomp. 200°. For purposes of comparison the following derivatives of 3 : 4 : 5-tribromophenol were prepared by similar methods : 3 : 4 : 5-*tribromo*-2 : 6-*dinitrophenol*, m. p. 135—136°; 3 : 4 : 5-*tribromo*-2 : 6-*di-iodophenol*, m. p. 207°; 3 : 4 : 5-*tribromo*-2 : 6-*di-iodoanisole*, m. p. 190—190·5°. J. W. Baker.

Bromophenols. XXIX. Molecular wandering in the preparation of tribromo-*o*-anisidine from *o*-nitroanisole. M. Kohn and H. Karlin (Monatsh., 1927, 48, 613—618).—Bromination of *o*-nitroanisole yields 4-bromo-*o*-nitroanisole, which on nitration yields 4-bromo-2 : 6-dinitroanisole, m. p. 85—85·5° (Meldola and Streatfeild, J.C.S., 1898, 73, 688, give 81—82°), and on reduction yields 4-bromo-*o*-anisidine. The latter, on bromination, yields 3 : 5 : 6-tribromo-*o*-anisidine (preceding abstract) instead of the expected 3 : 4 : 5-tribromo-compound, a bromine atom wandering from the 4- to the 6-position during bromination. Proof of the constitution of the product is adduced by its conversion consecutively into 3 : 5 : 6-tribromoanisole and 3 : 5 : 6-tribromophenol. Bromination of *p*-nitroanisole yields 2-bromo-*p*-nitroanisole. J. W. Baker.

Nitration of α-4-methoxy- and α-4-ethoxyphenyl-β-ethylcarbamide. H. F. J. Lorang (Rec. trav. chim., 1927, 46, 635—652).—*p*-Anisidine and ethylcarbimide condense to give α-p-*anisyl*-β-*ethylcarbamide*, m. p. 138°, which is nitrated by absolute nitric acid at −10° to α-*nitro*-β-2 : 3 : 5-*trinitro*-p-*anisyl*-α-*ethylcarbamide*, decomp. 50—60°, which gives nitroamine reactions. With water, the latter yields 2 : 3 : 5-trinitro-*p*-anisidine; with ethyl alcohol, 2 : 3 : 5-trinitro-*p*-anisylurethane (cf. Reverdin, A., 1926, 1243); with methyl alcohol, the corresponding *methylurethane*, m. p. 236—239° (decomp.); with alcoholic ammonia, 2 : 4-dinitro-6-methoxy-*m*-phenylenediamine; with aniline in ether, 2 : 6-*dinitro*-3-*anilino* - 4 - *methoxycarbanilide*, m. p. 182—183° (decomp.).

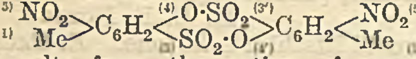
p-Phenetidine and ethylcarbimide condense to give α-p-*phenetyl*-β-*ethylcarbamide*, m. p. 152°, which is similarly nitrated to α-*nitro*-β-2 : 3 : 5-*trinitro*-p-*phenetyl*-α-*ethylcarbamide*, m. p. 92—98° (decomp.). This with water yields 2 : 3 : 5-trinitro-*p*-phenetidine, and also 3 : 5-dinitro-2-hydroxy-*p*-phenetidine; with methyl and ethyl alcohols, the 2 : 3 : 5-trinitro-*p*-phenetyl-methyl- and -ethyl-urethanes, m. p. 236—239° (decomp.) and 218—219°, respectively, each hydrolysed to the amine; with alcoholic ammonia, 2 : 4 - dinitro - 6 - ethoxy - *m* - phenylenediamine; with aniline, 2 : 6 - *dinitro* - 3 - *anilino* - 4 - *ethoxycarbanilide*, m. p. 216—217°.

m-Phenylenediamine reacts with ethylcarbimide to give m-*di*-β-*ethylcarbamidobenzene* (decomp. 120—126° to *s*-diethylcarbamide and *m*-dicarbamidobenzene). The product is nitrated to ββ′ : 2 : 4 : 6′-*pentanitro*-ββ′-*diethyl*-m-*dicarbamidobenzene*, $C_6H(NO_2)_3(NH{\cdot}CO{\cdot}NEt{\cdot}NO_2)_2$, decomp. 80—85°, which with water or alcoholic ammonia yields 2 : 4 : 6-trinitro-*m*-phenylenediamine; with ethyl alcohol, 2 : 4 : 6-*trinitrophenylene*-1 : 3-*diurethane*, m. p. 226°, of which the *methyl* analogue has m. p. 276° (decomp. from 260°); with aniline, 2 : 4 : 6-*trinitro*-1 : 3-*di*-β-*phenylcarbamidobenzene*, m. p. 276°. E. W. Wignall.

Equilibria in binary systems containing trinitro-*m*-cresol. N. N. Efremov and M. A. Tichomirova (J. Russ. Phys. Chem. Soc., 1927, 59, 373—389).—The nature of the binary systems formed by the addition of hydrocarbons and nitro-derivatives to trinitro-*m*-cresol was determined, with the view of utilising them on a technical scale in the manufacture of explosives. Trinitro-*m*-cresol and acenaphthene, phenanthrene, fluorene, and retene gave well-defined *compounds*, but no solid solutions. The acenaphthene *compound*, $C_{12}H_{10},C_6HMe(NO_2)_3{\cdot}OH$, has m. p. 117·9°; the eutectics are at 88·2° and 87·8°, with 9·1% and 79·8% of acenaphthene. The phenanthrene *compound*, $C_{14}H_{10},C_6HMe(NO_2)_3{\cdot}OH$, m. p. 113·1°, is deep red; eutectics 85·6° and 84·2° with 13·5% and 77·5% of phenanthrene. The fluorene *compound*, grey when solid, red when liquid, $C_{13}H_{10},C_6HMe(NO_2)_3{\cdot}OH$, grey solid, red liquid, has m. p. 107·2°; eutectics at 85·4° and 90·5° with 13·8% and 67·4% of fluorene. The retene *compound*, $C_{18}H_{18},C_6HMe(NO_2)_3{\cdot}OH$, violet, has m. p. 118·3°; eutectics at 89·5° and 73·5° with 6·7% and 88·6% retene. The system trinitro-*m*-cresol–anthracene was too unstable to be determined. Trinitro-*m*-cresol with tetranitromethylaniline forms a eutectic at 64·4° with 42·3% of the latter; with picric acid the eutectic point is at 52·5° and 35·6%, with *m*-dinitrobenzene, 55·4° and 44·8%, with trinitrotoluene, 41·3° and 42·3%.

There was no trace of compound or solid solution formation. The explosive properties of the systems are being investigated. M. Zvegintzov.

Rule for direct formation of free acid chlorides by action of phosphorus pentachloride on 6-substituted phenol-*o*-sulphonic acids. R. Anschütz and T. Cürten (Annalen, 1927, 457, 256—267; cf. L. Anschütz, this vol., 663).—A hydroxyl group is protected by the presence of two *ortho* substituents from attack by phosphorus pentachloride, so that 6-substituted phenol-2-sulphonyl chlorides may be prepared directly.

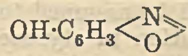
5-*Nitro*-p-*cresol*-3-*sulphonic acid* (discovered by Raschig but not hitherto described), m. p. 84° ($+1·5H_2O$) or 172° (anhyd.; *ammonium, sodium, potassium, silver, magnesium, barium, nickel,* and *cobalt* salts prepared), is converted by phosphorus pentachloride into 5-*nitro*-p-*cresol*-3-*sulphonyl chloride,* m. p. 86—87°, from which are obtained the *sulphonamide,* m. p. 210° (decomp.), *sulphonanilide,* m. p. 217°, and *sulphon*-p-*toluidide,* m. p. 226°. The acid gives the *anhydride,* m. p. 158—159°, when treated with thionyl chloride, and with acetyl chloride or acetic anhydride the *acetate,* which is converted by phosphorus pentachloride into 5-*nitro*-4-*acetoxytoluene*-3-*sulphonyl chloride,* m. p. 101·5° (*sulphonanilide,* m. p. 141·5°, and *sulphon*-p-*toluidide,* m. p. 113°, described). 5 : 5′ - *Dinitrotolylene* - 3 : 4 : 3′ : 4′-*sulphonylide,*

$\overset{(5)}{} NO_2, \overset{(1)}{} Me > C_6H_2 < \overset{(4)\ \ \ \ (3')}{O·SO_2} \underset{(3)\ \ \ \ (4')}{SO_2·O} > C_6H_2 < NO_2^{(5')}, Me^{(1')}$, m. p. 84·5°, results from the action of ammonia or diethylaniline on the acetoxy-sulphonyl chloride, or of phosphoryl chloride on the nitrocresolsulphonic acid.

p-Cresol-3 : 5-disulphonic acid, m. p. 115° ($+2H_2O$) or 145° (anhyd.; *silver,* potassium, and barium salts described), reacts with phosphorus pentachloride to form p-*cresol*-3 : 5-*disulphonyl chloride,* from which the *disulphonanilide,* m. p. 231°, *disulphon*-p-*toluidide,* m. p. 221°, and acetate, m. p. 116°, are prepared. The corresponding tolylene-3 : 4 : 3′ : 4′-sulphonylide-5 : 5′-disulphonyl chloride (Anschütz and Hodenius, A., 1918, i, 425) gives a *disulphonanilide,* m. p. 262—263°, and a *disulphon*-p-*toluidide,* m. p. 258—259°. C. Hollins.

Supposed isomerism of 9-methylfluorenol. H. Wieland and J. Cerezo (Annalen, 1927, 457, 249—255; cf. Wieland and Krause, A., 1925, i, 902).—The "isomeric 9-methylfluorenol," m. p. 84°, is shown to be 9-methylfluorenyl ethyl ether. It is best obtained by Nakamura's method by the action of alcohol on the *acetate* of the true 9-methylfluorenol (m. p. 175°), and is also formed by treating 9-methylfluorenyl chloride with sodium ethoxide. 9-*Methylfluorenyl benzoate,* m. p. 173°, is unchanged by boiling alcohol, but is converted by hot acetic acid into benzoic acid and diphenylene-ethylene [9-methylenefluorane]. C. Hollins.

Synthesis of the homologue of urushiol. II. S. Kawai (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 53—60).—Condensation of sodium phenoxide with geranyl chloride (obtained by Forster's method, J.C.S., 1913, 103, 1338) in toluene by Claisen's method (A., 1925, i, 656) yields o-*geranylphenol,* b. p. 126—130°/0·12—0·09 mm., d_4^{25} 0·97029, n_D^{25} 1·53414, *phenyl geranyl ether,* b. p. 102—106°/0·16 mm. (not quite pure), d_4^{25} 0·9551, n_D^{25} 1·52037, together with an unidentified terpene (cf. Forster, *loc. cit.*). By a similar condensation using pyrocatechol is obtained a mixture of 3-*geranylpyrocatechol,* b. p. 179—180°/0·16 mm., d_4^{20} 1·0566, n_D^{20} 1·55068, and *pyrocatechol monogeranyl ether,* which undergoes isomeric change on distillation in a high vacuum. Separation is effected by conversion into the *lead* salts, that of the former being insoluble in alcoholic lead acetate. Small quantities of a terpene and (?)pyrocatechol digeranyl ether are also obtained. The physiological action of 3-geranylpyrocatechol on the skin closely resembles that of urushiol, whilst *o*-geranylphenol and pyrocatechol monogeranyl ether have no such action. J. W. Baker.

Relative directive powers of groups of the form RO and RR′N in aromatic substitution. VIII. Nitration of 4-*n*-butoxyanisole. J. Clarke, R. Robinson, and J. C. Smith (J.C.S., 1927, 2647—2653).—Treatment of 3- and 2-nitro-4-methoxyphenols with *n*-butyl bromide in boiling methyl alcohol gives 2-*nitro*-4-n-*butoxyanisole* (I), m. p. 13·2°, b. p. 143°/1 mm., $n_D^{14·4}$ 1·5382, and 3-*nitro*-4-n-*butoxyanisole* (II), m. p. —9·7°, b. p. 137°/1 mm., n_D^{14} 1·5358, respectively. Thermal analysis shows that the nitration product of 4-n-*butoxyanisole,* m. p. 24·5—25·5°, obtained by butylation of quinol monomethyl ether, contains 65% of (II). This result is in harmony with the theory advanced previously (A., 1926, 397). A mixture of equal quantities of *n*-propyl gallate, m. p. 147—148°, and *n*-butyl gallate, m. p. 143—144° (lit. 133—134°), melts at 152—154°. Crystallographic data are given for 2-nitro-4-methoxyphenol, 2-nitro-4-ethoxyanisole, and 2-nitro-4-*n*-propoxyanisole. M. Clark.

Dyes and other compounds from 2 : 6-dihydroxytoluene. F. Henrich and W. Herold (Ber., 1927, 60, [*B*], 2053—2058; cf. A., 1921, i, 886; 1923, i, 145).—The development of fluorescence in alkaline solutions of hydroxybenzoxazole derivatives,  $OH·C_6H_3<{N \atop O}>CR$, is observed only when R is an aryl group directly united to the 2-carbon atom and when the hydroxyl group is in the *para*-position to the nitrogen atom. 5-*Nitroso*-2 : 6-*dihydroxytoluene,* m. p. (from benzene) 147° (from alcohol, m. p. 147° after darkening at 127°), is prepared by the action of amyl nitrite on 2 : 6-dihydroxytoluene in ethyl-alcoholic potassium hydroxide; the *potassium, copper, cobalt, nickel, lead, uranium,* and *zinc* salts are described. It is reduced by stannous chloride and hydrochloric acid to 5-amino-2 : 6-dihydroxytoluene, isolated as the *hydrochloride* ($+2H_2O$). The latter substance is converted by boiling benzoyl chloride into a mixture of 5-*benzamido*-2 : 6-*dibenzoyloxytoluene,* m. p. 211°, and 6-*benzoyloxy*-2-*phenyl*-7-*methylbenzoxazole,* m. p. 176°, hydrolysed to 6-hydroxy-2-phenyl-7-methylbenzoxazole, m. p. 206°.

Autoxidation of 3-amino-2 : 6-dihydroxytoluene in alkaline solution gives a blue dye which has not been fully investigated. H. Wren.

Action of ammonia on *iso*safrole oxide. K. Krassovsky and T. Kusner (Ukraine Chem. J., 1926, **6**, 376—381).—Ammonia reacts with *iso*safrole oxide in alcoholic solution at 100° after 10 hrs. to give an *amine* having the structure $CH_2O_2:C_6H_3\cdot CH(NH_2)\cdot CHMe\cdot OH$ or $CH_2O_2:C_6H_3\cdot CH(OH)\cdot CHMe\cdot NH_2$. The compound has an alkaline reaction, is soluble in alcohol and ether, and decomposes on distillation. The *chloroplatinate*, m. p. 195—196° (decomp.), and *picrate*, m. p. 204° (decomp.), are described. E. Rothstein.

Feeble activation of certain extended conjugated systems by doubly-bound oxygen. R. Robinson and A. Zaki (J.C.S., 1927, 2485—2490).—Phenyl 2-chlorostyryl ketone and ethyl 2-chloro-α-cyanocinnamate could not be converted into quinoline derivatives by reaction with carbamide nor would the chlorine atom react with aniline in presence of copper powder. 2-*Chlorobenzylidene*-1 : 3-*diketohydrindone*, m. p. 130—131°, from *o*-chlorobenzaldehyde and diketohydrindene, condenses with carbamide under drastic experimental conditions to give a very small yield of ketoindenoquinoline. 2′-*Chloro*-2 : 4-*dinitrostilbene*, m. p. 174°, and 2′-*methoxy*-2 : 4-*dinitrostilbene*, m. p. 176°, from 2 : 4-dinitrotoluene and *o*-chloro- or *o*-methoxy-benzaldehyde, show no reactivity of the chloro- or methoxyl groups. *Bromodihydrosafrole*, b. p. 160°/16 mm., prepared by the action of hydrobromic acid on safrole, yields *iso*safrole when heated with aniline. *iso*Safrole could not be nitrated directly, but bromodihydrosafrole on nitration in acetic acid solution and subsequent removal of hydrobromic acid yields 6-*nitroisosafrole*, m. p. 88°, the orientation of this compound being established by the preparation of 6-nitropiperonal. No conclusive evidence of reactivity of the methyl group in this compound could be obtained. 6-*Aminoisosafrole*, m. p. 68—69° (*hydrochloride*), may be diazotised and coupled with β-naphthol to give a crimson *azo*-derivative. 6-*Acetamidoisosafrole*, m. p. 206°, yields an oily *dibromide*, converted by alcoholic potassium hydroxide into 5 : 6-methylenedioxy-2-methylindole. It is therefore concluded that extended crotenoid systems may fail to exhibit the reactivity which might be assumed to be their characteristic. *o*-*p*-Substitution in styrene derivatives is probably due to a definite *o*-*p*-orienting influence of the unsaturated group. The views of Baker and Wilson (this vol., 550) regarding the *o*-*p*-orienting influence of ethenoid and benzenoid groups are controverted. M. Clark.

Tautomerism of phenols. X. Phenylhydrazine and naphthols of the α-series. W. Fuchs and F. Niszel (Ber., 1927, **60**, [*B*], 2058—2062; cf. this vol., 257).—The action of phenylhydrazine and sulphurous acid on 1 : 4-dihydroxynaphthalene gives an oily base which is conveniently isolated as the *benzoyl* derivative, m. p. 163°. The latter compound is not identical with the benzoyl compound of 4-benzenehydrazo-α-naphthol, m. p. 162° (conveniently prepared by benzoylation of benzeneazo-α-naphthol by the Schotten–Baumann method and reduction of the product by aluminium amalgam in alcohol). Reduction of 4-benzeneazo-α-naphthol by zinc dust and aluminium filings in alkaline solution followed by benzoylation of the product gives the compound, m. p. 163°. Since this compound loses one half of its nitrogen and affords a *compound*, $C_{23}H_{17}O_2N$, m. p. 202°, when treated with nitrous fumes in alcohol, it is considered to be 4-p-*aminoanilino*-2-*naphthyl benzoate*. H. Wren.

Constitution and colour. XIV. F. Kehrmann (Helv. Chim. Acta, 1927, **10**, 670—676).—The theory of Dilthey (A., 1925, i, 650) is insufficient alone to account for the properties of salt-forming dyes. For instance, the greenish-red diacid salts of azobenzene are represented as derivatives of the feebly-coloured hydrazobenzene, $[Ph\cdot\dot{N}H\cdot\dot{N}H\cdot Ph]A_2$. The formulæ ascribed to monoacid salts of *apo*safranine and other quinoneimine dyes contain amino-groups, whereas diazotisation experiments show that these are present only in polyacid salts.' Dilthey's formulæ fail to express the close chemical resemblance between quinones and dyes, *e.g.*, between *o*-benzoquinone and *N*-phenylphenazonium salts, neither do they account for the absence of triphenylmethane dyes related to *m*-quinones. If, however, the double linking is regarded as co-ordinatively univalent (cf. Piccard and Dardel, A., 1921, ii, 394) it is possible to introduce the classical chromophores into the co-ordination formulæ. Thus, the above azobenzene derivative is written $[Ph\cdot\dot{N}H:\dot{N}H\cdot Ph]A_2$, and dimethylfuchsimonium chloride, $[\dot{C}Ph_2:C_6H_4:\dot{N}Me_2]Cl$. H. E. F. Notton.

New derivative of Michler's ketone. E. Pace (Arch. Farm. sperim., 1927, **26**, 225—230).—pp′-*Tetramethyldiaminoethylbenzhydrol*, $OH\cdot CEt(C_6H_4\cdot NMe_2)_2$, obtained by the action of magnesium ethyl bromide on *pp*′-tetramethyldiaminobenzophenone, has m. p. 127°, and forms a *monohydrochloride*, m. p. 127°, a *monosulphate*, m. p. 144°, an *acetate*, an *oxalate*, and a *tartrate*. Its *benzoyl* derivative, m. p. 166·5°, is without anæsthetic action and passes almost unchanged into the fæces. T. H. Pope.

Stereoisomerism in trisubstituted α-glycols (phenyldialkylglycols and alkylhydrobenzoins). M. Tiffeneau and (Mlle.) J. Lévy (Bull. Soc. chim., 1927, [iv], **41**, 1351—1362).—The action of magnesium alkyl halides on ketols, according to the schemes $OH\cdot CHR\cdot CO\cdot R' \xrightarrow{R''MgX}$

$$OH\cdot CHR\cdot CR'R''\cdot OH \xleftarrow{R'MgX} OH\cdot CHR\cdot CO\cdot R'',$$

does not produce the same glycol, but results in the formation of stereoisomerides. Thus, propionylphenylcarbinol and magnesium methyl iodide yield a β-isomeride of α-*phenyl*-β-*methylbutane*-αβ-*diol*, m. p. 73—74°, whilst acetylphenylcarbinol and magnesium ethyl bromide give the α-isomeride, m. p. 83—84° (Fischer and Taube, A., 1926, 599). Both glycols are dehydrated by concentrated sulphuric acid to α-phenyl-*n*-propyl methyl ketone. Similarly, from acetylphenylcarbinol and magnesium *iso*propyl bromide there is produced an α-isomeride of α-*phenyl*-βγ-*dimethylbutane*-αβ-*diol*, m. p. 98—99°, whilst the β-*isomeride*, m. p. 124—125°, results from magnesium methyl iodide and *iso*butyrylphenylcarbinol. Pairs of isomeric (α- and β-) glycols have been prepared from the requisite ketols and magnesium alkyl halides as follows: α-*phenyl*-β-*ethylpentane*-αβ-*diols*, m. p. 94—95° and 99—100°; α-*phenyl*-β-iso*propylbutane*-αβ-*diols*, m. p. 75° and 113°; α-*phenyl*-β-*ethylhexane*-αβ-*diols*, m. p. 88—89° and 81—81·5° (α- and β-*acetonyl* derivatives, b. p. 155—158°/25 mm., d^0 0·999, and b. p. 170—173°/30 mm., d^0 0·992, respectively); α-*phenyl*-δ-*methyl*-β-*ethylpentane*-αβ-*diols*, m. p. 85—86° and 90—91°; α-*phenyl*-β-n-*propylhexane*-αβ-*diols*, m. p. 115° and 91—92°; α-*phenyl*-β-iso*propylhexane*-αβ-*diols*, m. p. 90° and 75—76°; and α-*phenyl*-β-*benzylpentane*-αβ-*diols*, m. p. 115—116°, and viscous oil. Dehydration of this last pair of glycols yields αβ-diphenylethyl propyl ketone.

Acetylphenylcarbinol and magnesium phenyl bromide yield α-methylhydrobenzoin, m. p. 94—95°, also formed by hydrating methylstilbene oxide. The β-isomeride is obtained from benzoin and magnesium methyl iodide, and has m. p. 104—105° (cf. Fischer and Taube, *loc. cit.*). Similarly, α-ethylhydrobenzoin, m. p. 105—106° (*acetonyl* derivative, m. p. 62—63°), is obtained from magnesium phenyl bromide and propionylphenylcarbinol, whilst the β-isomeride from benzoin and magnesium ethyl bromide has m. p. 116—117° (*acetonyl* derivative, m. p. 42°). Diacetyl and magnesium phenyl bromide yield α-dimethylhydrobenzoin, m. p. 121—122°, whereas benzil and magnesium methyl iodide give β-dimethylhydrobenzoin, m. p. 87°. Dehydration of the α- and β-isomerides gives αα-diphenylethyl methyl ketone.

H. Burton.

Constitution of *iso*campholic acid. P. Lipp and F. Reinartz (Helv. Chim. Acta, 1927, 10, 611—614).—Evidence is adduced in favour of the view that campholic and *iso*campholic acids are stereoisomeric 1 : 2 : 2 : 3-tetramethyl*cyclo*pentane-1-carboxylic acids, the carboxyl group and the 3-hydrogen atom being relatively *cis* and *trans*, respectively. The bromination of *iso*campholic acid by the method of Hell, Volhard, and Zelinsky (Rupe and Briellmann, A., 1922, i, 1017) is not conclusive evidence of the presence of an α-hydrogen atom, since campholic acid is also brominated under these conditions, giving a mixture of products, b. p. 65—75°/2 mm., containing less than 1 atom of bromine per mol. It is assumed that a 3-bromo-derivative is formed in each case, that of campholic acid being partly converted into the lactone, whilst that of *iso*campholic acid is stable. The optically active unsaturated acid obtained (*loc. cit.*) by treating the latter with alkali would, accordingly, be 1 : 2 : 2 : 3-tetramethyl-Δ^3-*cyclo*pentene-1-carboxylic acid. Attempts to isomerise campholic acid by heating at 170—180° with acetic and hydrochloric acids, or by means of ultra-violet light, were unsuccessful.

H. E. F. Notton.

Benzoylformhydroxamic acid oximes. XIV. C. Gastaldi (Gazzetta, 1927, 57, 620—621).—A final contribution to the controversy with Ponzio (cf. this vol., 462). Hydroxylamine is considered unlikely to cause an isomerisation of benzoylformhydroxamic acid to a nitronic acid; the α-oxime is still held to be stereoisomeric with the β-oxime.

E. W. Wignall.

Mechanism of the thermal decomposition of benzoyl peroxide. H. Erlenmeyer (Helv. Chim. Acta, 1927, 10, 620—627).—The formation of benzoic acid in the thermal decomposition of benzoyl peroxide (cf. Gelissen and Hermans, A., 1925, i, 379) may be due (*a*) to the formation of diphenyl which then reacts as follows (*R·H* scheme): $Ph·Ph+(Ph·CO·O)_2 \longrightarrow C_6H_4Ph_2+Ph·CO_2H$; or (*b*) to initial decomposition thus $(Ph·CO·O)_2 \longrightarrow (Ph·CO)_2O+O$, followed by hydrolysis. According to (*a*) the amount of benzoic acid formed should decrease in proportion as the peroxide is diluted with an inert material such as finely-divided carborundum; actually it is found to increase. Further evidence in favour of (*b*) is obtained by exploding the peroxide in air in a closed vessel when the atmospheric oxygen is converted into carbon monoxide, whilst in an atmosphere of carbon dioxide unsaturated gaseous hydrocarbons are formed. In air the reaction (*b*) is probably followed by complete oxidation: $(Ph·CO·O)_2+O+O_2 \longrightarrow CO_2+CO+H_2O$. This reaction provides the water necessary for the hydrolysis of the benzoic anhydride and the heat required for secondary decompositions, *e.g.*, $(Ph·CO·O)_2 \longrightarrow Ph·Ph+CO_2$. The formation of benzoic acid from iodine and benzoyl peroxide (A., 1926, 1138) is explained along similar lines, the *R·H* mechanism suggested by Reynhart (this vol., 356) being disproved by analysis of the reaction product, which contains no iododiphenyl. A further exception to the *R·H* scheme is the decomposition of perbenzoic acid which yields only benzoic acid and oxygen.

H. E. F. Notton.

Method of hydrolysing amides and nitriles. G. Berger and S. C. J. Olivier (Rec. trav. chim., 1927, 46, 600—604).—2 : 6-Dimethylbenzonitrile, which is not hydrolysed by 90% sulphuric acid, nor by a methyl- or amyl-alcoholic solution of potassium hydroxide, is hydrolysed by concentrated sulphuric acid merely to 2 : 6-*dimethylbenzamide*, m. p. 138·5—139° (corr.). This amide can be hydrolysed by 100% phosphoric acid at 145—150°, which is employed also for the hydrolysis of benzamide, benzonitrile, α-naphthonitrile, acetonitrile, and propionitrile, and gives good yields of the acids. Phosphoric acid forms a crystalline *compound* with acetonitrile, m. p. 51—53°.

E. W. Wignall.

Rearrangement of acid azides and hydroxamic acids of geometrical isomerides. L. W. Jones and J. P. Mason (J. Amer. Chem. Soc., 1927, 49, 2528—2536; cf. A., 1926, 279).—When allo*cinnamyl chloride*, obtained by the action of thionyl chloride on ethereal *allo*cinnamic acid at 0°, is treated with sodium azide in ethereal suspension, nitrogen is continuously evolved, indicating the decomposition and rearrangement of the allo*cinnamyl azide*. Treatment of the product with ammonia affords a *styrylcarbamide*, m. p. 143°, identical with that obtained similarly from *styrylcarbimide*, b. p. 107°/12 mm., which is the product of the rearrangement of cinnamyl azide (cf. Forster, J.C.S., 1909, 95, 437) in benzene at 75—80°. It is therefore concluded that the stable configuration is assumed during the rearrangement of *allo*cinnamyl azide. Treatment of styrylcarbimide with water at 50°, or of cinnamyl azide with boiling water, affords s-*distyrylcarbamide*, m. p. 214°. Treatment of ethereal crotonyl chloride with sodium azide affords *crotonyl azide*, a pungent liquid, which loses nitrogen at 75—85° with formation of *propenylcarbimide*, a liquid. Treatment of the latter with ethereal ammonia affords *propenylcarbamide*, m. p. 122°. iso*Crotonyl azide*, obtained similarly, undergoes slow rearrangement at 25—28°, and treatment of the product with ammonia affords propenylcarbamide, identical with the above, indicating that in this case also the stable configuration had been assumed during rearrangement. Cinnamhydroxamic acid is best prepared by the method of Jones and Hurd (A., 1922, i, 248). It has m. p. 119·5° (benzoyl derivative, m. p. 156·5°). When cinnamhydroxamic acid is treated with an equivalent of aqueous sodium carbonate, or when the potassium salt of the benzoyl derivative is warmed with water, a *product*, m. p. 152°, is obtained, which is not the expected disubstituted carbamide. F. G. Willson.

Derivatives of diphenylamine-2-carboxylic acid. III. H. Goldstein and M. de Simo (Helv. Chim. Acta, 1927, 10, 603—606; cf. this vol., 558).—2-Chloro-5-nitrobenzoic acid and *m*-phenylenediamine afford, in presence of potassium carbonate and catalytic copper (" Naturkupfer C "), 4-*nitro*-3′-*aminodiphenylamine*-2-*carboxylic acid*, decomp. about 250°. This is reduced by stannous chloride to 4 : 3′-*diaminodiphenylamine*-2-*carboxylic acid*, m. p. 221° (decomp.) (double *tin* salt; *dihydrochloride*; *methyl* ester, m. p. 120°; *diacetyl* derivative, decomp. 252°). Attempts to condense 2-chloro-4-nitrobenzoic acid with *p*-phenylenediamine yielded only *p*-nitrobenzoic acid. 4′-Diethylaminodiphenylamine-2-carboxylic acid, m. p. 215° (*methyl* ester, m. p. 61°), has been obtained crystalline (cf. Tuttle, A., 1923, i, 1011). 4-Nitro-4′-diethylaminodiphenylamine-2-carboxylic acid is reduced by stannous chloride to 4-*amino*-4′-*diethylaminodiphenylamine*-2-*carboxylic acid*, m. p. 194° (decomp.) (double *tin* salt; *dihydrochloride*; *methyl* ester, m. p. 86°). H. E. F. Notton.

3-Hydroxy*cyclo*hexylacetolactone. R. Robinson and A. Zaki (J.C.S., 1927, 2411—2413).—Reduction of *m*-hydroxyphenylacetic acid with hydrogen in the presence of platinum-black gives, as main product, hexahydrophenylacetic acid together with a small quantity of 3-*hydroxy*cyclo*hexylacetolactone*, b. p. 240—243°. The lactone contains a ring system similar (O instead of N) to that which occurs in the molecules of alkaloids of the morphine group (Gulland and Robinson, J.C.S., 1923, 123, 980). Treatment of ethyl acetonedicarboxylate with ethyl bromoacetate and an alcoholic solution of sodium ethoxide gives *ethyl* βδ-*dicarbethoxy*-γ-*ketopimelate*, b. p. 168—170°/1 mm., hydrolysed by dilute sulphuric acid to acetonediacetic acid. Further treatment with the same reagents gives *ethyl* αββ′-*tricarbethoxy*iso*butyrylsuccinate*, b. p. 189—191°/1 mm. M. Clark.

Beckmann rearrangement of salicylhydroxamic acid derivatives. A. W. Scott and J. H. Mote (J. Amer. Chem. Soc., 1927, 49, 2545—2549).—The *potassium* salt of the *acetyl* derivative, m. p. 142°, of salicylhydroxamic acid (cf. Jeanrenaud, A., 1889, 870) explodes at 85° without evolving any odour of phenylcarbimide. When boiled in aqueous solution, it yields oxycarbanil and acetic acid, whilst *o*-aminophenol could not be detected. The *sodium* and *potassium* salts of the *benzoyl* derivative, m. p. 153°, of salicylhydroxamic acid explode similarly when heated, without evolving odours of phenylcarbimide, and yield oxycarbanil and benzoic acid when boiled in aqueous solution. The results indicate that a carbimide is not formed during the Beckmann rearrangement of these derivatives. F. G. Willson.

Chlorination and bromination of hydroxybenzoic acids with a mixture of halogen acid and hydrogen peroxide. A. Leulier and L. Pinet (Bull. Soc. chim., 1927, [iv], 41, 1362—1370).—Treatment of *o*- and *p*-hydroxybenzoic acids with a mixture of hydrochloric or hydrobromic acid and hydrogen peroxide gives mono- or dihalogenated products according to the conditions employed. *m*-Hydroxybenzoic acid yields the tribromo-derivative. H. Burton.

Velocity measurements on the opening of the lactone ring in derivatives of phthalide. A. Tasman (Rec. trav. chim., 1927, 46, 653—698).—The solubilities, and velocities of ring-opening under the influence of 0·1*N*-potassium hydroxide solution have been determined at 25° for phthalide and its derivatives. For phthalide, $k_{25}\times10^4=49$; for derivatives containing the following substituents the respective values for the solubilities in g. per 100 c.c. of water at 25° and for the velocity coefficient $k_{25}\times10^4$ are: 5-nitro- (new m. p. 147°), 0·0420, 520; 5-amino- (new m. p. 182°), 0·1356, 15; 5-acetamido-, 0·0480, 37; 5-chloro-, 0·0556, 65; 5-bromo-, 0·0480, 75; 5-iodo-, 0·0160, 98; 5-*cyano*- (m. p. 194°, obtained from phthalidediazonium chloride), 0·0316, 280; 5 : 6-dimethoxy- (meconine), 0·2548, 32; 3-nitro-5 : 6-dimethoxy-, 0·0148, 440; 3-amino-5 : 6-dimethoxy-, 0·1752, 29; 3-bromo-5 : 6-dimethoxy-, 0·0032, insufficiently soluble; 3-*cyano*-5 : 6-*dimethoxy*- (m. p. 233·5°, decomp.), 0·0072, insufficiently soluble; 2-methyl- (b. p. 284—285·5°), 0·1012, 34; 5-nitro-2-methyl-, 0·0468, 210; 5-amino-2-methyl-, 0·2652, 22; 5-*cyano*-2-*methyl*- (m. p. 117°), 0·0540 (at 17·5°), 360; 2-ethyl- (b. p. 294·5—295·5°, 151—152°/17 mm.), 0·2904, 30; 5-nitro-2-ethyl-, 0·0584, 160; 5-amino-2-ethyl-, 0·0568, 7·9; 5-*cyano*-2-*ethyl*- (m. p. 90°), 0·0912, 230; 2-*propyl*- (m. p. 20°, b. p. 150°/14 mm., d_{15}^{15} 1·1073, $n_D^{17\cdot5}$ 1·5327; prepared by reducing *propylidenephthalide*, obtained from phthalic and butyric anhydrides and sodium butyrate), 0·0030, 12; 2-iso*propyl*- (m. p. 36°, b. p. 166·5°/24 mm.; obtained from 2-iso*propylidenephthalide*, m. p. 95°), 0·0976, 18; 2-*butyl*- (b. p. 178—180°/16 mm., volatile in steam; prepared from phthalaldehydic acid and butyl iodide), 0·0480, 9·3; 2-phenyl-, 0·0040, ring-opening not detected; 2 : 2-dimethyl-, 0·2196, 11; 5-nitro-2 : 2-dimethyl-, 0·0184, 83; 5-amino-2 : 2-dimethyl- (m. p. 117°), 0·2164, 8·7; 5-*cyano*-2 : 2-*dimethyl*- (m. p. 159°), 0·0232, 67; 2 : 2-diethyl-, 0·0260, and 5-nitro-2 : 2-diethyl-, 0·052, ring-opening not detected; 2 : 2-diphenyl- (m. p. 116°), 0·0040, insufficiently soluble.

The results are compared with those of Teppema (A., 1923, i, 256) on ring-opening under the action of hydrazine. It is observed that the stability of the ring increases as the size and number of substituents in the α-position increase. In the case of nuclear substitution, results obtained using hydrazine are not directly comparable with those obtained using potassium hydroxide; thus the ring of 5-nitrophthalide, opened by potassium hydroxide and giving a velocity coefficient three times as great as that for phthalide itself, is not opened by hydrazine. Attempts are made to explain the effects of nuclear substitution on the basis of (the discarded form of) Lapworth, Kermack, and Robinson's theory of induced alternate polarities, but with little success; it is, however, concluded that the general effect is more powerful than the alternating effect. In the case of phthalide substituted in the 5-position by halogen, it is found that ring-opening is accelerated most by iodine, less by bromine, and least by chlorine.

The great stability of a phthalide ring containing two substituents in the 2-position leads the author to question the view that the red colour produced by the action of alkali on phenolphthalein is due to opening of the ring and formation of a quinonoid structure (cf. the failure on the part of Bassett and Bagnall, A., 1924, i, 856, to isolate coloured salts of phenolphthalein). It is suggested that a keto–enol change at the *p*-hydroxyl group may be concerned in the colour change. E. W. WIGNALL.

Chlorohydrin formation in glycerol and glycol and esterification of hydroxy- and 2 : 5- and 2 : 6-dihydroxy-benzoic acids and of phenylacetic acid in glycerol. A. KAILAN and E. GOITEIN (Monatsh., 1927, 48, 405—443; cf. A., 1925, ii, 49).—The velocity of chlorohydrin formation and of esterification of benzoic, *o*-, *m*-, and *p*-hydroxybenzoic, and phenylacetic acids in absolute glycerol and in glycerol containing varying amounts of water in the presence of hydrogen chloride as a catalyst at 25° is investigated, and the results are compared with those of the corresponding reactions in glycol and alcohol. Esterification in the absence of a catalyst is also studied. At 25°, in glycerol containing 0·01 mol. of water per litre, the unimolecular coefficient for chlorohydrin formation is more than twice as great as that for glycolchlorohydrin in glycol, the ratio being reversed in the presence of 1·35 mols. of water per litre. The influence of water on the velocity in glycerol is large, the presence of 0·66 mol. of water per litre lowering the velocity coefficient to one tenth of its value in absolute glycerol. In the presence of salicylic, anthranilic, and *o*-hydroxybenzoic acids the velocity is increased in both media, and in the presence of 0·03 mol. of water per litre with an acid concentration of 0·1 mol., approximately the same values of the coefficient are obtained with each acid. A comparison of the velocity of chlorohydrin formation in glycol and glycerol with the formation of ethyl chloride in alcohol shows that the effect of water is much smaller in glycol than in alcohol, but is three times as great in glycerol as in alcohol. Esterification in both absolute and moist glycerol is almost quantitative. The unimolecular velocity coefficients for the esterification of *o*-, *m*-, and *p*-hydroxybenzoic and phenylacetic acids in absolute and moist glycerol in the presence of hydrogen chloride as a catalyst are, in all cases, proportional to the concentration of the hydrogen chloride; interpolation formulæ showing the relationship between the values of the velocity coefficients and varying concentration of water are given. In the presence of *N*/6-hydrogen chloride the velocity of esterification of salicylic acid with a water concentration of 0·03 and 0·065 mol. per litre is greater in glycerol than in alcohol, whilst with the other organic acids the velocity is respectively 72—221% and 49—186% greater in alcohol than in glycerol for the same concentrations of water. With water concentrations of 0·73 and 1·35 mols. per litre, the velocity in alcohol is only 55—71% and 37—49%, respectively, of that in glycerol, except with phenylacetic acid, in which case, with a water concentration of 0·73 mol. per litre, it is 40% greater in alcohol than in glycerol. As in the case of butyric and benzoic acids, the velocity of esterification of *o*-, *m*-, and *p*-hydroxybenzoic acids is less in glycerol than in glycol, the ratios of the values of the velocity coefficients for benzoic acid and its *o*-, *m*-, and *p*-hydroxy-derivatives (*N*/6-hydrogen chloride) being, in ethyl alcohol 1·0 : 0·37 : 1·17 : 0·43; in glycol 1·0 : 0·073 : 1·15 : 0·39; and in glycerol 1·0 : 0·081 : 1·23 : 0·38, the relative values for the *o*-, *m*-, and *p*-hydroxybenzoic acids in the three solvents being, respectively, 1·0 : 31·5 : 11·7; 1·0 : 15·8 : 5·4; and 1·0 : 15·3 : 4·8. The velocity of esterification of 2 : 6-dihydroxybenzoic acid in glycerol is less than one half that of the isomeric 2 : 5-acid, whilst the latter is esterified at one fourteenth the rate of salicylic acid. The velocity coefficients for esterification of *o*-, *m*-, and *p*-hydroxybenzoic and phenylacetic acids in the absence of a catalyst at 83° indicate that the reaction is "sesquimolecular" in type, the values of the coefficients for benzoic acid and *o*-, *m*-, and *p*-hydroxybenzoic acids in glycerol containing 0·03—0·05 mol. of water per litre being in the ratios 1·0 : 0·267 : 0·095 : 0·097. In glycerol containing 2 mols. of water per litre the value of the velocity coefficient is 20% smaller than in absolute glycerol, whilst in the case of the fatty acids such water addition has very little effect on the value. J. W. BAKER.

Isomerism of halogenohydroxybenzoyltoluic acids. M. HAYASHI (J.C.S., 1927, 2516—2527).—β-5′-*Chloro*-2′-*hydroxy*-2-*benzoyl*-m-*toluic acid*, m. p. 238—239° [*sodium* salt ($+6H_2O$); *barium* salt ($+8H_2O$)], is obtained by condensation of 3-methylphthalic anhydride and *p*-chloroanisole (or *p*-chlorophenol) in presence of aluminium chloride. It isomerises in presence of concentrated sulphuric acid at the ordinary temperature to α-5′-*chloro*-2′-*hydroxy*-2-*benzoyl*-m-*toluic acid*, m. p. 169—171° [*sodium* salt ($+4H_2O$); *barium* salt ($+2H_2O$)]. Treatment of either isomeride with concentrated sulphuric acid at 100° gives an equilibrium mixture of the two forms (containing only about 1% of the β-isomeride) together with partial conversion into 5-*chloro*-8-*hydroxy*-1-*methylanthraquinone*, m. p. 223—224°. The last-named compound is converted by heating with a solution of boric acid in concentrated sulphuric acid into 5 : 8-dihydroxy-1-methylanthraquinone (A., 1922, i, 946). β-5′-*Bromo*-2′-*hydroxy*-2-*benzoyl*-m-*toluic acid*, m. p. 246—246·5° [*sodium* salt ($+6H_2O$); *potassium* salt ($+3H_2O$)], is similarly isomerised to α-5′-*bromo*-2′-*hydroxy*-2-*benzoyl*-m-*toluic acid*, m. p. 163·5—164° [*sodium* salt ($+4H_2O$); *potassium* salt ($+H_2O$)]. 5-*Bromo*-8-*hydroxy*-1-*methylanthraquinone* has m. p.

198—198·5°. When 5′-chloro-2′-hydroxy-*o*-benzoylbenzoic acid is heated with concentrated sulphuric acid at 100°, 4-chloro-1-hydroxyanthraquinone is obtained in 90% yield; at the ordinary temperature reaction is incomplete (5% yield), and an isomeric form of the acid was not produced. Two theories, one postulating stereoisomerism, the other structural isomerism of the halogenohydroxybenzoyltoluic acids, are advanced. The absence of isomerism in the corresponding benzoic series lends support to the latter explanation. M. Clark.

Catalytic hydrogenations with platinum oxide. I. Salicylic acid and phthalic anhydride. F. Díaz Aguirreche (Anal. Fís. Quím., 1927, **25**, 313—331).—By the hydrogenation of salicylic acid using platinum oxide as catalyst, hexahydrosalicylic acid is obtained, together with a small quantity of pimelic acid. Phthalic acid, similarly, yields hexahydrophthalic acid. G. W. Robinson.

Ether of a ketone hydrate. α-Benzylidene-β-(β-phenylethyl)succinic and benzyl-β-phenylethylmaleic acids. J. Bougault (Compt. rend., 1927, **185**, 717—718).—When benzyl-β-phenylethylmaleic acid (I) (this vol., 665) is boiled for 10 hrs. with sodium hydroxide solution, some *benzyl-β-phenylethylfumaric acid* (?) (II), m. p. 194°, is formed, which is separated from (I) by the greater solubility of its calcium salt. The action of acetic anhydride at 100° for 30 min. on the acid (II) produces the anhydride of (I), showing (II) to be the *trans*-isomeride of (I). The acid (II), on prolonged boiling with acetic anhydride, reverts to the parent anhydride. B. W. Anderson.

Keto- and lactone forms of benzil-*o*-carboxylic acid. A. Hantzsch (J. pr. Chem., 1927, [ii], **117**, 151—153).—Polemical against Meerwein (this vol., 875). J. W. Baker.

Synthesis of *dl*-2 : 5-dihydroxyphenylalanine. K. Hirai (Biochem. Z., 1927, **189**, 88—91).—Gentisaldehyde (2 : 5-dihydroxybenzaldehyde) is prepared by the method of Neubauer and Flatov (A., 1907, i, 771), converted into the dimethyl ether, b. p. 50—51°, and condensed with glycine anhydride by Sasaki's method. 2 : 5-*Dimethoxybenzylidineglycine anhydride* crystallises from hot acetic acid, m. p. 278—279°, and on treatment with red phosphorus and hydrogen iodide gives *dl*-2 : 5-dihydroxyphenylalanine, m. p. 203—204° (decomp.) (cf. this vol., 56). P. W. Clutterbuck.

Products of conversion of *peri*-cyanonaphthalenesulphonic acids [1 : 8-hydroxy- and amino-naphthoic acids]. I. G. Farbenind. A.-G.—See B., 1927, 808.

Manufacture of salts of *o*-aminophenylpropionic acids, its homologues, substitution products, and analogues. I. G. Farbenind. A.-G.—See B., 1927, 810.

Sulphur derivatives of substituted benzaldehydes. H. H. Hodgson and H. G. Beard (J.C.S., 1927, 2423—2428).—Sodium disulphide reacts with 4- and 6-chloro-3-nitrobenzaldehyde in alcoholic solution giving respectively 3 : 3′-*dinitrodibenzaldehyde* 4 : 4′-*disulphide* (I), m. p. 237—238° [*dioxime* (II), m. p. 260—261°; *di*-p-*nitrophenylhydrazone*, m. p. 305—310° (decomp.)], and 3 : 3′-*dinitrodibenzaldehyde* 6 : 6′-*disulphide* (III), m. p. 257° [*dioxime* (IV), explodes 140—160°; *di*-p-*nitrophenylhydrazone*, m. p. 283—284° (decomp.)]. The stable yellow dioxime (II) is converted by cold aqueous sodium hydroxide into an isomeride of deeper colour, m. p. 230—232° (decomp.), which explodes like the dioxime (IV) if suddenly heated at 170°. Compounds (I) and (II) are converted by reduction with alkaline sodium sulphide and subsequent treatment with methyl sulphate into 3-*nitro*-4-*methylthiolbenzaldehyde* (V), m. p. 141—142° [*oxime*, m. p. 210° (*sodium* salt); p-*nitrophenylhydrazone*, m. p. 294—296° (decomp.)], and 3-*nitro*-6-*methylthiolbenzaldehyde* (VI), m. p. 159—160° [*oxime*, m. p. 187° (*sodium* salt); p-*nitrophenylhydrazone*, m. p. 250—252°]. 3-*Nitroso*-4-*methylthiolbenzyl alcohol* (?), m. p. 127°, is obtained as a by-product in the preparation of (V). Reduction of (V) and (VI) with sodium hyposulphite gives unstable amino-derivatives, which diazotise normally in acid solution giving, on treatment with cuprous chloride, 3-*chloro*-4-*methylthiolbenzaldehyde*, m. p. 58—59° [*oxime*, m. p. 134°; p-*nitrophenylhydrazone* (VII), m. p. 222—223°], and 3-*chloro*-6-*methylthiolbenzaldehyde*, m. p. 65° [*oxime*, m. p. 114°; p-*nitrophenylhydrazone* (VIII), m. p. 246°]. The phenylhydrazones (VII) and (VIII) are scarlet and orange respectively and give bluish-purple and reddish-purple colorations with alkali hydroxides, showing the much more pronounced bathochromic effect of the methylthiol group when *para* than when *ortho* to the hydrazine group (cf. A., 1926, 515). Reduction of the oximes of (V) and (VI) with alkaline ferrous sulphate gives 3-*amino*-4-*methylthiolbenzaldoxime* (IX), m. p. 100°, and 3-*amino*-6-*methylthiolbenzaldoxime* (X), m. p. 140°. Treatment with bromine displaces the methylthiol group from (IX), giving 2 : 4 : 5 : 6-*tetrabromo*-3-*aminobenzaldoxime*, m. p. 202—203°, whereas (X) is decomposed. M. Clark.

Preparation of protocatechualdehyde and vanillin. N. Fröschl and P. Bomberg (Monatsh., 1927, **48**, 571—575).—The method of Dimroth and Zoeppritz (A., 1902, i, 293) has been applied to the synthesis of protocatechualdehyde and vanillin from pyrocatechol and veratrole, respectively. By the method of Wallach and Wüster (Ber., 1883, **16**, 145) the authors obtained no formanilide but only diphenylformamidine, it being assumed that at the high temperature employed (>220°) the formanilide is partly decomposed with the liberation of aniline which reacts with unchanged formanilide thus : $NHPh\cdot CHO+NH_2Ph=NHPh\cdot CH{:}NPh+H_2O$. At 190°, however, formanilide is obtained. When equimolecular quantities of dry pyrocatechol and formanilide are fused together in the absence of solvents and with rigid exclusion of moisture, the product treated with phosphorus oxychloride, hydrolysed with alkali, distilled with steam to remove the aniline produced, and the residue acidified and extracted with ether, a mixture of *protocatechualdehyde* in 5% yield (*phenylhydrazone*, m. p. 174—175°) and unchanged pyrocatechol is obtained, the latter being removed by extraction with cold benzene. Vanillin is similarly prepared. An explanation of the mechanism of the reaction is given. J. W. Baker.

Hadromal. C. Hoffmeister (Ber., 1927, **60**, [*B*], 2062—2068).—The treatment of wood powder with boiling stannous chloride solution according to Czapek's method ("Lotosberichte," 1898, No. 7) gives hadromal if interrupted at a suitable time, but if prolonged gives vanillin and pyrocatechol and is thus difficult to control on a considerable scale. Better results are achieved in an apparatus which permits the mixture to be heated by benzene vapour and the product to be extracted simultaneously by benzene. Hadromal is most readily obtained by allowing wood meal, previously extracted with alcohol and benzene, to remain in contact with lead acetate solution and subsequently treating an alcoholic suspension of the insoluble compound of hadromal and lead thus formed with hydrogen sulphide (cf. Combes, A., 1907, i, 839). Gentle treatment of hadromal with potassium permanganate gives vanillin and (?) pyrocatechol, whereas cautious oxidation with very dilute potassium ferricyanide affords 4-hydroxy-3-methoxycinnamic acid. Its identity with 4-hydroxy-3-methoxycinnamaldehyde is confirmed by synthesis of the latter from vanillin and acetaldehyde in the presence of sodium hydroxide. It appears to be present in wood to the extent of about 3% in the form of a cellulose ester. H. Wren.

Derivatives of orcinol. I. E. L. Hirst (J.C.S., 1927, 2490—2495).—The constitutions of the two isomeric orcylaldehyde monomethyl ethers are established by condensation with acetophenone and acetylanisole. Everninaldehyde (Hoesch, A., 1913, i, 474) readily forms pyrylium salts and must therefore be orcylaldehyde 5-methyl ether, in which the hydroxyl group is *ortho* to the aldehyde group. The isomeric ether (Gattermann, A., 1908, i, 31) fails to yield pyrylium salts and is accordingly the 3-methyl ether. The 4′ : 7-dimethoxy-2-phenyl-5-methylbenzopyrylium salts show greatly enhanced fluorescence ascribed to the simultaneous presence of the two methoxy-groups. Orcylaldehyde condenses with acetophenone in presence of hydrogen chloride, giving 7-*hydroxy*-2-*phenyl*-5-*methylbenzopyrylium chloride*, m. p. 206° (decomp.) [*perchlorate*, m. p. indefinite, below 245°; *iodide*, m. p. 225° (decomp.); *mercurichloride*, m. p. 229—230° (decomp.); *ferrichloride*, m. p. 147—148° (decomp.)]. Precipitation with sodium acetate gives the *anhydro-base*, m. p. 156—165° (decomp.), which, after methylation and treatment with ferric chloride, yields 7-*methoxy*-2-*phenyl*-5-*methylbenzopyrylium ferrichloride*, m. p. 181° (decomp.). Orcylaldehyde undergoes similar condensation with acetylanisole, giving 7-*hydroxy*-4′-*methoxy*-2-*phenyl*-5-*methylbenzopyrylium chloride* ($+1\frac{1}{2}H_2O$), m. p. 242—243° (decomp.) [*iodide*, m. p. 235—236° (decomp.); *ferrichloride*, m. p. 149—150° (decomp.)]. Everninaldehyde condenses with acetophenone, giving 7-*methoxy*-2-*phenyl*-5-*methylbenzopyrylium chloride* ($+1\frac{1}{2}H_2O$), m. p. 173—174° (decomp.) [*iodide*, m. p. 191—192° (decomp.)], and with acetylanisole giving 4′ : 7-*dimethoxy*-2-*phenyl*-5-*methylbenzopyrylium chloride*, m. p. 214—215° (decomp.) [*ferrichloride*, m. p. 177° (decomp.)]. Orcylaldehyde 3-methyl ether condenses with acetylanisole in presence of potassium hydroxide solution giving p-*anisyl* 4-*hydroxy*-2-*methoxy*-6-*methylstyryl ketone*, m. p. 194—195°. An acetone solution of orcylaldehyde 3-methyl ether reacts with methyl chloroformate giving 5-*methylcarbonato-orcylaldehyde* 3-*methyl ether*, m. p. 80—81° (phototropic). This compound is oxidised in neutral solution by potassium permanganate to 5-methylcarbonato-orsellinic acid 3-methyl ether, converted by alkali into orsellinic acid 3-methyl ether. M. Clark.

Cyclic thioketones. E. Fromm (Ber., 1927, **60**, [*B*], 2090—2094).—Successive treatment of *cyclo*pentanone dissolved in alcohol with hydrogen chloride and hydrogen sulphide yields *trithio*cyclo*pentanone*, $(C_5H_8S)_3$, m. p. 99°, oxidised by potassium permanganate to the corresponding *trisulphone*, m. p. 172°. *Trithio*cyclo*hexanone*, m. p. 101—102°, is oxidised to the *sulphidedisulphone*, $C_{18}H_{30}O_4S_3$, m. p. 175·5—176·5°, and converted when heated at 160° into hydrogen sulphide and the *compound*, $C_{18}H_{28}S_2$, m. p. 182°. *cyclo*Hexanone and ethyl mercaptan afford 1 : 1-diethylthiol*cyclo*hexane (cf. Rècsei, this vol., 750) oxidised to 1 : 1-diethylsulphonyl*cyclo*hexane, m. p. 118—119°. *p*-Methyl*cyclo*hexanone is converted successively into *trithio*-p-*methyl*cyclo*hexanone*, m. p. 94·5—95·5°, and the corresponding *sulphidedisulphone*, m. p. 253—254°; *diethylthiol*-p-*methyl*cyclo*hexane* and *diethylsulphonyl*-p-*methyl*cyclo*hexane*, m. p. 112—113°, are described. Pulegone is converted by hydrogen sulphide and hydrogen chloride into *trithio*-m-*methyl*cyclo*hexanone*, m. p. 182—183°, and trithioacetone; the corresponding *sulphidedisulphone*, m. p. 266—267°, *diethylthiol*-m-*methyl*cyclo*hexane*, and *diethylsulphonyl*-m-*methyl*cyclo*hexane*, m. p. 107—108°, have been isolated. H. Wren.

Carbon rings. IX. Degradation of civetone, civetol, and civetane. L. Ruzicka, H. Schinz, and C. F. Seidel (Helv. Chim. Acta, 1927, **10**, 695—706).—Civetone is reduced, (*a*) by sodium and alcohol to *civetol* (Δ^{θ}-cyclo*heptadecenol*), b. p. 157—158°/1 mm., m. p. 65°; (*b*) by hydrogenation in presence of platinum-black in glacial acetic acid to *dihydrocivetol* (cyclo*heptadecanol*), m. p. 80°, b. p. 155°/0·5 mm.; (*c*) by Wolff's method through the semicarbazone to a mixture of civetol, removed as the hydrogen phthalate, and *civetane* (*cyclo*heptadecene), b. p. 120—125°/1 mm., m. p. 47°; (*d*) by Clemmensen's method to a mixture (I) of civetane and *cyclo*heptadecane (A., 1926, 727), from which the former is removed by oxidation with permanganate. Dihydrocivetol is oxidised by aqueous chromic acid to dihydrocivetone (A., 1926, 615) and dehydrated by potassium hydrogen sulphate to civetane. With phosphorus tribromide it yields *bromo*cyclo*heptadecane*, b. p. 150—160°/0·5 mm., which gives civetane with alcoholic potassium hydroxide. Oxidation of any of the above samples of civetane or of the mixture (I) with permanganate yields mainly tetradecane-αξ-dicarboxylic acid together with suberic and sebacic acids; whilst ozonisation affords pentadecane-αο-dicarboxylic acid and other products. Civet contains about 3% of civetol, which may be isolated as the hydrogen phthalate from the fraction of b. p. 160—170°/1 mm. after removing the civetone as semicarbazone. In order to establish the identity of natural and synthetic civetol, the former was oxidised with chromic acid to civetone and with permanganate to θ-*ketopentadecane-αο-dicarboxylic acid* (*methyl* ester, m. p. 60°), identical with the keto-acid previously obtained (*loc. cit.*) from civetone and erroneously described as η-ketotetradecane-αξ-dicarboxylic acid. The synthesis of both acids will be described later. The constitutions of civetol and civetone are thus completely established.

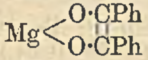
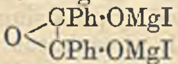
H. E. F. NOTTON.

Mechanism of molecular rearrangements. (MME.) RAMART-LUCAS (Compt. rend., 1927, 185, 718—721).—Theoretical. An explanation of the mechanism of the Beckmann and pinacolin rearrangements and of the dehydration of alcohols in terms of the migration of valency electrons between neighbouring atoms (cf. this vol., 1051; Perrin, *ibid.*, 1009).

B. W. ANDERSON.

Reduction of benzophenone by magnesium amalgam. Correction. M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1927, 49, 2666; cf. following abstract).—Benzophenone is reduced by a mixture of magnesium and mercury, but not by magnesium amalgam previously prepared by heating the metals together (cf. Schlenk and Thal, A., 1913, i, 1205).

F. G. WILLSON.

Reduction of benzil by the binary system, magnesium–magnesium iodide (or bromide). M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1927, 49, 2584—2592; cf. this vol., 245).—When metallic magnesium is added to a solution of benzil in ether–benzene containing magnesium iodide or bromide, an amount of magnesium is dissolved, corresponding with 1 atom per mol. of benzil, and the solution contains the colourless *halomagnesium glycoloxide*, [Hal·Mg·O·CPh:]$_2$, in quantitative yield. The reaction proceeds more slowly, but completely, in presence of only traces of the magnesium halide, with production of the *magnesium glycoloxide*,  $Mg{<}\begin{matrix}O{\cdot}CPh\\ \Vert\\ O{\cdot}CPh\end{matrix}$. Whilst the reaction mixture is finally only pale yellow, deep green and brown colorations are produced as the reaction proceeds, and these are ascribed to the formation of derivatives of the quinhydrone type, or alternatively, to the presence of free radicals. The glycoloxides react vigorously with oxygen, with production, on subsequent hydrolysis, of benzil (40%), a polymeride of benzilic acid anhydride (40%), and benzoic acid (13%) (cf. Staudinger and Binkert, A., 1922, i, 1016), apparently through the intermediate formation of the *oxide*,  $O{<}\begin{matrix}CPh{\cdot}OMgI\\ |\\ CPh{\cdot}OMgI\end{matrix}$. The production of both benzil and benzilic acid probably indicates the existence of this oxide in two stereoisomeric forms. Treatment of the magnesium glycoloxide with water affords benzoin, whilst acetyl chloride and benzoyl chloride yield, respectively, diacetoxy- and dibenzoyloxy-stilbene. Benzyl chloride and methyl iodide are without action on the glycoloxide, but triphenylmethyl chloride affords a small proportion of a yellow *product*, m. p. 180—190°, probably the corresponding triphenylmethyl ether, together with oxidation and reduction products of triphenylmethyl. Bromine and iodine oxidise the glycoloxide, with production of benzil. A solution of benzil and magnesium bromide in ether–benzene deposits the *compound* $(CPhO)_2,MgBr_2,Et_2O$, which dissociates in presence of water. The addition of benzil to a solution of magnesium iodide in ether–benzene causes liberation of iodine. Subsequent treatment with oxygen affords the above oxide, indicating the formation, from the benzil and magnesium iodide, of the iodomagnesium glycoloxide. The latter can also be demonstrated by treating the magnesium iodide–benzil mixture with molecular silver, mercury, or zinc, which displace the equilibrium by removal of the iodine. A similar result is obtained with magnesium bromide, although bromine is not liberated from the latter and benzil alone. Similar results can be obtained with benzil and beryllium and beryllium iodide, and with magnesium amalgam. These reactions probably proceed through an intermediately-formed magnesium subhalide.

F. G. WILLSON.

Nitrogen trichloride and unsaturated ketones. G. H. COLEMAN and D. CRAIG (J. Amer. Chem. Soc., 1927, 49, 2593—2596).—Treatment of phenyl styryl ketone with nitrogen trichloride in carbon tetrachloride affords the *hydrochloride*, m. p. 206—208°, of *phenyl α-chloro-β-amino-β-phenylethyl ketone* (*benzoyl* derivative, m. p. 186—187°). On reduction with sodium amalgam, this yields *α-amino-γ-hydroxy-αγ-diphenylpropane*, m. p. 122—124°, which is also obtained similarly from the monoxime of dibenzoylmethane.

F. G. WILLSON.

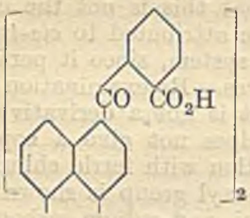
Perylene and its derivatives. XIII. A. PONGRATZ (Monatsh., 1927, 48, 585—591).—3 : 9-Dibromo- and 3 : 9-dichloro-perylene (Zinke, Linner, and Wolfbauer, A., 1925, i, 383) when heated with cuprous cyanide (in the former case with quinoline as a solvent) are converted into 3 : 9-*dicyanoperylene*, not melting at 360°, which when heated with alcoholic potassium hydroxide at 200° yields *perylene*-3 : 9-*dicarboxylic acid*, sintering and decomp. about 360° (*diethyl* ester, m. p. 264—265°). Perylene when treated with acetyl, *p*-chlorobenzoyl, and *o*-toluoyl chlorides in carbon disulphide with aluminium chloride as a catalyst yields, respectively, 3 : 9-*diacetyl*-, m. p. 300—301°, 3 : 9-*di*-p-*chlorobenzoyl*-, m. p. 284—285°, and 3 : 9-*di*-o-*toluoylperylene*, m. p. 280—282°. Similar treatment of 3 : 9-dichloroperylene with acetyl and propionyl chlorides yields, respectively, 3 : 9-*dichloro*-4 : 10-*diacetyl*-, decomp. above 320°, and 3 : 9-*dichloro*-4 : 10-*dipropionyl-perylene*.

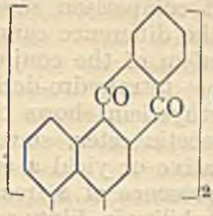
J. W. BAKER.

Perylene and its derivatives. XIV. A. ZINKE, G. GORBACH, and O. SCHIMKA (Monatsh., 1927, 48, 593—598).—The action of phthalic anhydride on perylene in the presence of anhydrous aluminium chloride in solvents under varying conditions yields a mixture of mono- and di-carboxybenzoylperylenes (I). Retreatment of the product with aluminium chloride at 170° for 2 hrs., or heating perylene, phthalic anhydride, and aluminium chloride together at 170° for 3 hrs. yields 3 : 9-*diphthaloylperylene* (II). The action of 4-chlorophthalic anhydride on perylene in carbon disulphide in the presence of aluminium chloride yields a mixture of 4-*chloro*-2-*carboxybenzoyl*-

perylene, m. p. 263°, and *di-(4-chloro-2-carboxybenzoyl)-perylene*, m. p. 350° (decomp.), which are separated

(I.)



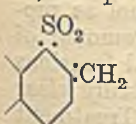


(II.)

by extraction with boiling benzene, the mono-com pound being soluble. When the dibenzoyl compound is heated with aluminium chloride at 170° for 2 hrs. it yields *dichlorodiphthaloylperylene*. J. W. BAKER.

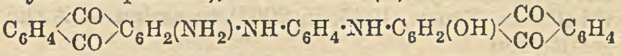
Formation of anthraquinone by vapour-phase oxidation of toluene and petroleum distillates containing toluene. A. R. BOWEN and A. W. NASH (Nature, 1927, 120, 621).—Small amounts of anthraquinone, together with benzoic acid and benzaldehyde, have been obtained by passing air mixed with the vapour of toluene or a petroleum distillate containing toluene (12 litres per hr.) over a catalyst, consisting of aluminium grains coated with vanadium pentoxide, at 400°. A. A. ELDRIDGE.

1-Nitro-2-methylanthraquinone. A. LOCHER and H. E. FIERZ (Helv. Chim. Acta, 1927, 10, 642—670).—Nitration of 2-methylanthraquinone (cf. Eder, A., 1924, i, 528) with sulphuric acid and potassium nitrate at 0° yields a mixture from which pure 1-nitro-2-methylanthraquinone (82% of theoretical) is obtained by boiling with 10% sodium sulphite, the other isomerides being converted into sulphonic acids. Bromination of 1-amino-2-methylanthraquinone at the ordinary temperature affords 4-*bromo*-1-*amino*-2-*methylanthraquinone*, m. p. 346—347° (decomp.). This is converted by diazotisation and heating into 4-*bromo*-1-*hydroxy*-2-*methylanthraquinone*, m. p. 176—177°, and by boiling with *p*-toluenesulphonamide in presence of sodium and copper acetates into 1-*amino*-4-*toluenesulphonamido*-2-*methylanthraquinone*, m. p. 271—272°, hydrolysed by sulphuric acid to 1 : 4-*diamino*-2-*methylanthraquinone*, m. p. 247—248°. 1-Amino-4-hydroxy-2-methylanthraquinone is obtained by heating the bromo-derivative at 150° with sulphuric and boric acids. 2-Methylanthraquinone-1-sulphonic acid ($+2H_2O$) [*potassium*, *sodium* ($+2H_2O$), and *barium* salts] is obtained (60% yield) together with 2-methylanthraquinone by heating 1-nitro-2-methylanthraquinone with 15% sodium sulphite at 135—140° (cf. Ullmann and Bincer, A., 1916, i, 483). Unlike other anthraquinonesulphonic acids, this loses the sulphonic group when heated at 120—130° with sulphuric acid or oleum. The formation in the direct sulphonation of 2-methylanthraquinone of a mixture of sulphonic acids from which none of the 2-derivative can be isolated is thus explained. 2-*Methylanthraquinone*-1-*sulphonyl chloride*, m. p. 165° (decomp.), loses hydrogen chloride when heated in indifferent solvents, giving yellow 2-*methyleneanthraquinone*-1-*sulphene* (annexed formula), m. p. 221—222°. This is converted by water into the sulphonic acid and by aniline into 2-*methylanthraquinone*-1-*sulphonanilide*, m. p. 132—133°. 1 : 5-Dinitro-2-methylanthraquinone, m. p. 346—347° (cf. Eder, *loc. cit.*), is not attacked by boiling sodium sulphite solution, but 1 : 8-dinitro-2-methylanthraquinone gives 2-*methylanthraquinone*-1 : 8-*disulphonic acid* ($+5H_2O$) (*sodium* and *lead* salts). 1 : 5-Diamino-2-methylanthraquinone (*dibenzoyl* derivative, m. p. 286—287°) has m. p. 213—214° (cf. Schaarschmidt, A., 1913, i, 95).



Careful bromination of 1-nitro-2-methylanthraquinone in nitrobenzene at about 160° affords 80% of 1-*nitro*-2-*bromomethylanthraquinone* (I), m. p. 210—211° (decomp.), which is oxidised by nitric and chromic acids to 1-nitroanthraquinone-2-carboxylic acid, and gives on further treatment with bromine (?) 1-*nitro*-2-*dibromomethylanthraquinone*, m. p. 245—246°. The compound (I) undergoes a remarkable intramolecular oxidation–reduction when heated in dichlorobenzene, giving 1-aminoanthraquinone-2-carboxylic acid, and when heated with aqueous sulphuric acid at 155° it gives 3-*bromo*-1-*aminoanthraquinone*-2-*carboxylic acid* (II), m. p. 326—327°. The mechanism of these reactions is discussed (cf. Scholl, Monatsh., 1913, 34, 1011). (II) is quantitatively converted by sulphuric and boric acids into 1-*amino*-3-*hydroxyanthraquinone*-2-*carboxylic acid*, m. p. 322—323° (*silver* salt, which gives phthalic anhydride on heating). 1 : 3-*Diaminoanthraquinone*-2-*carboxylic acid*, m. p. 320—325°, with sublimation (*sulphate*), is prepared from (II) through the insoluble 3-p-*toluenesulphonamido*-derivative. 4-Bromo-1-aminoanthraquinone-2-carboxylic acid has m. p. 324—325° (cf. Scholl, *loc. cit.*). The bromo-derivative (I) is converted by 15% sodium sulphite at 120° into 2-*sulphomethylanthraquinone*-1-*sulphonic acid*, the *potassium* salt of which is converted by water at 200° into *potassium* 1-*hydroxy*-2-*methylanthraquinone*-ω-*sulphonate*. H. E. F. NOTTON.

New class of vat dyes of the anthraquinone series. H. T. BUCHERER and T. MAKI (Ber., 1927, 60, [*B*], 2068—2078).—The action of concentrated sulphuric acid on aminoanthraquinones and nitro-compounds leads to the production, *inter alia*, of vat dyes. For the reaction, 2-aminoanthraquinone is the most important component, followed by 2 : 6-diamino- and 1-amino-anthraquinone, whilst *m*-nitroaniline, nitrobenzene, and *p*-nitroaniline are most serviceable as nitro-compounds. With concentrated sulphuric acid the reaction is frequently violent and is then accompanied by production of ammonia as well as of sulphur dioxide. The change may be moderated by employing a large excess of acid; with 80—90% acid the reaction is less violent but condensation is incomplete. Inorganic addenda appear to offer no advantages. 2-Aminoanthraquinone and nitrobenzene yield unchanged amino-compound, products soluble in alkali hydroxide (mainly 2-amino-1-hydroxyanthraquinone), a *substance* (?)



$$C_6H_4{<}{\begin{smallmatrix}CO\\CO\end{smallmatrix}}{>}C_6H_2(NH_2){\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_2(OH){<}{\begin{smallmatrix}CO\\CO\end{smallmatrix}}{>}C_6H_4$$

soluble in quinoline but not in dimethylaniline, the actual *dye*, $C_{62}H_{39}O_{11}N_5$, insoluble in quinoline, and traces of anthraquinone. The *dye*, $C_{68}H_{39}O_{10}N_5$, obtained from 2-aminoanthraquinone, nitrobenzene, and 84% sulphuric acid is more violet in colour and less sensitive to acids than that obtained with the concentrated acid. The brownish-black *dye* derived from 2-aminoanthraquinone, *p*-nitroaniline, and concentrated sulphuric acid resembles that obtained with nitrobenzene and appears to be a mixture of di- and tri-hydroxy-compounds. From 2-aminoanthraquinone, *p*-nitrosophenol, and 80% sulphuric acid the *substance* $C_{60}H_{32}(CO)_8(NH)_5(NH_2){\cdot}OH$ is derived in poor yield. With *m*-nitroaniline and 1-nitronaphthalene, 2-aminoanthraquinone and concentrated sulphuric acid yield respectively the *dyes* $C_{68}H_{40}O_9N_4$ and $C_{76}H_{43}O_{11}N_5$, the latter being produced in small yield. If nitrobenzene is replaced by *o*-nitrotoluene, the *compound* $C_{70}H_{41}O_{10}N_5$ is produced, the methyl group of the *o*-nitrotoluene suffering oxidation. Anthraquinone, nitrobenzene, and concentrated sulphuric acid give the *dye* $C_{46}H_{23}O_7N_3$ in good yield. Nitrobenzene, 1-aminoanthraquinone, and concentrated sulphuric acid yield unchanged aminoanthraquinone, products soluble in alkali hydroxide (? aminohydroxyanthraquinones), a *substance*, $C_{40}H_{23}O_5N_3$, soluble in quinoline but insoluble in dimethylaniline, and a *dye*, $C_{68}H_{39}O_{10}N_5$, in much poorer yield than is the case when 2-aminoanthraquinone is used. Substitution of *p*-nitroaniline for nitrobenzene makes little difference in the character of the dye produced, whereas a bluish-grey vat dye with much better affinity for cotton is prepared by using *m*-nitroaniline. From aniline, nitrobenzene, and concentrated sulphuric acid a black dye, insoluble in alkali hydroxide, is produced which, in paste form, dissolves in alkaline hyposulphite but loses this property after being dried. H. WREN.

New products of the anthraquinone series [hexahydroarylaminoanthraquinones, acid wool dyes]. I. G. FARBENIND. A.-G.—See B., 1927, 809.

Constituents of kawa root. V. Synthesis of yanganol. W. BORSCHE and C. WALTER (Ber., 1927, 60, [*B*], 2112—2113; cf. this vol., 664).—*p*-Methoxycinnamic acid, prepared in 80—90% yield by heating a mixture of anisaldehyde, malonic acid, pyridine, and piperidine, is converted by thionyl chloride into the corresponding chloride, m. p. 50°, which with methyl sodioacetoacetate affords *methyl* p-*methoxycinnamoylacetoacetate*, m. p. 80—81° (*copper* derivative, m. p. 196—197°). The latter substance is converted by water at 130° into βδ-diketo-ζ-*p*-methoxyphenyl-Δ^{ϵ}-hexene, m. p. 93°, identical with yanganol (cf. Borsche and Gerhardt, A., 1915, i, 438). *Methyl* p-*methoxycinnamoylacetate*, m. p. 84—85°, is prepared by the action of aqueous ammonia (*d* 0·91) on the corresponding acetoacetate. H. WREN.

Constituents of kawa root. VI. Constitution of methysticin. W. BORSCHE, C. H. MEYER, and W. PEITZSCH (Ber., 1927, 60, [*B*], 2113—2120; cf. this vol., 563, 664).—The observation of optical activity in methysticin has led Murayama and Shinozaki (Chem. Zentr., 1925, ii, 2062) to assign to it the constitution

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH<\genfrac{}{}{0pt}{}{CH_2-CO}{O{\cdot}C(OMe)}\geqslant CH$$

in place of the Pomeranz structure, $CH_2O_2{:}C_6H_3{\cdot}[CH{:}CH]_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Me$, which they attribute to *iso*methysticin. The latter substance might therefore be identical with the *allo*methysticin prepared by Borsche, Rosenthal, and Meyer (*loc. cit.*) by deacetylation of methyl piperonoylacetoacetate. Direct comparison shows that this is not the case and the difference cannot be attributed to *cis–trans* isomerism of the conjugate system, since it persists in the tetrahydro-derivatives. Re-examination of *iso*methysticin shows that it is not a derivative of acetoacetic ester, since it does not give a copper derivative or yield a coloration with ferric chloride. The presence of a free carboxyl group is shown by its solubility in dilute ammonia and sodium carbonate and the evolution of 1 mol. of carbon dioxide without loss of methoxyl when heated above its m. p. The identity of methystic acid of Pomeranz and Winzheimer (A., 1908, i, 805), which has the composition $C_{15}H_{14}O_5$, and not $C_{14}H_{12}O_5$ as previously supposed, with the *iso*methysticin of Murayama and Shinozaki (*loc. cit.*) is established and the substance is therefore β-methoxy-ζ-methylenedioxyphenyl-$\Delta^{\alpha\gamma\epsilon}$-heptatrienoic acid, which accords with its hydrolysis by dilute acids into methyl alcohol, carbon dioxide, and methysticol and accounts for the impossibility of converting methystic acid into methysticin by methyl-alcoholic hydrogen chloride. The conversion of *iso*methysticin into *allo*methysticin is accomplished by methylation with diazomethane followed by cautious treatment of the product with alcoholic hydrogen chloride, whereby only the enolic methoxyl group is affected. The transformation of methysticin into methystic acid (=*iso*methysticin) is not a case of hydrolysis, but of the isomerisation of a dihydro-α-pyrone to a trebly unsaturated acid, and as there is no analogy for the simultaneous displacement of the methyl group from the α- to the γ-oxygen atom the constitution

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH<\genfrac{}{}{0pt}{}{CH_2{\cdot}C(OMe)}{O\text{———}CO}\geqslant CH$$

must be assigned to methysticin. Similarly, kawaic acid is probably to be regarded as β-methoxy-ζ-phenyl-$\Delta^{\alpha\gamma\epsilon}$-heptatrienoic acid.

The following new compounds are incidentally described: *ammonium methystate*; *tetrahydro*iso*methysticin*, m. p. 137—138°, identical with tetrahydromethystic acid of Goebel (A., 1922, i, 657); *copper* compound of *allo*methysticin, $(C_{15}H_{13}O_5)_2Cu$, decomp. about 220° after darkening; *tetrahydro*allo*methysticin*, isolated as the *copper* compound, $(C_{15}H_{17}O_5)_2Cu$, m. p. 130°. H. WREN.

Caoutchouc. III. Preparation of homogeneous caoutchouc hydrocarbons. R. PUMMERER and H. MIEDEL (Ber., 1927, 60, [*B*], 2148—2152).—Extraction of caoutchouc with acetone combined with repeated intermediate precipitation of the material from benzene by alcohol or acetone removes oxygenated impurities soluble in acetone, but does not eliminate albumins and sugars. Systematic extension of the fractional precipitation method of Pummerer and Koch (A., 1924, i, 1214), in which benzene, hexahydrotoluene, light petroleum, and ether are used as solvents and acetone or alcohol as precipitants, does not lead to the certain removal of nitrogenous impurities, although individual fractions are free from nitrogen and soluble to initially clear solution in hexahydrotoluene or ether. Treatment of caoutchouc with methyl-alcoholic potassium hydroxide removes nitrogenous and acidic substances completely, but the loss of material and the difficulty of removing the last traces of alkali render the method suitable only on a small scale. The portion of caoutchouc soluble in ether can be obtained by fractional dissolution (cf. Feuchter, B., 1926, 100), but "smoked sheet" and "crêpe caoutchouc" are unsuitable for this purpose. Crude, preserved latex is subjected to dialysis to remove salts, carbohydrates, etc. soluble in water, coagulated, and extracted with acetone to remove water and resinous material. The finely-divided material gives a solution of nitrogen-free "diffusion caoutchouc" in ether which is readily freed from oxidation products by precipitation with acetone. The portion insoluble in ether contains the impurities present originally in the caoutchouc which may amount to 33% of its weight. H. Wren.

Caoutchouc. IV. Preparation of pure caoutchouc from latex by means of alkali and its division into sol and gel caoutchouc. R. Pummerer and H. Pahl (Ber., 1927, 60, [*B*], 2152—2163; cf. preceding abstract).—Rubber latex, preserved with ammonia, is agitated with aqueous sodium hydroxide (2%) during 2 days at 50°, the cream is separated, and the operation repeated until the biuret and ninhydrin reactions are negative and the aqueous solution reacts only slowly with permanganate. The cream is washed with water, dialysed, and coagulated by acetone or acetic acid. Extraction of the product with acetone serves essentially to remove the water, thus giving "total caoutchouc" which retains the double linkings of the original material and contains 0·077% of ash. All the actual hydrocarbons of the latex, including the sparingly soluble portions, are present. Systematic treatment of "total caoutchouc" with ether in an atmosphere of carbon dioxide leads to its division into "sol caoutchouc" and "gel caoutchouc," the latter of which contains the integument components of the latex droplet. "Sol," "gel," and "total" caoutchouc soften at 115—130°, 145—160°, and 130—145°, respectively. "Gel caoutchouc" behaves normally towards iodine monochloride, requiring 1 mol. of iodine for each C_5H_8 group. Prolonged rolling renders "gel caoutchouc" soluble in ether. Similar solubility is conferred by treatment with benzene, toluene, xylene, chlorobenzene, or, particularly, cumene, but the regenerated "gel caoutchouc" is not identical with "sol caoutchouc." A well-defined end-point to the solubility of "total caoutchouc" in ether as assumed by Feuchter does not exist. "Sol" and "total" caoutchouc give closely similar hydrochlorides. When treated in hexahydrotoluene with tetranitromethane at 0° the caoutchoucs give additive products stable at 60° in a high vacuum. With the technical varieties such as crêpe or smoked sheet or the authors' pure caoutchouc the ratio of tetranitromethane to isoprene groups is 1 : 5. This ratio is also observed with "gel caoutchouc" whether suspended or rendered soluble, but with "sol caoutchouc" the ratio is 1 : 6. It is uncertain whether the reaction affords a definite chemical method of distinguishing between "sol" and "gel" caoutchouc. The additive compounds are not crystalline; when heated they become yellow at 150°, brown at 175°, and ultimately carbonise. Vulcanisation with 10% of sulphur under 3½ atm. of steam converts pure caoutchouc into a product very similar to that derived from the best technical varieties, whereas with 7½% of sulphur vulcanisation of the pure material occurs more slowly owing to the absence of albumins. "Sol" and "gel" caoutchouc appear to be vulcanised much more slowly than "total" caoutchouc with 7·5% of sulphur. Vulcanisation of pure caoutchouc with 30% of sulphur gives a product with better insulating properties than that obtained from crêpe rubber. H. Wren.

Caoutchouc. V. Absorption of caoutchouc and guttapercha in the ultra-violet region of the spectrum. G. Scheibe and R. Pummerer (Ber., 1927, 60, [*B*], 2163—2167).—Comparison of the absorption curves of caoutchouc at various stages of purification dissolved in hexahydrotoluene in an atmosphere of carbon dioxide allows the elucidation of the true curve for caoutchouc. This, when considered in conjunction with the curves of trimethylethylene and diallyl, leads to the conclusion that not more than one conjugated double linking can be present in the caoutchouc molecule for every thousand ordinary double linkings. Optical observations are in harmony with Harries' formulation of caoutchouc, but scarcely reconcilable with Staudinger's assumption of the presence of tervalent carbon atoms in considerable number. The varying behaviour of solutions of caoutchouc in hexahydrotoluene towards hydrogenation (cf. Pummerer and Burkard, A., 1923, i, 49) does not appear to be due to difference in the number of double linkings in the molecule. The absorption curve of purified guttapercha in hexahydrotoluene is completely identical with that of caoutchouc; the number and type of double linkings in the two compounds must therefore be very similar. "Sol," "gel," and "total" caoutchouc have been examined in hexane solution after addition of piperidine. In the lower portion of the curve "gel" caoutchouc exhibits a rather more pronounced absorption; otherwise the curves are identical. H. Wren.

Caoutchouc. VI. Cryoscopic determinations of the mol. wt. of caoutchouc. R. Pummerer, H. Nielsen, and W. Gündel (Ber., 1927, 60, [*B*], 2167—2175; cf. A., 1924, i, 1214).—When precautions are taken to secure a true solution of the caoutchouc in camphor (by spreading the material in a film over the inside of the tube by evaporation of a solution and subsequently adding the camphor) every purified sample has approximately the same mol. wt., varying from 1100 to 1600. Variation of the concentration of the solutions between 1 in 4 and 1 in 10 is without effect. In spite of the high m. p. of camphor, the caoutchouc does not appear to be changed chemically. In benzylidenecamphor, m. p. 98°, the observed mol. wts. are generally higher than in camphor (1400—2500), but the depression constant is much smaller and the results are less accurate. In menthol (using Beckmann's apparatus) the mol. wt. of caoutchouc is 1200—1600 at concentrations of 1 in 50, whereas in 1% solution the mol. wt. sinks to 520—620 and remains constant at greater dilutions as far as the method permits of accurate measurement. This corresponds with the presence of eight isoprene components in the molecule. It is remarkable that "sol" and "gel" caoutchouc which differ most widely in their solubilities have exactly the same mean mol. wt. in camphor and menthol. The decisive factor in the different caoutchouc fractions cannot therefore be the mean mol. wt.

Abnormalities in the hydrogenation of caoutchouc have been observed by Pummerer and Koch (A., 1924, i, 1214) whereby double linkings disappear without absorption of hydrogen, presumably owing to ring formation. Almost quantitative ring formation is recorded in the case of a sample of "sol" caoutchouc exposed to hydrogen at 60 atm. pressure in the presence of spongy platinum. In the presence of purified caoutchouc spongy platinum frequently acquires the ability to absorb very large quantities of hydrogen whilst the caoutchouc is not invariably actually hydrogenated; the platinum passes partly into colloidal solution. Hydrocaoutchouc, containing 14% of hydrogen and traces of colloidal platinum, is autoxidisable, containing more than 20% of oxygen after exposure to the air during 5—8 weeks. Dehydrogenation is not caused thereby. The older experiments of Pummerer and Burkard (A., 1923, i, 49) were not performed with isolated material.

H. WREN.

Oxidation of santonin. I. S. S. MEDVEDEV (Trans. Karpov Inst. Chem., 1924, No. 3, 41—53).—Oxidation of santonin (10 g.) with ammonium persulphate in acetic acid yields a *compound*, $C_{10}H_{12}O_3$, m. p. 80—90° (2·6 g.); chromic acid and acetic acid give santeninic acid, m. p. 130—131° (*bromo*-derivative $C_{15}H_{16}O_4Br_2$, m. p. 120° [decomp.]; *oxime*, decomp. 190°). At 125—130° in a vacuum, santeninic acid loses 2 mols. of water, affording santenin, m. p. 135—136°, yellow (*acetyl* derivative, m. p. 112·5°; *oxime*, decomp. 190—200°). Santeninic acid is regarded as 1 : 4-dimethyl-3 : 7-diketohexahydronaphthylpropionic acid, and santenin the lactone.

CHEMICAL ABSTRACTS.

Two sterol-like substances from *Asclepias syriaca*. II. L. SCHMID and E. LUDWIG (Monatsh., 1927, 48, 577—583).—The mixture of two sterol-like substances, m. p. 176°, isolated by Schmid and Stohr from *Asclepias syriaca* (this vol., 248) has now been separated and shown by comparison of a series of derivatives to be identical with α- and β-amyrin isolated by Rollett (cf. this vol., 248) from *Manila elemi* resin. The mixture is benzoylated and from the product the pure β-benzoate, m. p. 231° (corr.), is obtained, from which are prepared the *alcohol*, m. p. 199·5—200°, *acetate*, m. p. 238—239°, and *formate*, m. p. 238—239°, identical with the corresponding derivatives obtained from β-amyrin benzoate. Treatment of the mother-liquor from the β-benzoate with bromine in acetic acid yields the bromo-α-benzoate, m. p. 239°, identical with bromoamyrin α-benzoate (Zinke, Friedrich, and Rollett, A., 1921, i, 39, give m. p. 229°) obtained by the same method from the mixture of amyrin α- and β-benzoates. From the bromo-α-benzoate are obtained the *bromo-α-alcohol*, m. p. 180°, and the *bromo-α-acetate*, m. p. 263°, identical with the preparations from bromoamyrin α-benzoate. All m. p. are corrected.

J. W. BAKER.

Strophanthin. XI. Hydroxyl groups of strophanthin. XII. Oxidation of trianhydrostrophanthidin. XIII. *iso*Strophanthidin and its derivatives. XIV. Isomerisation in the *iso*strophanthidin series. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1927, 74, 795—804, 805—810, 811—827, 829—837).—XI. Methyl strophanthidinate (cf. A., 1926, 73) was oxidised by chromic acid to a monoketo-ester, *methyl strophanthidonate*, $C_{24}H_{32}O_7$, m. p. 161—162°, $[\alpha]_D$ +26° in pyridine, which no longer gave a benzoate; the acylatable carbinol group of strophanthidin is therefore secondary. On warming with methyl-alcoholic hydrochloric acid, the above ester lost $1H_2O$ to give *methyl monoanhydrostrophanthidonate*, m. p. 210°, $[\alpha]_D$ +123° in pyridine (*oxime*, m. p. 290—291°); this, on hydrogenation, yielded a *dihydro*-derivative, m. p. 209°, which gave a nitroprusside reaction, indicating the persistence of the βγ-unsaturated linking. On similar, but more drastic, treatment with methyl-alcoholic hydrochloric acid, methyl strophanthidinate yielded an *anhydro*-derivative, m. p. 205—206°, $[\alpha]_D$ +25° in pyridine, which, with chromic acid, gave *methyl dianhydrostrophanthidonate*, $C_{24}H_{28}O_5$, m. p. 202—203°, $[\alpha]_D$ +131° in pyridine. Dihydrostrophanthidinic lactone gave a *benzoate*, m. p. 271—272°; strophanthidinic lactone, a *benzoate*, m. p. 263—264°. The enhanced lability of one hydroxyl group in methyl strophanthidonate indicates that the latter is an αβ-unsaturated ketone; in the dehydration of methyl strophanthidinate the third hydroxyl group must be involved. The results further indicate that the action of concentrated hydrochloric acid in forming ψ-strophanthidin from strophanthidin (A., 1925, i, 566), and the neutral dilactone, now designated strophanthidinic lactone, from strophanthidinic acid (A., 1926, 73), involves one of the tertiary carbinol groups, and must cause a rearrangement of the aldehyde (or carboxyl) group into the *cis*-position with respect to this carbinol group.

XII. Trianhydrostrophanthidin gave, with potassium permanganate in acetone, an *acid*, $C_{20}H_{24}O_3$, m. p. 206—208°, which did not contain a lactone group, failed to give the nitroprusside reaction, and did not absorb bromine; the substance was therefore formed by oxidation of the βγ-unsaturated lactone linking, which is probably the lactone of an aldehydo-acid, of which the β- or γ-carbon atom is linked to the benzene ring of trianhydrostrophanthidin. Oxidation of the latter with chromic acid gave an *acid*, $C_{23}H_{24}O_6$, m. p. 236—237° (*methyl* ester, m. p. 144—146°), which retained the unsaturated lactone group and the benzene ring of trianhydrostrophanthidin, and contained, in addition, a new lactone group; this result is explained by oxidative cleavage of the second ring between the carbon atom carrying the acylatable carbinol group of strophanthidin (which now becomes a lactone carbon atom) and the adjoining CH_2 group, which is oxidised to carboxyl.

XIII. Methyl α-*iso*strophanthate gave, with chromic acid, *methyl α-isostrophanthonate*, $C_{25}H_{34}O_8$, m. p. 254—255°, $[\alpha]_D$ −6·2° in pyridine, which gave no benzoate, but yielded an *oxime*, m. p. 228°, and, with alcoholic hydrochloric acid, readily gave an *anhydro*-derivative, $C_{25}H_{32}O_7$, m. p. 210°, $[\alpha]_D^{25}$ +74° in pyridine; the latter, with sodium hydroxide, gave the *methyl hydrogen* ester, m. p. 260°, and, on hydrogenation, *methyl deoxy*-α-iso*strophanthonate*, m. p. 206°, $[\alpha]_D$ −4° in pyridine. Methyl strophanthidinate, with methyl-alcoholic potassium hydroxide, gave *methyl* α-iso*strophanthidinate*, m. p. 270—271°, $[\alpha]_D^{25}$ +84° in pyridine, from which was obtained α-iso*strophanthidindiacid methyl hydrogen* ester, m. p. 204—206°; this gave the *methyl* ester, m. p. 226—228° (*semicarbazone*, m. p. 144—146°). On prolonged contact with cold methyl-alcoholic potassium hydroxide, methyl strophanthidinate gave the *methyl half-acetal* of *methyl oxido*-α-iso*strophanthidinate*, m. p. 219—220°. After hydrolysis of the lactone group, α-*iso*strophanthidindiacid methyl hydrogen ester gave, with hypobromite, α-*iso*strophanthic methyl hydrogen ester; the methyl ester, with chromic acid, yielded methyl α-*iso*strophanthonate (see above). The results indicate that on hydrolysis of the lactone group of α-*iso*strophanthidin a second aldehyde group is liberated, which, on oxidation, is converted into carboxyl and forms a lactone with the same (tertiary) carbinol group as was involved in the original lactone grouping; this original lactone grouping of α-*iso*strophanthidin is a βγ-unsaturated lactone of a β-aldehydo-acid.

XIV. From the mixture of substances produced by boiling α-*iso*strophanthidic acid in dilute sodium hydroxide, there was isolated, by means of its insoluble ammonium salt, β-iso*strophanthidic acid*, m. p. 175—180°, $[\alpha]_D$ −14° in alcohol, which on oxidation with permanganate gave β-iso*strophanthic acid*, m. p. 280°, $[\alpha]_D^{26}$ −24° in methyl alcohol, and, with hypobromite, the previously described acid, $C_{23}H_{30}O_7$ (A., 1924, i, 1331), which is now shown to be β-iso*strophanthic lactone acid*; α-*iso*strophanthidic acid could not be oxidised in the above manner and therefore does not exist in the oxidic form; the aldehyde and secondary carbinol groups must therefore be in the *cis*-position in the β-acid and *trans*- in the α-acid. On treatment with concentrated hydrochloric acid, α-*iso*strophanthic acid gave γ-iso*strophanthic acid*, m. p. 231—232°, $[\alpha]_D$ +90° in alcohol (*methyl* ester, m. p. 227°, $[\alpha]_D$ +120° in pyridine, giving, on oxidation, *methyl* γ-iso*strophanthonate*, m. p. 235°, $[\alpha]_D$ +106° in pyridine, *anhydro*-derivative, m. p. 168—171°, $[\alpha]_D$ +160° in pyridine). β-*iso*Strophanthic acid gave similarly δ-iso*strophanthic lactone acid*, m. p. 230—231°, $[\alpha]_D^{17}$ +29° in pyridine, which, on hydrolysis, yielded δ-iso*strophanthic acid*, m. p. 209—210°, $[\alpha]_D^{17}$ +72° in methyl alcohol.

C. R. HARINGTON.

Crossed dismutation between aldehydes and ketones. I. Benzaldehyde and menthone in relation to the menthone–menthol reactions in *Mentha piperita*, L. S. M. GORDON (J. Biol. Chem., 1927, 75, 163—168).—*l*-Menthone condenses with benzaldehyde in presence of aluminium ethoxide, giving l-*neomenthyl benzoate*, b. p. 165—170°/10 mm., $[\alpha]_D^{25}$ −20·24°; *l*-neomenthol gives an α-*naphthylcarbamate*, m. p. 32°, and a 3 : 5-*dinitrobenzoate*, m. p. 94°.

C. R. HARINGTON.

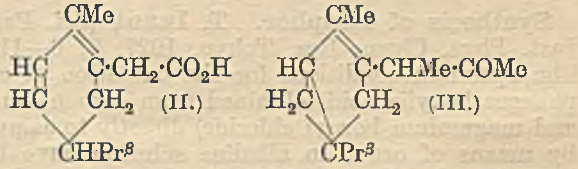
Existence of menthone in the enol form. S. M. GORDON (Amer. J. Pharm., 1927, 99, 599—603).—Mixtures of menthone with acetic anhydride, prepared in 1910, have been analysed for the amount of ester present. This was greatest for the mixture containing equimolecular proportions.

S. I. LEVY.

Chemistry of the three-carbon system. XV. Pulegone and *iso*pulegone. W. E. HUGH, G. A. R. KON, and R. P. LINSTEAD (J.C.S., 1927, 2585—2594).—The conditions are defined for the oxidation of *iso*pulegol to *iso*pulegone. The pure ketone is regarded as having b. p. 101—102°/17 mm., $d_4^{20\cdot4}$ 0·92177, $n_D^{20\cdot4}$ 1·46787, α_D +24·7° in methyl alcohol. A small quantity of the inactive ketone is also obtained by this method. No *iso*pulegone could be found in oil of pennyroyal as stated by Grignard (A., 1926, 408); the fraction of the oil corresponding with Grignard's *iso*pulegone consists principally of menthone. The equilibrium between pulegone and *iso*pulegone was studied in the presence of sodium ethoxide, barium hydroxide, sodium carbonate, piperidine, and sulphuric acid. In the first two cases, equilibration is rapid and the final product is indistinguishable from pure pulegone within the limits of experimental error. The iodometric method of Linstead and May (this vol., 1167) serves for accurate determination of the proportion of pulegone and *iso*pulegone in mixtures of the two ketones.

M. CLARK.

Chemistry of the three-carbon system. XVI. Effect of bridged and unsaturated rings on tautomerism. W. E. HUGH and G. A. R. KON (J.C.S., 1927, 2594—2600).—Dehydration of β-thujolacetic acid with acetic anhydride gives β-*thujylideneacetic acid* (I), m. p. 103—104° (*acid chloride*, b. p. 136—138°/14 mm.; *ethyl* ester, b. p. 136—137°/10 mm., $d_4^{17\cdot8}$ 0·95995, $n_D^{17\cdot8}$ 1·47800; *anilide*, m. p. 118·5°), oxidised by potassium permanganate in a current of steam to oxalic acid and β-thujone. Dehydration of ethyl β-thujolacetate gives, instead of the βγ-isomeride of (I), an *acid* (II), m. p. 169° (*sodium* and *silver* salts).



(II.) (III.)

The αβ-acid (I), on treatment with alkali, is partly converted into the liquid βγ-isomeride, but the extent of conversion (75% of βγ-isomeride) is much less than in *cyclo*hexylideneacetic acid (cf. this vol., 356). β-*Thujylideneacetone*, b. p. 120°/10 mm., $d_4^{17\cdot4}$ 0·93111, $n_D^{17\cdot4}$ 1·48464 (*semicarbazone*, m. p. 191°), obtained by the action of zinc methyl iodide on the chloride of β-thujylideneacetic acid, has the αβ-structure, although the corresponding *cyclo*hexane compound has the double linking in the ring. Methylation yields a *ketone* (III), b. p. 122°/14 mm., $d_4^{17\cdot8}$ 0·91690, $n_D^{17\cdot8}$ 1·47339 (*semicarbazone*, m. p. 194°), with the βγ-structure. β-Thujone condenses with acetone, giving 2-iso*propylidene*-β-*thujone*, m. p. 78·5° (*semicarbazone*, m. p. 208°). It is concluded that bridged rings in which the strain of the *cyclo*hexane ring is already relieved have a much diminished tendency to acquire a double linking. When one double linking is already present in the ring, the tendency to produce a conjugated system with two double linkings in the ring is so great that, as in the case of dihydro-*m*-tolylacetic acid, the βγ-form alone is stable.

M. Clark.

Catalytic action of reduced copper on *iso*borneol. T. Ikeda (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 1—5).—The action of reduced copper on the vapour of *iso*borneol has been investigated at various temperatures and pressures. At 135—140°/1 atm. the main product is camphene together with 10—15% of camphor. At 170° only a trace of camphor is obtained, whilst at 210—220° camphene is the sole product. At 350—360° terpenes and high-boiling substances are also produced by the action of the copper on the camphene. At 190—200° or 270—280°/3—4 mm., *iso*borneol gives a little camphor, but is otherwise unaffected.

J. W. Baker.

Oxidation of *iso*bornyl acetate with ozone. T. Ikeda and Y. Fujita (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 12—20).—No appreciable amount of oxidation occurs when *iso*bornyl acetate is treated in glacial acetic acid with twice the theoretical quantity of ozone at temperatures between 1° and 100°, and under similar conditions in acetone solution a substance chemically identical with *iso*bornyl acetate but with a much higher b. p., 153—154°/10 mm., is obtained. A large excess of ozone in acetic acid solution gives rise to *keto*iso*bornyl acetate*, b. p. 150—155°/10 mm., d_4^{20} 1·0657, n_D^{20} 1·47131 (*semicarbazone*, m. p. 187°), which is not identical with acetoxycamphor. Hydrolysis of the semicarbazone with aqueous sodium carbonate yields the *semicarbazone*, m. p. 224°, of keto*iso*borneol. A second *semicarbazone*, m. p. 197—198°, was obtained from the residues of the original oxidation product. Ozonolysis of *iso*bornyl acetate in cold acidified acetone gave a small quantity of a viscous *substance*, b. p. 135—140°/8 mm.

J. W. Baker.

Synthesis of camphor. T. Ikeda (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 6—11).—The optimum conditions for the oxidation of camphanecarboxylic acid (obtained from carbon dioxide and magnesium bornyl chloride) directly to camphor by means of ozone in alkaline solution have been investigated. No oxidation occurs at the ordinary temperature (or in glacial acetic acid) and the velocity of formation of camphor is greater the more concentrated the alkali. The best catalysts found for the oxidation were manganese borate and ferrous sulphate; with a 10% solution of the potassium salt in *N*-potassium hydroxide with the addition of 2% of the former catalyst at 90—95°, a 15% yield of camphor was obtained in 9 hrs.

J. W. Baker.

Action of potassium cyanide on pernitroso-derivatives. M. Passerini and (Signa.) G. Bruscoli (Gazzetta, 1927, 57, 598—605).—See this vol., 670: a more detailed account is now given.

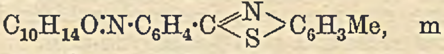
E. W. Wignall.

New compounds of camphor with amines. P. Saccardi and E. Romagnoli (Arch. Farm. sperim., 1927, 26, 197—204).—*Camphanylidene*-p-*aminophenol*, $C_{10}H_{16}{:}N\cdot C_6H_4\cdot OH$, prepared by the interaction of pernitrosocamphor and *p*-aminophenol, has m. p. 144°, and forms unstable, soluble *sodium* and *potassium* compounds, also a *hydrochloride*, m. p. 212° (decomp.); an *oxalate*, m. p. 190° (decomp.); an *acetate*, and an insoluble *ferrocyanide*, which turns brown at 105° and chars at above 200°.

Camphanylidene-p-*phenetidine*, m. p. 207°, similarly obtained, forms an unstable *hydrochloride*, an *oxalate*, m. p. 175° (decomp.), and a *ferrocyanide* which turns brown at 150° and chars at above 200°.

T. H. Pope.

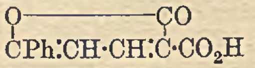
Influence of the sulphur atom on optical rotatory power. P. P. Shukla (J. Indian Inst. Sci., 1927, 10A, 33—41; cf. Hilditch, J.C.S., 1908, 93, 1618).—The depression in rotatory power due to the introduction of a bivalent sulphur atom was found to vary considerably in some thio-derivatives of arylbisiminocamphors. The following compounds were prepared by boiling alcoholic solutions of camphorquinone and the appropriate thio-base (modifications of the published methods for the preparation of these thio-bases had to be adopted to obtain good yields) in presence of anhydrous sodium sulphate: *thiodiphenylenebisiminocamphor*, $(C_{10}H_{14}O{:}N\cdot C_6H_4\cdot)_2S$, m. p. 215° $[\alpha]_D$ 947°; *methylbenzthiazolebenzenyliminocamphor*,



$C_{10}H_{14}O{:}N\cdot C_6H_4\cdot C{<}\genfrac{}{}{0pt}{}{N}{S}{>}C_6H_3Me$, m. p. 182°, $[\alpha]_D$ 564·8°; pp′-*dithiodiphenylenebisiminocamphor*, $(C_{10}H_{14}O{:}N\cdot C_6H_4\cdot S\cdot)_2$, m. p. 201—202° (colour changes at 160° and 195°), $[\alpha]_D$ +820°; pp′-*thioditolylenebisiminocamphor*, m. p. 216°, $[\alpha]_D$ +407·6°; and a brown *compound*, m. p. 216°, formed in the attempt to condense dithio-*p*-toluidine with camphorquinone. Dinitrodiphenyl disulphide has m. p. 182°.

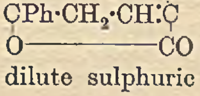
B. W. Anderson.

Synthesis of phenylcoumalin and of a quinoline derivative. J. Kalff (Rec. trav. chim., 1927, 46, 594—599).—Attempts to synthesise phenylcoumalin (6-phenyl-α-pyrone) by condensing benzoylacetaldehyde with malonic acid or by condensing phenylglyoxal with succinic anhydride and sodium succinate were unsuccessful. The mixed anhydride of crotonic and benzoic acids cannot be obtained from crotonyl chloride and sodium benzoate, and the product of the action of sodamide on acetophenone when treated with ethyl phenylpropiolate gives only 2 : 6-diphenyl-γ-pyrone. Phenylpropargylaldehyde, obtained by the action of alcoholic potassium hydroxide solution on the acetal of bromocinnamaldehyde, followed by hydrolysis by dilute sulphuric acid (Weigand, Diss., Kiel, 1902), condenses, however, with malonic acid to give *propargylidenemalonic acid*. This is obtained in two forms: at the ordinary temperature (I), soluble in sodium hydrogen carbonate solution, m. p. 208—218° (corr., decomp.), and at 100° (II), insoluble, m. p. 218° (corr., decomp.), are obtained. For these the respective formulæ



$$\begin{array}{l}O\text{———————}CO\\ CPh{:}CH\cdot CH{:}C\cdot CO_2H\end{array}$$

and



$$\begin{array}{l}O\text{————}CO\\ CPh\cdot CH_2\cdot CH{:}C\\ O\text{————}CO\end{array}$$

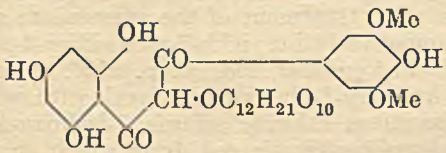
are suggested. On heating in dilute sulphuric acid, (I) is largely converted into

(II), stable to sulphuric acid, but also loses carbon dioxide to give phenylcoumalin, m. p. 68°, identical with that obtained from Coto bark.

When phenylpropargylaldehyde is warmed with β-naphthylamine in acetic acid, 1-phenyl-β-naphthaquinoline is obtained. E. W. Wignall.

2 : 3 : 4′-[6 : 7 : 4′-]Trihydroxyflavone. G. Bargellini and A. Grippa (Gazzetta, 1927, 57, 605—609).—When 2 : 4 : 5-trimethoxyacetophenone is condensed with methyl anisate in presence of sodium, 2 : 4 : 5 : 4′-*tetramethoxybenzoylacetophenone*, m. p. 138—140°, is obtained, which when heated with hydrobromic acid gives 6 : 7 : 4′-*trihydroxyflavone*, $(+H_2O)$, decomp. 300° (*triacetyl* derivative, m. p. 234—236°). Heating with hydriodic acid gives, however, a mixture containing also mono-, di-, and tri-methoxy-compounds. A *dimethyl ether* of 6 : 7 : 4′-trihydroxyflavone $(+H_2O)$, m. p. 158—162° (decomp.) (*acetyl* derivative, m. p. 164—166°), can thus be isolated. 6 : 7 : 4′-*Trimethoxyflavone*, m. p. 184—186°, is obtained by methylation of the latter or of the trihydroxyflavone. E. W. Wignall.

Vegetable colouring matters. IV. Anthocyanins and anthocyanidins. P. Karrer, R. Widmer, A. Helfenstein, W. Hürliman, O. Nievergelt, and P. Monsarrat-Thoms (Helv. Chim. Acta, 1927, 10, 729—757; cf. this vol., 252, 571).—Malvin chloride is oxidised by 15% hydrogen peroxide to *malvone*, $C_{29}H_{36}O_{19},H_2O$ (65% of theoretical), m. p. 220—230°, sintering from 100°, and traces of syringic and phloroglucinolcarboxylic acids. Malvone reduces Fehling's solution and yields 2 mols. of dextrose on acid hydrolysis. It is very readily hydrolysed by boiling alkali to syringic acid (70% of theoretical). At the same time the disaccharide residue is detached entire and converted into a product which has no further reducing properties, but gives 1 mol. of dextrose when boiled with acid. Since the glucosides of phloroglucinol and of syringic acid are not hydrolysed by alkali, malvone is represented by (I), the



(I.)

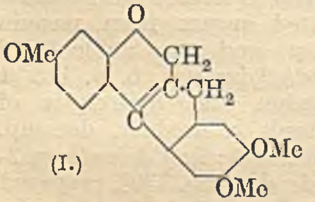
extra H_2O (above) being probably attached to one of the keto-groups. With phenylhydrazine and sodium acetate, malvone gives a *phenylhydrazone*, $C_{23}H_{20}O_7N_2(OC_6H_{11}O_5),H_2O$, m. p. indef., losing 1 mol. of dextrose as phenylglucosazone. After prolonged treatment with diazomethane the ketone gives a crystalline *product* which contains 7 methoxyl groups and is hydrolysed to 3 : 4 : 5-trimethoxybenzoic acid. When other anthocyanins and anthocyanidins are oxidised with 15% hydrogen peroxide, the latter yield secondary oxidation products much more readily than the former. Ketones resembling malvone have not been isolated. Thus, syringidin gives syringic acid, pæonidin vanillic acid, and pelargonidin, *p*-hydroxybenzoic acid in fair yield, whilst malvin and pæonin give only traces and pelargonin none of the corresponding acids. This is due to the disaccharide residue in the 3-position (cf. Atree and Perkin, this vol., 231) which prevents the pyrylium nucleus from assuming tautomeric forms in which it is more readily oxidised. Proof of this explanation is furnished by comparing the behaviour of 3 : 5 : 7-trimethoxy-2-phenylbenzopyrylium chloride (Pratt and Robinson, A., 1924, i, 306) towards hydrogen peroxide with that of 3-*hydroxy*-5 : 7-*dimethoxy*-2-*phenylbenzopyrylium chloride*, prepared by Robinson's method from 2-hydroxy-4 : 6-dimethoxybenzaldehyde and ω-hydroxyacetophenone. Under similar conditions the former gave a trace, the latter a considerable amount of benzoic acid. The hydrogen peroxide method is not suitable for the degradation of anthocyanins with adjacent hydroxyl groups, which usually yield black, insoluble products.

In order further to determine the position and nature of the disaccharide residue, pæonin and cyanin have been methylated with methyl sulphate and alkali, then thrice with methyl iodide and silver oxide. When the amorphous product is hydrolysed with methyl-alcoholic hydrochloric acid, the same methylated dye is formed in both cases. It is identified as 3-*hydroxy*-5 : 7 : 3′ : 4′-*tetramethoxy*-2-*phenylbenzopyrylium chloride*, m. p. 138°, sintering from 113°, by the formation of an insoluble *carbinol base* when its concentrated aqueous solution is treated with sodium hydroxide. The methylated sugars from pæonin contain tetramethylglucose and an unidentified syrupy *trimethylglucose* (*methylglucoside*, b. p. 118°/1 mm.). Similarly methylation and hydrolysis of monardin (pelargonin) affords a product, decomp. 120°, identified with 3-*hydroxy*-5 : 7 : 4′-*trimethoxy*-2-*phenylbenzopyrylium chloride*, decomp. 130°, prepared from ω-hydroxy-4-methoxyacetophenone and 2-hydroxy-4 : 6-dimethoxybenzaldehyde. 5-*Hydroxy*-3 : 7 : 4′-*trimethoxy*-2-*phenylbenzopyrylium chloride* and 7-hydroxy-3 : 5 : 4′-trimethoxy-2-phenylbenzopyrylium chloride (Pratt and Robinson, *loc. cit.*) were synthesised for comparison. Methylation and hydrolysis of malvin give 3-*hydroxy*-5 : 7 : 3′ : 4′ : 5′-*pentamethoxy*-2-*phenylbenzopyrylium chloride*. In all four anthocyanins, therefore, the disaccharide residue is in the 3-position. In spite of their apparent homogeneity and crystalline nature, most of the methylated dyes described in this and the following abstract have methoxyl contents 1—3% below the theoretical and probably contain traces of impurities. Attempts to hydrogenate anthocyanins in presence of platinum-black or platinum oxide were unsuccessful. Since all anthocyanins known at present have a 4′-hydroxyl group their colour in the plant will depend on the p_H of the cell-sap. This is confirmed by analyses of 3 species of blue and 4 of red flowers, the former having a higher ash content than the latter, on account of the presence of more alkali. The presence of the sugar residue in the 3-position renders the molecule more stable towards alkali. H. E. F. Notton.

Vegetable colouring matters. V. Primula colouring matters. P. Karrer and R. Widmer (Helv. Chim. Acta, 1927, 10, 758—763; cf. preceding abstract).—The colouring matter of *Primula viscosa* is identical with malvin, which is also present with compounds of lower methoxyl content in *P. integrifolia*. *P. hirsuta* contains an anthocyanin, *hirsutin*, the *chloride*, $C_{30}H_{37}O_{17}Cl$, of which is hydrolysed by acids to *hirsutidin* (a delphinidin trimethyl ether) and 2 mols. of dextrose, and oxidised by hydrogen peroxide to *hirsutone*, $C_{30}H_{38}O_{19},H_2O$, which gives syringic acid on hydrolysis. The new products differ only slightly in colour and chemical properties from malvin, syringidin, and malvone, respectively. Hirsutin is, therefore, the 3-*diglucoside* of 5(?7) : 4'-*dihydroxy*-7(?5) : 3' : 5'-*trimethoxy*-2-*phenylbenzopyrylium chloride*.

H. E. F. Notton.

Brazilin and hæmatoxylin question. V. Synthesis of a trimethylanhydrobrazilin. P. Pfeiffer and H. Oberlin (Ber., 1927, **60**, [*B*], 2142—2148; cf. A., 1925, i, 1303).—The reduction of 7 : 3' : 4'-trimethoxy-3-benzylidene-2 : 3-dihydro-γ-benzopyrone by hydrogen in the presence of platinum-black to 7 : 3' : 4'-trimethoxy-3-benzyl-2 : 3-dihydro-γ-benzopyrone is confirmed (cf. Pfeiffer and Emmer, A., 1920, i, 562); the ketone has m. p. 90—90·5° after purification through the *oxime*, m. p. 143·5—144·5°, and is not identical with the 7 : 3' : 4'-trimethoxy-3-benzylchroman described by Perkin, Rây, and Robinson (A., 1926, 732). 7 : 3' : 4'-Trimethoxy-3-benzylidene-2 : 3-dihydro-γ-benzopyrone is converted by phosphoric oxide in the presence of boiling benzene into trimethylanhydrobrazilin (I), m. p. 167—170°, identical with trimethyldeoxybrazilone (cf. Gilbody and Perkin, J.C.S., 1902, **81**, 1046; Herzig and Pollak, A., 1905, i, 605). The constitution of the compound is confirmed by its oxidation by ferric chloride to *iso*brazilein ferrichloride trimethyl ether (cf. Crabtree and Robinson, J.C.S., 1918, **113**, 872).



(I.)

H. Wren.

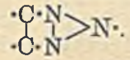
Fission of the heterocyclic compounds of coal tar. R. Weissgerber and C. Seidler (Ber., 1927, **60**, [*B*], 2088—2090).—The use of sulphuric acid for the removal of heterocyclic compounds from coal-tar distillates involves considerable losses of material and usually transforms the heterocyclic substances into worthless resins. The application of potassium hydroxide promises better results. Thus thionaphthen is transformed by solid potassium hydroxide at 300—310° into *o*-thiocresol in 83% yield and formic acid, which suffers oxidation to carbon dioxide. Similarly, coumarone affords *o*-cresol without appearance of by-products. Indene gives a black, amorphous mass together with hydrindene, a little *o*-xylene, and (?)chrysene and truxene. Indole at 200° yields unchanged material and pure *o*-toluidine. Diphenylene oxide, diphenylene sulphide, and thiophen are stable towards potassium hydroxide at 300°.

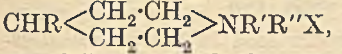
H. Wren.

Diphenylthiophens. E. Fromm, P. Fantl, and E. Leibsohn (Annalen, 1927, **457**, 267—277; cf. Baumann and Fromm, Ber., 1897, **30**, 117; Steinkopf, A., 1921, i, 630).—The non-identity of the two isomeric diphenylthiophens obtained by heating cinnamic acid with sulphur (Baumann and Fromm, *loc. cit.*) is shown by the preparation of derivatives. The identical mercurichlorides described by Steinkopf are accounted for by the presence of 2 : 4-diphenylthiophen in the 2 : 5-isomeride used; the latter gives no mercurichloride.

The mixture of products obtained by Baumann and Fromm's method gives by repeated purification pure 2 : 5-diphenylthiophen, m. p. 153°, and the pure 2 : 4-isomeride, m. p. 124°. Bromination of these in chloroform yields *tetrabromo*-derivatives, m. p. 203° and 150°, respectively. In the absence of solvent the 2 : 5-compound gives the tetrabromo-derivative, m. p. 203°, whilst the 2 : 4-compound is converted into a *substance*, m. p. 245°, with much higher sulphur content. The 2 : 4-compound is also degraded by concentrated nitric acid, with formation of a nitrogenous *substance*, m. p. 271°, with high sulphur content, whereas the 2 : 5-isomeride gives *trinitro*-2 : 5-*diphenylthiophen*, m. p. 243°, in 80% yield, together with a *dinitro*-compound, m. p. 189°. 2 : 4-Diphenylthiophen yields a *picrate*, m. p. 133—134°; the 2 : 5-compound gives no picrate. By condensation with acetyl chloride the isomerides form, respectively, 2 : 5-*diphenyl*-3-*thienyl methyl ketone*, m. p. 214°, and a 2 : 4-*diphenylthienyl methyl ketone*, m. p. 94°. 2 : 4-Diphenylthiophen gives with mercuric chloride Steinkopf's mercurichloride, m. p. 222°, and with mercuric acetate a mixture, m. p. 207—208°, of *mercuriacetate* and *mercury tetraphenyldithienyl*. The pure 2 : 5-isomeride does not react with mercuric chloride or acetate.

C. Hollins.

Comparison of heterocyclic systems with benzene. II. Reduction potentials of quinones containing the pyridine, glyoxaline, triazole, and thiophen rings. L. F. Fieser and L. A. Ames (J. Amer. Chem. Soc., 1927, **49**, 2604—2617; cf. A., 1926, 625).—Treatment of 4-nitroso-5-hydroxy-2-phenylbenztriazole (cf. Fries and Roth, A., 1912, i, 656) with aqueous sodium hydrogen sulphite affords the *sodium* 4-*amino*-5-*hydroxy*-2-*phenylbenztriazole*-7-*sulphonate* ($1\frac{1}{2}H_2O$), which is oxidised by 25% nitric acid to 2-*phenylbenztriazole*-4 : 5-*quinone*-7-*sulphonic acid* (*potassium* salt), treatment of the ammonium salt of which in aqueous solution yields 7-p-*toluidino*-2-*phenylbenztriazole*-4 : 5-*quinone*, red, m. p. 215°. Condensation of 5-hydroxy-1-phenylbenztriazole with aqueous benzenediazonium chloride affords 5-*hydroxy*-4-*benzeneazo*-1-*phenylbenztriazole*, red, from which an amine could not be obtained by reduction. αβ-Naphthatriazolequinone (cf. Zincke and Noack, A., 1897, i, 355) is obtained by the oxidation of αβ-naphthatriazole with chromium trioxide in glacial acetic acid. αβ-*Naphthiminazole*-4 : 5-*quinone*, orange, darkening at 210°, m. p. not below 250°, is obtained by heating 1 : 2-diamino-3 : 4-dihydroxynaphthalene dihydrochloride with sodium acetate and formic acid, with subsequent oxidation of the resulting quinol with nitric acid. The reduction potentials of the above quinones, as well as of 2-phenyl-αβ-naphthatriazole-4 : 5-quinone, 3-phenyl-αβ-naphthatriazole-4 : 5-quinone, α-naphthaquinolinequinone, phenanthraquinone, 1-phenyl-ββ-naphthatriazole-4 : 9-quinone, 1-*p*-tolyl-ββ-naphthatriazole-4 : 9-quinone, 3-phenyl-2-methyl-ββ-naphthiminazole-4 : 9-quinone, thionaphthenquinone, and thiophenanthrenquinone, were measured by electrometric titration with titanous chloride in aqueous 50% alcohol in presence of $0{\cdot}1M$-hydrogen chloride and $0{\cdot}2M$-lithium chloride. The results obtained indicate a marked similarity between the 2-phenyltriazole ring and benzene. The 3-phenyltriazole grouping exhibits greater reactivity than the 2-phenyl- or unsubstituted triazole groupings, and it is therefore concluded that both these have the structure  $\begin{matrix}\cdot C\cdot N \\ | \quad | \\ \cdot C\cdot N\end{matrix}\!\!>\!N\cdot$. The effects of the pyridine and glyoxaline nuclei are not comparable with that of the phenylene group, but the observed results are probably modified by the basicities of these groups. Heterocyclic analogues of anthraquinone do not bear the same relationship to the latter as is observed between phenanthraquinone and the corresponding heterocyclic isomerides. It is suggested that this observation is connected with the abnormally low reduction potential of anthraquinone, which may possibly be ascribed to an *o*-quinonoid structure of anthraquinol, which would increase the tendency of the latter to revert to the quinone. If the *o*-quinonoid phenylene group be now replaced by a more stable system, such as dihydroglyoxaline (cf. Fries, this vol., 778) the tendency of the whole molecule to assume the *p*-quinonoid structure by oxidation will be greatly reduced. The results obtained with thionaphthenquinone indicate that the thiophen ring has a much greater tendency than benzene to assume the quinonoid structure. F. G. WILLSON.

Configuration of the ammonium ion. II. Geometrically isomeric quaternary ammonium salts derived from 4-phenyl- and 4-hydroxypiperidine. W. H. MILLS, J. D. PARKIN, and W. J. V. WARD (J.C.S., 1927, 2613—2626; cf. Mills and Warren, A., 1926, 178).—The tetrahedral configuration of the quaternary ammonium ion is demonstrated by the existence of pairs of stereoisomerides in piperidinium salts,  $CHR<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>NR'R''X$, only when R′ and R″ are different, and the absence of isomerism when R′=R″, whereas a pyrimidal configuration requires pairs of stereoisomerides whether R′ and R″ are different or identical, and the isomerides would in the former case be racemic compounds.

By the action of alkyl iodide and sodium hydroxide 4-phenylpiperidine is converted into its 1-*methyl* [m. p. 9°, b. p. 122—123°/11 mm.; *hydrochloride*, m. p. 196—198°; *perchlorate*, m. p. 106—107°; *picrate*, m. p. 244° (decomp.)], 1-*ethyl* (m. p. 11°, b. p. 137°/11 mm.; *hydrochloride*, m. p. 203—205°; *perchlorate*, m. p. 112°), and 1-n-*propyl* [m. p. 13°, b. p. 150°/11 mm.; *hydrochloride*, m. p. 250° (decomp.); *perchlorate*, m. p. 160—162·5°] derivatives. α-4-*Phenyl*-1-*methyl*-1-*ethylpiperidinium iodide*, m. p. 180—181° (*perchlorate*, m. p. 135°), is isolated from the mixture formed by the action of ethyl iodide on 4-phenyl-1-methylpiperidine. The dimorphous β-*isomeride*, m. p. 140° and 146° (*perchlorate*, m. p. 159°), is best obtained from the mixed methiodides of 4-phenyl-1-ethylpiperidine (from which the α-compound may also be isolated). Addition of benzyl chloride to 4-phenyl-1-ethylpiperidine yields a mixture of α- and β-4-phenyl-1-benzyl-1-ethylpiperidinium salts, separable as *perchlorates*, m. p. 208° (α) and 189° (β). The β-*iodide*, m. p. 210—215°, is converted, when kept above its m. p., into the α-*iodide*, m. p. 240° (decomp.); both are obtainable from the perchlorates. On the other hand, 4-*phenyl*-1 : 1-*diethylpiperidinium iodide*, m. p. 177°, and 4-*phenyl*-1 : 1-*di*-n-*propylpiperidinium iodide*, m. p. 190°, show no separation into isomerides when fractionated.

4-Hydroxy-1-methylpiperidine, m. p. 28°, b. p. 105°/18 mm. (*hydrochloride*, m. p. 157—158°; *hydrobromide*, m. p. 139—140°), reacts with ethyl bromoacetate to give a mixture, m. p. 204°, of *ethyl* 4-*hydroxypiperidylacetate methobromides*. The α-isomeride, m. p. 221° (decomp.; *picrate*, m. p. 152—153°), is converted by silver oxide into the α-*methylbetaine*, m. p. 271—272°, from which by treatment with hydrobromic acid α-4-*hydroxypiperidylacetic acid methobromide*, m. p. 170—172°, is obtained. With less hydrobromic acid the betaine gives a basic *salt*, $C_{16}H_{31}O_6N_2Br$, m. p. 215—218° (decomp.). The β-*methylbetaine*, m. p. 266—267° (anhyd. and $+H_2O$), similarly yields β-4-*hydroxypiperidylacetic acid methobromide*, m. p. 210° [decomp.; *picrate*, m. p. 126°; *ethyl* ester, m. p. 206°; *ethyl* ester *methochloride*, m. p. 206° (decomp.)], and a basic *salt*, m. p. 220—221° (decomp.). Neither the α- nor the β-methobromide of 4-hydroxypiperidylacetic acid shows any tendency to lactone formation, and an attempt to convert 4-*bromoacetoxy*-1-*methylpiperidine* (*hydrobromide*, m. p. 172°) into a lactone was unsuccessful. C. HOLLINS.

Condensation products of isatin. I. M. KOTAKE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 61—65).—Condensation of isatin with hydantoin in the presence of acetic anhydride and fused sodium acetate at 100° yields the *diacetyl* derivative, decomp. 245°, of *oxindolidenehydantoin*, not decomp. below 310°; the latter is obtained crystalline on hydrolysis with cold dilute ammonia. Reduction of the diacetyl derivative with excess of sodium amalgam in potassium hydroxide yields *oxindolylhydantoin*, m. p. 283—284° (*diacetyl* derivative, m. p. 220—224°), whilst reduction with acetic acid and zinc at 100° yields a supposed intermediate *substance*, $C_{11}H_{13}O_2N_3$, which yields oxindolylhydantoin on reprecipitation from its solution in alkali by means of acid. On prolonged hydrolysis with barium hydroxide at 100° oxindolylhydantoin yields 3-*hydroxy*-2-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*-4-*carboxylic acid*, m. p. above 310° (*copper* and *silver* salts) and not oxindolylglycine. On heating the silver salt of the latter, 2-keto-1 : 2-dihydroquinoline is obtained. J. W. BAKER.

Facile ring-closure to a derivative of dihydro*iso*quinoline contrasted with the difficulty of analogous formation of a derivative of *iso*indole. J. MALAN and R. ROBINSON (J.C.S., 1927, 2653—2657).—When the compound $CHO{\cdot}N(CH_2{\cdot}C_6H_3{\cdot}O_2CH_2)_2$ (I), which might by cyclisation yield an *iso*indole or a dihydro*iso*quinoline, is treated with phosphoryl chloride only the six-membered ring is formed. This result is attributed to the field associated with the positive charge of the nitrogen atom (become quinquevalent), which is more effective on the nearer nucleus in preventing condensation with the aldehydic group.

(Piperonylmethyl)amine [*chloroplatinate*; *picrate*,

m. p. 198°; *piperonylmethyltrimethylammonium iodide*, m. p. 219° (decomp.); *benzylidene* derivative, m. p. 51—52° (*picrate*, m. p. 206°)], condenses with methyl opianate at 150° to form a 2-*carbomethoxyveratrylidene* derivative, m. p. 181°, which by the action of sodium methoxide in hot methyl alcohol loses the elements of methyl alcohol, yielding a *compound*, $C_{18}H_{15}O_5N$, m. p. 159°. This is probably not the expected 4-hydroxy-5 : 6-dimethoxy-3-piperonyl*iso*quinoline, since with methyl iodide it gives an *iodide*, m. p. 72°, having nearly the composition of (piperonylmethyl)-methylamine hydriodide. In the preparation of the primary amine by reduction of piperonaldoxime a by-product is *di*(*piperonylmethyl*)*amine*, m. p. 114°, b. p. 230°/50 mm. *Acetopiperonylmethylamide*, m. p. 103°, and the corresponding benzamide (Mannich and Kuphal, A., 1912, i, 850) are not cyclised by phosphoryl chloride, phosphorus pentoxide, sulphuric acid, zinc chloride, or stannic chloride. Phenacyl veratrate, $C_6H_3(OMe)_2\cdot CO_2\cdot CH_2Bz$, m. p. 122°, prepared from phenacyl bromide and silver veratrate, could not be converted into an *iso*coumarin derivative.

Piperonylmethyl-β-*piperonylethylamine* (as I), m. p. 53° (*hydrochloride*; *nitroso*-derivative, m. p. 127—128°; *dinitro*-derivative, m. p. 134—135°), is obtained by reduction of piperonylidene-β-piperonylethylamine with sodium and alcohol. The formyl derivative (I), m. p. 89—90°, is converted by phosphoryl chloride into 6 : 7-*methylenedioxy*-2-*piperonylmethyl*-3 : 4-*dihydro*iso*quinoline* salts (*picrate*, m. p. 184—185°). The *bromide*, m. p. 230°, which gives the same picrate, is synthesised from 6 : 7-methylenedioxy-3 : 4-dihydro*iso*quinoline and piperonylmethyl bromide. The bromide and the picrate both combine with nitromethane to form 6 : 7-*methylenedioxy*-1-*nitromethyl*-2-*piperonylmethyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, m. p. 124—125°, and the bromide or *chloride* with potassium cyanide gives the corresponding 1-*cyano*-compound, m. p. 151°.

C. Hollins.

Preparation of 2 : 3-diaminopyridine by amination of 3-aminopyridine. A. Konopnicki and E. Plażek (Ber., 1927, 60, [*B*], 2045—2047).—2 : 3-Diaminopyridine, m. p. 113°, is prepared in poor yield by the action of an excess of sodamide in boiling *p*-cymene on 3-aminopyridine, the bulk of which suffers resinification; the *picrate*, m. p. 262—264°, is described. The diamine is more conveniently prepared by the method of Tschitschibabin and Kirsanov (this vol., 466).

H. Wren.

***p*-Hydroxy- and *p*-amino-phenyl-lutidine.** B. Emmert, E. Diefenbach, and R. Eck (Ber., 1927, **60**, [*B*], 2216—2222).—Ethyl 4-phenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate is converted by nitric acid (*d* 1·51) and concentrated sulphuric acid at 60—70° into a mixture of *ethyl* 4-p-*nitrophenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, m. p. 117°, and ethyl 4-*m*-nitrophenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate, m. p. 63°. The former compound is reduced by tin and hydrochloric acid to *ethyl* 4-p-*aminophenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, m. p. 146° (*dihydrochloride*; *chlorostannate*), transformed by nitrous acid into *ethyl* 4-p-*hydroxyphenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, m. p. 171°. The constitution of the latter compound is established by its production (together with ethyl 2 : 6-dimethylpyridine-3 : 5-dicarboxylate) by the action of nitrous fumes on *ethyl* 4-p-*hydroxyphenyl*-2 : 6-*dimethyldihydropyridine*-3 : 5-*dicarboxylate*, m. p. 226—227°, obtained from *p*-hydroxybenzaldehyde, ethyl acetoacetate, and ammonia. *Ethyl* 1-*phenyl*-4-p-*hydroxyphenyl*-2 : 6-*dimethyldihydropyridine*-3 : 5-*dicarboxylate*, m. p. 155—156°, is prepared from *p*-hydroxybenzylideneaniline and ethyl acetoacetate in cold alcohol. Anisaldehyde, ethyl acetoacetate, and ammonia afford *ethyl* 4-p-*methoxyphenyl*-2 : 6-*dimethyldihydropyridine*-3 : 5-*dicarboxylate*, m. p. 159°, oxidised by nitrous acid to *ethyl* 4-p-*methoxyphenyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, m. p. 51—53°. 4-Phenyl-2 : 6-dimethylpyridine is converted by concentrated nitric and sulphuric acids at 65—70° into a mixture of 4-p-*nitrophenyl*-2 : 6-*dimethylpyridine*, m. p. 165—166° (*hydrochloride*), and a 4-*nitrophenyl*-2 : 6-*dimethylpyridine*, m. p. 122—123°. 4-p-*Aminophenyl*-2 : 6-*dimethylpyridine*, m. p. 132—133° (*dihydrochloride*, m. p. 85°; *methiodide*), and a *compound*, m. p. 223°, are obtained by reduction of the nitro-compound with tin and hydrochloric acid. The colourless solutions of ethyl 4-*p*-aminophenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate and 4-*p*-aminophenyl-2 : 6-dimethylpyridine become intensely yellow when a small proportion of hydrochloric acid is added, whereas the bases and their dihydrochlorides are colourless. The cause of the halochromy is not established.

H. Wren.

Quinoline derivatives. IV. Substituted 2-styrylquinoline-4-carboxylic acids. H. John (J. pr. Chem., 1927, [ii], **117**, 214—224).—These have been prepared by an extension of Friedländer's quinoline synthesis, substitution products of isatin and of styryl methyl ketone being condensed together in presence of concentrated aqueous potassium hydroxide at 100°. 2-Styrylquinoline-4-carboxylic acid (cf. Doebner and Peters, A., 1890, 176) (*ethyl* ester, m. p. 76°) is reduced by hydriodic acid to 2-β-*phenylethylquinoline*-4-*carboxylic acid*, m. p. 219—220°. The following derivatives of 2-styrylquinoline-4-carboxylic acid are described: 6-*methyl*-, m. p. 271°; 6-*chloro*-, m. p. 242—243°; 6-*bromo*-, m. p. 287°; 6-*iodo*-, m. p. 295—296° (decomp.); 6 : 8-*dibromo*-, m. p. 238—240°; 5-*chloro*-6-*bromo*-, m. p. 279°; p-*methyl*-, m. p. 271—272°; p-*chloro*-, m. p. above 300°; p-*dimethylamino*-, m. p. 260—261°; o-*hydroxy*-, m. p. above 300°; p-*methoxy*-, m. p. 285°; mp-*dihydroxy*-, m. p. above 300°; p-*hydroxy*-m-*methoxy*-, m. p. 282—283°; mp-*dimethoxy*-, m. p. 253—254°; mp-*methylenedioxy*-, m. p. 270—271°; p-*dimethylamino*-6-*bromo*-, m. p. 264—265°; mp-*methylenedioxy*-6-*bromo*-, m. p. above 305°. The solubility and appearance of a large number of metallic salts of each of the new acids are listed.

H. E. F. Notton.

Syntheses of quinoline and quinazoline derivatives; attempts to synthesise eight-membered rings containing nitrogen. J. Tröger and J. Bohnekamp (J. pr. Chem., 1927, [ii], **117**, 161—184).—When 2-amino-3-methoxybenzaldehyde (I) (cf. A., 1926, 68) and ethyl benzoylacetate are heated together at 160°, 2-*hydroxy*-8-*methoxy*-3-*benzoylquinoline*, m. p. 206° (*phenylhydrazone*, m. p. 159°), is formed, but in presence of sodium hydroxide at 100° they give *ethyl* 8-*methoxy*-2-*phenylquinoline*-3-*carboxylate*, m. p. 129°, which is hydrolysed by acid to 8-*methoxy*-2-*phenylquinoline*-3-*carboxylic acid*, m. p. 210° (*chloroplatinate*), whilst under other conditions 2-amino-3-methoxybenzoic acid (?) and anhydrobis-2-amino-3-methoxybenzaldehyde are obtained. In alkaline solution the aminoaldehyde gives, (*a*) with ω-cyanoacetophenone, 8-*methoxy*-3-*cyano*-2-*phenylquinoline*, m. p. 192° (*hydrochloride, chloroplatinate*), which is hydrolysed by alkali to the corresponding acid; (*b*) with malononitrile, 2-*amino*-3-*cyano*-8-*methoxyquinoline*, m. p. 225°, which is easily hydrolysed to 2-*amino*-8-*methoxyquinoline*-3-*carboxylic acid*, m. p. 268° (decomp.) (*chloroplatinate*). The aldehyde (I) and ethoxalyl chloride yield *ethyl* 2-*aldehydo*-6-*methoxyanilinoglyoxylate*, m. p. 138°, which is hydrolysed to the corresponding *glyoxylic acid*, m. p. 161° [*potassium*, *silver*, and *barium* ($+3H_2O$) salts], and converted by alcoholic ammonia into *di*-(8-*methoxyquinazoline*-2-*carboxyl*)*imide*, $(OMe{\cdot}C_8H_4N_2{\cdot}CO)_2NH$, m. p. 230° (*picrate*, *perchlorate*, and *silver nitrate* derivative, $C_{20}H_{15}O_4N_5,AgNO_3$), which, when hydrolysed, gives 8-methoxyquinazoline. Similarly, ethyl 2-aldehydoanilinoglyoxylate (m. p. 196°, not 106° as given by Bischler and Lang, A., 1895, i, 250) affords *di*(*quinazoline*-2-*carboxyl*)*imide*, m. p. 198° (*picrate*, *perchlorate*, and *silver nitrate* derivative). When the aldehyde (I) is fused with carbamide at 120—125°, amorphous 8-*methoxy*-2-*quinazolone*, m. p. 205° (*chloroplatinate*), is formed, and at 150°, a *substance*, m. p. 196°, probably a biuret derivative, $NH_2{\cdot}C_6H_3(OH){\cdot}CH(OH){\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$. Treatment of the methylcarbonato-derivative of (I) with alcoholic ammonia gave condensation products of (I) and an amorphous *substance*, m. p. 238—240°. Attempts to prepare eight-membered rings of the type probably present in anhydrobis-2-amino-3-methoxybenzaldehyde, $C_{16}H_{16}O_3N_2$ (Tröger and Sabewa; cf. Bamberger, this vol., 361), by condensing 2-amino-3-methoxybenzaldehyde with isatoic acid, anthranilic acid, or 2-amino-8-methoxyquinoline-3-carboxylic acid, were unsuccessful.

H. E. F. NOTTON.

Unsymmetrical phenanthridones. II. Preparation of 7-nitrophenanthridone by Beckmann rearrangement of 2-nitrofluorenoneoxime. F. J. MOORE and E. H. HUNTRESS (J. Amer. Chem. Soc., 1927, 49, 2618—2624; cf. this vol., 665).—2-Nitrofluorenone and hydroxylamine hydrochloride in aqueous alcohol afford, in 75% yield, an *oxime*, m. p. 269—270° (decomp.), which appears to undergo partial rearrangement when heated with solvents. When boiled with a mixture of phosphorus pentachloride and phosphoryl chloride (which converts fluorenoneoxime into phenanthridone), it yields what is apparently a mixture of 2-*nitrofluorenone*-9-*iminochloride* with 9-*chloro*-7-*nitrophenanthridine*. When boiled with aqueous 50% sulphuric acid, this mixture affords a 90% yield of 7-nitrophenanthridone.

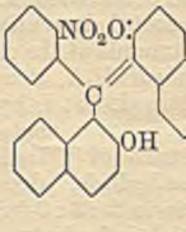
F. G. WILLSON.

Carbazine syntheses. III. H. GOLDSTEIN and M. DE SIMO (Helv. Chim. Acta, 1927, 10, 607—610).—Methyl 4 : 3′-diaminodiphenylamine-2-carboxylate and magnesium phenyl bromide (cf. A., 1926, 1151; this vol., 575) give 2 : 7-*diamino*-5 : 5-*diphenyldihydroacridine* (*diacetyl* derivative, decomp. 295°). The *dihydrochloride* of this is oxidised by ferric chloride to 2-*amino*-5 : 5-*diphenyldihydroacridine*-7-*immonium chloride*, from which the bluish-violet *imide base*, decomp. above 300°, is liberated by ammonia. Similarly, methyl 4-diethylaminodiphenylamine-2-carboxylate yields 3-*diethylamino*-5 : 5-*diphenyldihydroacridine* [*hydrochloride*, m. p. 245° (decomp.)], which is oxidised to 5 : 5-*diphenyldihydroacridine*-3-*diethylimmonium chloride* (orange *perchlorate*, decomp. 114°). 3-*Amino*-7-*diethylamino*-5 : 5-*diphenyldihydroacridine* (*dihydrochloride*, *monoacetyl* derivative, m. p. 209°), from methyl 4-amino-4′-diethylaminodiphenylamine-2-carboxylate (this vol., 1186), is oxidised by ferric chloride to green 3-*diethylamino*-5 : 5-*diphenyldihydroacridine*-7-*immonium chloride*, from which the violet *imide base*, m. p. 325°, blackening at 81°, is prepared.

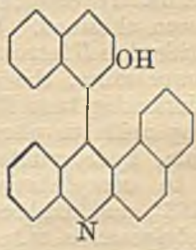
H. E. F. NOTTON.

***o*-Nitrobenzylidene-di-β-naphthol [*o*-nitrophenyldi-(2-hydroxy-α-naphthyl)methane].** O. DISCHENDORFER (Monatsh., 1927, 48, 543—557). The yield of *o*-nitrophenyldi-(2-hydroxy-α-naphthyl)methane [*diacetate*, m. p. 196—197°; *dibenzoate*, m. p. 213—214°; *dimethyl ether*, m. p. 191° (decomp.)] prepared by Zenoni's method (A., 1894, i, 136) is increased to 85% by the use of a larger amount of sulphuric acid and by avoiding rise in temperature during condensation, ring closure during crystallisation being prevented by using as a solvent boiling acetic acid containing a little sodium acetate. On oxidation in alcoholic solution with bromine and alkali at the ordinary temperature it yields *dehydro*-*o*-*nitrophenyldi*-(2-*hydroxy*-α-*naphthyl*)*methane* (I), m. p. 206° [*oxime*, m. p. 197° (decomp.): *dinitro*-derivative, m. p. 295° (decomp.)]. On reduction with zinc and acetic acid in benzene solution it yields a hydroacridine derivative which during purification is converted into 12-(2-*hydroxy*-α-*naphthyl*)-β-*phennaphthacridine* (II), m. p. 352° (decomp.) (*acetate*, m. p. 194°). The action of hydrochloric or sulphuric acid on a boiling acetic acid solution of *o*-nitrophenyldi-(2-hydroxy-α-naphthyl)methane yields *ms*-*o*-nitrophenyldinaphthaxanthen (Zenoni, *loc. cit.*), which is best prepared by the direct action of concentrated sulphuric acid on a solution of *o*-nitrobenzaldehyde and β-naphthol in acetic acid at 100°. This compound when heated with concentrated sulphuric acid at 100° for 0·5 hr. is converted into ms-*o*-*nitrophenyldinaphthaxanthhydrol*, m. p. 235° (decomp.) [*pyrylium chloride hydrochloride*, m. p. 310°; *mercurichloride*, m. p. 268° (decomp.); *perbromide*; *perchlorate*, m. p. 308° (decomp.); *ethyl ether*, m. p. 255—256° (decomp.); *methyl ether*, m. p. 260°], which is better prepared by the decomposition of the pyran *ferrichloride*, m. p.

(I.)



(II.)



chloride, m. p. 51° (cf. Erdmann and Huth, A., 1898, i, 35); *NN′*-diphenyl-*N*-benzylcarbamide, m. p. 85° (cf. Mailhe, A., 1919, i, 395); *phenylbenzylcarbamyl azide*; 1-benzylbenzpyrazolone (Milrath, A., 1908, i, 1014); *phenyl-α-naphthylcarbamyl chloride*, m. p. 102°, b. p. 245—250°/18 mm., and *azide*, m. p. 79°; 1-*phenyl*-6 : 7-*benzobenzpyrazolone* [1-*phenyl*-αβ-*naphthpyrazolone*], m. p. 267°; *phenyl*-β-*naphthylcarbamyl azide;* 1-*phenyl*-4 : 5(?5 : 6)-*benzobenzpyrazolone* [1-*phenylnaphthpyrazolone*], m. p. 234°; *di*-β-*naphthylcarbamyl azide*, m. p. 124° (decomp.); 1-β-*naphthyl*-4 : 5(?5 : 6)-*benzobenzpyrazolone* [1-β-*naphthylnaphthpyrazolone*], m. p. 254°. From di-*p*-tolylcarbamyl chloride are prepared as-*di*-p-*tolylcarbamide*, m. p. 163°, and *di*-p-*tolylcarbamyl azide*, which is converted in boiling xylene into 1-p-*tolyl*-5-*methylbenzpyrazolone*, m. p. 202°, together with *bis*-as-*carbonyldi*-p-*tolylhydrazine*, $[(C_6H_4Me)_2N\cdot N\colon CO]_2$, m. p. 202°. α-*Naphthylethylcarbamyl azide*, m. p. 100°, from α-*naphthylethylcarbamyl chloride*, m. p. 73°, gives in boiling xylene a mixture of 1-*ethyl*-6 : 7-*benzobenzpyrazolone* [1-*ethyl*-αβ-*naphthpyrazolone*], m. p. 195°, and s-*di*-α-*naphthyldiethylcarbazide*, $(C_{10}H_7\cdot NEt\cdot NH)_2CO$, m. p. 212°. *Dimethylcarbamyl azide*, b. p. 59°/15 mm., is similarly decomposed into a product which yields ammonia, dimethylamine, and *as*-dimethylhydrazine on hydrolysis. *Di*iso*butylcarbamyl chloride*, b. p. 115°/15 mm., gives with aniline carbanilide, instead of the expected N-*phenyl*-N′N′-*di*iso*butylcarbamide*, m. p. 110°, and with sodium azide, *di*iso*butylcarbamyl azide*, b. p. 113—115°/15 mm., which is transformed in tetrahydronaphthalene at 180—190° into a *substance*, m. p. 81°. Similarly, *di*iso*amylcarbamyl azide*, b. p. 146—149°/15 mm., from the corresponding *chloride*, b. p. 136—140°/15 mm., gives a *substance*, (?)$C_{22}H_{47}O_2N_5$, m. p. 138°. Benzaldehydephenylhydrazone-*N*-carboxyl chloride (Busch and Walter, A., 1903, i, 522) and sodium azide in acetone yield the corresponding *azide*, m. p. 133° (decomp.), which decomposes in boiling xylene into cyanuric acid, an impure *substance*, m. p. 365°, a *substance*, (?)$C_{21}H_{16}ON_4$, m. p. 182°, and a *substance*, $C_{14}H_{11}ON_3$, m. p. 229°, which may be 1-benzylideneaminobenzpyrazolone or 4-hydroxy-2 : 5-diphenyl-1 : 2 : 5-triazole; whilst the *azide*, m. p. 160°, of *o*-chlorobenzaldehydephenylhydrazone-*N*-carboxylic acid [*methyl* ester, m. p. 159°; *acid chloride*, m. p. 86°; *anilide* (o-*chlorobenzaldehyde*-2 : 4-*diphenylsemicarbazone*), m. p. 209°] is similarly decomposed into cyanuric acid, a *substance*, m. p. 240°, and 1-o-*chlorobenzylideneaminobenzpyrazolone* (?4-*hydroxy*-2-*phenyl*-5-o-*chlorophenyl*-1 : 2 : 5-*triazole*), m. p. 193°.

H. E. F. Notton.

Manufacture of *cyclo*trimethylenearylpyrazolones. C. Mannich.—See B., 1927, 869.

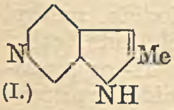
4-Hydroxypyrazoles and their tautomerism. A. Bertho and H. Nüssel (Annalen, 1927, 457, 278—307).—A series of 4-hydroxypyrazoles has been synthesised by the condensation of ethyl diazoacetate with malonic esters, and the amount of enol form in each product determined. The results show that the 4-hydroxypyrazoles exist in solution as an equilibrium of keto- and enol tautomerides, the amount of each depending on the substituents present.

Ethyl diazoacetate and ethyl malonate condense below 0° in presence of sodium ethoxide to give *ethyl 4-hydroxypyrazole*-3 : 5-*dicarboxylate*, m. p. 151°, which with silver nitrate yields the *silver* salt of the dicarboxylic acid. The ester is converted by hot hydrochloric acid into 4-hydroxypyrazole-5-carboxylic acid, m. p. 204°, which when heated gives 4-hydroxypyrazole. By using sodium methoxide in the condensation, or by heating the ethyl ester with sodium methoxide, the *methyl* ester, m. p. 232°, is obtained. *Ethyl* 4-*hydroxy*-3-*benzylpyrazole*-5-*carboxylate*, m. p. 169°, results directly from the condensation of ethyl diazoacetate with ethyl benzylmalonate, and is converted into 4-*hydroxy*-3-*benzylpyrazole*-5-*carboxylic acid*, m. p. 183·5° (decomp.), and 4-*hydroxy*-3-*benzylpyrazole*. From ethyl *iso*amylmalonate are similarly prepared *ethyl* 4-*hydroxy*-3-iso*amylpyrazole*-5-*carboxylate*, m. p. 115° [free *acid*, m. p. 186° (decomp.)], and 4-*hydroxy*-3-iso*amylpyrazole*, m. p. 85°. *Ethyl* 4-*hydroxy*-3-*phenylpyrazole*-5-*carboxylate*, m. p. 162°, is obtained in only minute quantities from ethyl phenylmalonate, the main product being phenylacetic acid. Ethyl diazoacetate condenses with ethyl cyanoacetate in presence of sodium ethoxide to form *ethyl* 4-*aminopyrazole*-3 : 5-*dicarboxylate*, m. p. 144°, which by diazotisation and coupling with α-naphthol gives a red *dye*, decomp. 210°. 4-*Aminopyrazole*-5-*carboxylic acid*, m. p. 212·5° (decomp.), may also be diazotised and coupled with α-naphthol; it is converted at 220° into 4-aminopyrazole (picrate, m. p. 195—196°).

All the 4-hydroxypyrazoles above mentioned give an enol colour reaction with ferric chloride, and silver salts with silver nitrate. The ferric chloride coloration is deeper with the acids than with the esters, and least intense with the pyrazoles themselves. The enol reaction depends also on the solvent, being most intense in water and decreasing in the order: ethyl alcohol, methyl alcohol, acetone, ether, chloroform, benzene. Ethyl 4-hydroxypyrazole-3 : 5-dicarboxylate is 91·7% enolised in water, but only 3·5% in ethyl alcohol (indirect bromine titrations by K. Meyer's method). A variety of methods of determining the extent of enolisation is examined. C. Hollins.

Internally complex salts of 2 : 2′-pyridylpyrrole and picolinamide. B. Emmert and F. Brandl (Ber., 1927, 60, [*B*], 2211—2216).—1 : 2′-Pyridylpyrrole is prepared by the action of potassium pyrrole on 2-chloropyridine in benzene at 160° and becomes isomerised when its vapour is superheated into 2 : 2′-pyridylpyrrole (cf. Tschitschibabin and Bylinkin, A., 1923, i, 954; Wibaut and Dingemanse, *ibid.*, 1232). The latter compound is converted by tetramminecopper sulphate or copper acetate in aqueous alcohol or by copper powder at 145° into the complex *copper* salt, $C_{18}H_{14}N_4Cu$, m. p. 149—150°. The corresponding *zinc* compound, $C_{18}H_{14}N_4Zn$, m. p. about 260° (decomp.), is prepared from 2 : 2′-pyridylpyrrole and zinc powder or zinc oxide in boiling naphthalene. The *iron* salt, $C_{27}H_{21}N_6Fe$, is obtained by the use of iron powder and boiling naphthalene or ferric chloride in alcoholic solution. The *cobalt* derivative, $C_{27}H_{12}N_6Co$, is prepared from pyridylpyrrole and cobaltic oxide in boiling naphthalene. Like the chlorophyll derivatives, the metallic compounds of pyridylpyrrole are very stable towards alcoholic alkali. Alcoholic solutions of the zinc and copper compounds are rapidly decomposed by acids which affect the iron compound more slowly. The zinc salt is unstable towards water. In the salts the pyrrole hydrogen atom is replaced by metal as shown by the evolution of hydrogen during the preparation, the formation when the metallic oxide is used, and the non-production when the hydrogen atom of the NH group is replaced by methyl. Similar complex salts might be expected from picolinamide, which contains a similar arrangement of the nitrogen atoms. The properties of the *copper* compound, $C_{12}H_{10}O_2N_4Cu$, differ so widely from those of the pyridylpyrrole complexes as to render its place in the series improbable. Internally complex salts of pyrrole-2-carboxylamide could not be prepared. H. WREN.

2-Methyl-βγ-pyrindole. E. KOENIGS and A. FULDE (Ber., 1927, 60, [*B*], 2106—2111).—3-Nitro-4-hydroxypyridine, m. p. 280—281°, free from the corresponding dinitro-derivative, is prepared by a modification of the method of Koenigs and Freter (A., 1924, i, 990) and converted by phosphorus pentachloride into 4-chloro-3-nitropyridine (unstable *hydrochloride*, m. p. 156°). The 4-chloro-atom is so labile that the base cannot be obtained from the hydrochloride by treatment with sodium ethoxide, which affords unchanged material and 3-nitro-4-ethoxypyridine, m. p. 49—50°. Condensation of 4-chloro-3-nitropyridine hydrochloride with ethyl disodiomalonate in the presence of alcohol yields *ethyl* 3-*nitro*-4-*pyridylmalonate* (*sodium* salt, decomp. about 250° after darkening at 80°), which is transformed by boiling 20% hydrochloric acid into the very hygroscopic 3-*nitro*-4-*methylpyridine* (*hydrochloride*, m. p. 178°; *chloroplatinate*, m. p. 267°; *picrate*, m. p. 118°). Reduction of the nitro-compound with stannous chloride and hydrochloric acid or with ammonium sulphide gives 3-*amino*-4-*methylpyridine*, m. p. 106°, b. p. 254°/735 mm., in 80% yield; the hygroscopic *hydrochloride*, m. p. 180°, *chloroplatinate*, m. p. 227°, and *picrate*, m. p. 179—180°, are described. 4-*Acetamido*-4-*methylpyridine*, m. p. 84° (*picrate*, m. p. 194°), and 3-*benzamido*-4-*methylpyridine*, m. p. 81° (*chloroplatinate*, m. p. 240°; *picrate*, m. p. 164°), have been prepared. The acetyl compound is converted when heated with sodium ethoxide into 2-*methylpyrindole* (I), m. p. 183°, which is not alkaline or volatile with steam. It does not give the pine-shaving reaction or red coloration with nitrite in nitric acid solution. The *hydrochloride*, m. p. 225—226°, *chloroplatinate*, m. p. 221°, and *picrate*, m. p. 193°, are described.



(I.)

H. WREN.

Quinazolines. XXXVIII. Synthesis of some new analogues of cinchophen and intermediate products. M. T. BOGERT and E. M. MCCOLM (J. Amer. Chem. Soc., 1927, 49, 2650—2654; cf. A., 1924, i, 1238).—2-*o*-*Nitrobenzamidoacetophenone* (I), m. p. 156°, and 2-*m*-*nitrobenzamidoacetophenone*, m. p. 170°, are obtained by the Schotten–Baumann reaction from *o*-aminoacetophenone. *o*-*Salicyloylamidoacetophenone*, m. p. 135°, is obtainable only by boiling *o*-aminoacetophenone with salicoyl chloride. Treatment of *o*-aminoacetophenone with *p*-acetoxybenzoyl chloride and alkali affords 2-*p*-*acetoxybenzamidoacetophenone*, m. p. 97·5°, which, when treated with cold aqueous 5% sodium hydroxide, or with ethyl alcohol and a trace of concentrated sulphuric acid, yields 2-*p*-*hydroxybenzamidoacetophenone*, m. p. 219°. Oxidation of (I) with alkaline permanganate affords *o*-*nitrobenzoylisatoic acid*, and this, when heated with alcoholic ammonia for 10 hrs. at 140°, yields 2-*o*-*nitrophenylquinazoline*-4-*carboxylic acid*, m. p. 235° (impure). *Salicyloylisatoic acid*, yellow, m. p. about 209—210° (decomp.), depending on the rate of heating, *p*-*hydroxybenzoylisatoic acid*, m. p. similar, 2-*o*-*hydroxyphenylquinazoline*-4-*carboxylic acid*, yellow, m. p. 171° (*ethyl* ester, yellow, m. p. 115°), and 2-*p*-*hydroxyphenylquinazoline*-4-*carboxylic acid*, yellow, m. p. 251° (*ethyl* ester, yellow, m. p. 159°), obtained analogously, are described. The *disodium* salt of 2-*o*-carboxyphenylquinazoline-4-carboxylic acid (cf. Bogert and Nabenhauer, A., 1924, i, 993) was prepared.

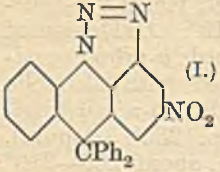
F. G. WILLSON.

Comparison of heterocyclic systems with benzene. II. Reduction potentials of quinones containing the pyridine, iminazole, triazole, and thiophen rings. L. F. FIESER and L. A. AMES.—See this vol., 1198.

Condensation of nitrobenzene with *o*-phenylenediamine. G. B. CRIPPA and P. CASTELLI (Gazzetta, 1927, 57, 621—625).—Whereas *p*-phenylenediamine condenses with nitrobenzene to give *p*-aminoazobenzene (this vol., 352), *o*-phenylenediamine gives under the same conditions 2-phenyl-4 : 5-benz-1 : 2 : 3-triazole in 10—15% yield, with *o*-aminoazobenzene. It is suggested that α-2-aminoazoxybenzene, $O\!:\!NPh\!:\!N{\cdot}C_6H_4{\cdot}NH_2$, is an intermediate product. E. W. WIGNALL.

Dicyanotriazole. J. A. FIALKOV (Bull. Soc. chim., 1927, [v], 41, 1209—1217).—The tetrameride of hydrocyanic acid (Bedel, A., 1923, i, 190) on treatment with nitrous acid gives yellow dicyanotriazole, m. p. 145—150°, which is transformed by sublimination at 140°/20—30 mm. into a colourless *isomeride*. These two substances are strong acids comparable with the mineral acids and form *sodium* salts which may be converted into the original substance. Measurements of the conductivity of the isomerides and their sodium salts show that the colourless modifications have the lower values. It is suggested that the coloured form is 4 : 5-dicyano-1 : 2 : 3-triazole and the colourless, 4 : 5-dicyano-2 : 1 : 3-triazole. The weak acid, m. p. 214—215°, produced by hydrolysis of the yellow form, is probably 4-cyano-1 : 2 : 3-triazole-5-carboxylic acid. G. A. C. GOUGH.

Coloured derivatives of tetraphenylmethane. X. Derivatives of diphenylcarbazine. F. KEHRMANN and M. ROHR (Helv. Chim. Acta, 1927, 10, 596—603).—When polynitrodiphenyldihydroacridines are partly reduced with alcoholic ammonium or potassium sulphide (A., 1926, 526), 1- and 9-nitro-groups are always attacked first. The constitutions of the resulting nitroamines are established by diazotisation and boiling with alcohol, when 1- or 9-amino-groups give stable yellow *peri*azimines, whilst those in other positions are eliminated. The azimines are reduced by stannous chloride to amines. In this way 1 : 3-dinitro-5 : 5-diphenylcarbazine (1 : 3-dinitro-5 : 5-diphenyldihydroacridine, A., 1921, i, 600) is reduced to 3-*nitro*-1-*amino*-5 : 5-*diphenylcarbazine*, m. p. 269°, which is converted by nitrous acid into 3-*nitro*-1 : 10-*azimino*-5 : 5-*diphenylcarbazine* (I.), m. p. 216°. 1 : 7-Dinitro-5 : 5-diphenylcarbazine yields 7-*nitro*-1-*amino*-, m. p. 270° (decomp.), and 7-*nitro*-1 : 10-*azimino-diphenylcarbazine*, m. p. indef. 3-Nitro-7-aminodiphenylcarbazine is deaminated to 3-nitrodiphenylcarbazine. 3 : 7-Dinitro-1-amino-5 : 5-diphenylcarbazine, obtained together with a little 3 : 7 : 3′ : 7′-*tetranitro*-1 : 1′-*azodiphenylcarbazine* by reducing 1 : 3 : 7-trinitrodiphenylcarbazine, gives with nitrous acid and alcohol 3 : 7-*dinitro*-1 : 10-*azimino*-5 : 5-*diphenylcarbazine* (II), m. p. 300° (decomp.), whilst its reduction product, 7-*nitro*-1 : 3-*diaminodiphenylcarbazine*, decomp. 280°, gives the 7-nitro-1 : 10-azimino-derivative (above). Similarly, nitrous acid and alcohol convert 3 : 7-dinitro-1 : 9-diamino-5 : 5-diphenylcarbazine, m. p. 266° (not 180° as previously stated, A., 1926, 526), into the azimine (II), and 3 : 7-*dinitro*-1 : 9-*diamino*-5 : 5-*dinitrodiphenylcarbazine*, prepared from hexanitrodiphenylcarbazine (A., 1919, i, 551), into 3 : 7-*dinitro*-1 : 10-*azimino*-5 : 5-*dinitrodiphenylcarbazine* (explodes on heating), from which a blue *dye* is obtained by reduction and aërial oxidation. H. E. F. Notton.



(I.)

Synthesis of β-*iso*coproporphyrin and of opsopyrrolecarboxylic acid. H. Fischer and H. Andersag (Annalen, 1927, **458**, 117—148).—Coproporphyrin (complex *copper* salt; *tetraethyl* ester, m. p. 225—226°) is conveniently separated from ethereal solutions of porphyrins (cf. A., 1926, 1261) by conversion into the *hydrochloride* (crystallographic data by Steinmetz), from which colloidal solutions of coproporphyrin may be prepared. The residues from the synthesis of *iso*coproporphyrin (complex *copper* salt; *tetramethyl ester hæmin*, $C_{40}H_{44}O_8N_4ClFe$; *tetraethyl* ester, m. p. 258°) contain the isomeric β-*iso*coproporphyrin, isolated as the *tetramethyl* ester, m. p. 135° (complex *copper* salt, m. p. 177°; *hæmin*, $C_{40}H_{44}O_8N_4ClFe$), and traces of a substance with an absorption band at λ 645. The ester is hydrolysed by sodium hydroxide to amorphous β-iso*coproporphyrin* (? a mixture) (*tetraethyl* ester, m. p. 124°; complex *copper* salt). A second synthesis of *iso*coproporphyrin has been effected by brominating cryptopyrrolecarboxylic acid and heating the resulting *bis*-(5-*bromo*-4-*methyl*-3-β-*carboxyethyl*-2-*pyrryl*)*methene hydrobromide*, m. p. 200° (decomp.), with bis-(4 : 5-dimethyl-3-β-carboxyethyl-2-pyrryl)methene and succinic acid at 220°. Bromination of 5-carbethoxy-2 : 4-dimethyl-3-pyrrylpropionic acid (*loc. cit.*) affords a *substance*, m. p. 275°, as well as 5-carbethoxy-4-methyl-2-bromomethyl-3-pyrrylpropionic acid. The latter product is converted by potassium cyanide in aqueous alcohol into 5-*carbethoxy*-4-*methyl*-2-*cyanomethyl*-3-*pyrrylpropionic acid*, m. p. 176°, by aniline into 5-*carbethoxy*-4-*methyl*-2-*anilinomethyl*-3-*pyrrylpropionic acid*, m. p. 162°, and by oxidation with lead nitrate or chromic acid into 2-*aldehydo*-5-*carbethoxy*-4-*methyl*-3-*pyrrylpropionic acid*, m. p. 173°, which is hydrolysed by alcoholic potassium hydroxide to 2-*aldehydo*-5-*carboxy*-4-*methyl*-3-*pyrrylpropionic acid*, decomp. 230° with formation of porphyrin. The synthesis of opsopyrrolecarboxylic acid previously described (*loc. cit.*) has been confirmed. Ethyl 2 : 4-dimethylpyrrole-5-carboxylate condenses with ethyl cyanoformate in ether–chloroform in presence of hydrogen chloride, giving *ethyl* 5-*carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylglyoxylate*, m. p. 127·5°. The methyl esters of copro-, *iso*copro-, and β-*iso*copro-porphyrin are reduced by hydrogen iodide in glacial acetic acid at 100°, giving in each case principally 2 : 3-dimethyl-β-4-pyrrylpropionic acid, identified as the methyl ester picrate (cf. A., 1914, i, 429); uroporphyrin octamethyl ester yields small quantities of the same product. These examples illustrate the tendency to the formation of 2 : 3-dimethylpyrroles in the reduction of pyrrylmethenes (cf. A., 1926, 962). The absorption spectra of the three coproporphyrins, their methyl esters, and of the "hæmins," "phyllins," and complex copper salts of the latter, also of the complex *iron* salt, $C_{40}H_{37}O_{16}N_4Fe$, of uroporphyrin, are tabulated. Evidence in favour of the view that the coproporphyrins differ only in the disposition of the double linkings is furnished by the identity of the absorption spectra of corresponding derivatives. H. E. F. Notton.

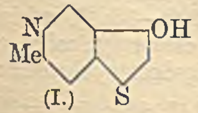
Porphyrin syntheses. XI. Ætioxantho- and mesoxantho-porphinogens. H. Fischer and A. Triebs (Annalen, 1927, **457**, 209—248; cf. this vol., 365, 469).—An attempt to obtain an analogue of dehydroindigo (Kalb, A., 1909, i, 966) from ætioporphyrin further confirms the rejection of the "indigoid" structure in favour of Küster's formula. Oxidation of ætioporphyrin in chloroform and acetic acid shaken with lead peroxide gives an intensely yellow compound, *ætioxanthoporphinogen*, $C_{32}H_{38}O_4N_4$, decomp. 318°, crystallising with $6H_2O$ or $3COMe_2$ [crystallographic data by Steinmetz] (*sodium* and *potassium* salts, *hydrochloride*, and *hydrobromide* described; no metal complex salts, no perchlorate, no picrate). Bromine gives *perbromides* with 4Br and 8Br. The substance is very stable to hydriodic acid (probably owing to the sparing solubility of the *hydriodide*), to water at 220°, and to potassium methoxide at 220°. It does not react with phenylhydrazine, hydroxylamine, benzoyl chloride, acetyl chloride, methyl iodide, methyl sulphate, methyl-alcoholic hydrogen chloride, ethyl mercaptan, keten (at 15°), phosphorus tri- or pentachloride, thionyl chloride, hydrogen cyanide, or nitrous acid. Dry distillation at 320—350° (bath temperature) yields opsopyrrole. The substance is oxidised by ozone to oxalic acid and ammonia, the amount of the latter accounting for half the nitrogen (ætioporphyrin behaves similarly), and by lead peroxide in sulphuric acid, or by nitric acid, to methylethylmaleinimide. The four oxygen atoms of ætioxanthoporphinogen are removed by reduction with sodium amalgam in methyl alcohol and acetic acid, regenerating ætioporphyrin. Magnesium and acetic acid give the same result, but iron and aluminium in boiling acetic acid have no effect, whilst reduction with zinc dust and hot acetic acid removes only two oxygen atoms, forming a colourless, crystalline *compound*, $C_{32}H_{42}O_2N_4$, decomp. 297° (*hydrochloride*; no sodium salt), which is reduced by sodium amalgam to ætioporphyrin. It is suggested that ætioxanthoporphinogen contains two *N*-oxide groups and two tertiary carbinol groups.

When lead tetra-acetate is used in place of lead peroxide for the oxidation of ætioporphyrin, no xanthoporphinogen can be isolated, and the product is a *dichloroætioporphyrin*, m. p. 305° (Pregl block). A *monobromoætioporphyrin*, m. p. 392° (Pregl block), is isolated by fractionation of Fischer and Klarer's synthetic ætioporphyrin (A., 1926, 962). An analytical method for following the course of bromination of ætioporphyrin and of cryptopyrrole is described.

Oxidation of mesoporphyrin dimethyl ester with lead peroxide in chloroform and acetic acid gives *mesoxanthoporphinogen dimethyl* ester, $C_{36}H_{42}O_8N_4$, which regenerates the same porphyrin ester on reduction with sodium amalgam. The absence of isomerides from the reduction products of both the xanthoporphinogens has an important bearing on the question of constitution. Xanthoporphinogens have also been obtained from coproporphyrin ester and tetramethyltetrapropylporphin.

[With P. Halbig and B. Walach.]—*Ethyl 2-dibromomethyl-4-hydroxymethylpyrrole-3 : 5-dicarboxylate*, m. p. 130—131°, obtained from the 2 : 4-dimethyl ester using bromine and sodium bromate in acetic acid, gives with phenylhydrazine and hydrazine a bromine-free *phenylhydrazone*, m. p. 199°, and *hydrazone*, m. p. 143°, respectively. Reduction with zinc and acetic acid removes bromine, forming *ethyl 2-methyl-4-hydroxymethylpyrrole-3 : 5-dicarboxylate*, m. p. 132° (*acetate*, m. p. 40°), which is also obtained when ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate is oxidised with chromic–acetic acid. The compound shows only one reactive hydrogen atom when treated with magnesium methyl iodide. Ætioxanthoporphinogen has according to the same criterion only the same number of active hydrogen atoms as ætioporphyrin. C. Hollins.

New "thiopyrindigotin" and a pyrindoxyl. E. Koenigs and H. Kantrowitz (Ber., 1927, 60, [*B*], 2097—2105).—Ethyl 4-chloro-2 : 6-dimethylpyridine-3-carboxylate is hydrolysed by a slight excess of dilute aqueous-alcoholic potassium hydroxide at 130° and the resulting solution is treated with potassium hydrogen sulphide at 160—170°, whereby 4-thiol-2 : 6-dimethylpyridine-3-carboxylic acid, m. p. 235°, is obtained in good yield. It is transformed by sodium hydroxide and chloroacetic acid into *3-carboxy-2 : 6-dimethylpyridyl-4-thiolacetic acid*, $CO_2H{\cdot}C_5NHMe_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, m. p. 247° (*hydrochloride*, m. p. 221°), which, with acetic anhydride, affords *3-hydroxy-4 : 6-dimethylpyridothiophen* (I), m. p. 49° (*hydrochloride*, m. p. 94°; *chloroplatinate*, decomp. above 300°; *semicarbazone*, decomp. above 300°; *compound*, $C_{16}H_{15}ON_3S$, m. p. 98°, obtained by coupling with diazotised *p*-toluidine). Oxidation of the thiophen derivative in alkaline solution at 70° in the presence of spongy platinum affords "*4 : 6 : 4′ : 6′-tetramethylthiopyrindigotin*" (II) (unstable *hydrochloride*; *chloroplatinate*, decomp. above 300°), which can be reduced by alkaline hyposulphite or tin and hydrochloric acid and dyes cotton a dull pink. The "thiopyrindigotin" is more readily prepared by the action of concentrated sulphuric acid at 210—215° on 3-carboxy-2 : 6-dimethylpyridyl-4-thiolacetic acid (cf. Plazek and Sucharda, A., 1926, 1263).



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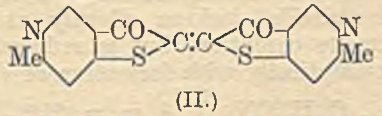
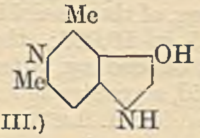


(II.)

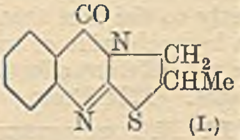
Ethyl 4-chloro-2 : 6-dimethylpyridine-3-carboxylate is converted by aminoacetonitrile at 150° into the *anhydride* of *3-carboxy-2 : 6-dimethyl-4-pyridylaminoacetic acid*, m. p. 100—101° (*hydrochloride*, m. p. 221°); the corresponding *acid*, m. p. 184°, and its *hydrochloride*, m. p. 282°, are described. Acetic anhydride transforms the acid or its anhydride into *4 : 6-dimethylpyrindoxyl* (III), m. p. 67°, in moderate yield; the *hydrochloride*, m. p. 243°, *chloroplatinate*, decomp. above 300°, *semicarbazone*, m. p. 63°, and *p-tolueneazo*-derivative, m. p. 92°, are described. Attempts to oxidise it to the corresponding "pyrindigotin" were unsuccessful. H. Wren.



(III.)

Dioximes. XLV. I. De Paolini (Gazzetta, 1927, 57, 656—660).—3 : 4-Dibenzoyl-1 : 2 : 5-furazan, prepared by Angeli (A., 1893, i, 355) by the action of alcohol on dibenzoylglyoxime, is better obtained from the peroxide of the latter by the action of stannous chloride. When treated with sodium hydroxide it yields oximinobenzoylacetonitrile; the action of nitrogen tetroxide on dibenzoylfurazandioxime, m. p. 180°, yields the *peroxide* of the latter, m. p. 171—172° (decomp.). Similarly, *3 : 4-di-p-toluoyl-1 : 2 : 5-furazan*, m. p. 128—129°, is obtained from di-*p*-toluoylglyoxime peroxide; it yields a *dioxime*, m. p. 181—182° (decomp.), a *diphenylhydrazone*, m. p. 200—201° (decomp.), and, by the action of sodium hydroxide, oximino-*p*-toluoylacetonitrile, m. p. 137° (cf. Lublin, A., 1907, i, 213). E. W. Wignall.

Condensation of anthranilic acid with allylthiocarbimide. G. Rossi (Gazzetta, 1927, 57, 625—632).—Pawlewski (A., 1906, i, 542) considered the product, m. p. 208—210° (I), of the interaction of anthranilic acid with allylthiocarbimide to be 4-keto-2-thion-1-allyltetrahydroquinazoline, since it was not identical with the 3-allyl compound; when treated with alkaline hydrogen peroxide it gave a product, m. p. 187—189°, (II), regarded as the 2 : 4-diketo-compound. The migration which the formulation of (I) involves is improbable; also the substance $C_{18}H_{15}O_3N_3$, m. p. 211—212°, (III), obtained by the same reaction and wrongly regarded (Rossi, A., 1914, i, 1169; Gazzetta, 1914, 44, [2], 267) as the dianilide of 3-nitrophthalic acid, would on Pawlewski's scheme be 2-*o*-carboxyanilo-4-keto-1-allyltetrahydroquinazoline, but it contains no carboxyl group. Hydrolysis of (III) by hydrochloric acid yields (II), with a *substance*, $C_{11}H_{12}O_3N_2$, m. p. 180°; hydrolysis by potassium hydroxide solution yields a product $C_{11}H_{10}O_2N_2$, of which part has m. p.



(I.)

172—174°, and the residue m. p. 194—198°. It is suggested that (I) has the structure formulated.

E. W. Wignall.

Volatile alkaloid of pepper. A. Pictet and R. Pictet (Helv. Chim. Acta, 1927, 10, 593—595).—The alkaloid, C_5H_9N (*hydrochloride*, $[\alpha]_D$ +2·77°; *picrate*, m. p. 165°), obtained by steam-distilling black pepper (A., 1907, i, 954) gives an oily nitroso-derivative, and is reduced by tin and hydrochloric acid to racemic 3-methylpyrrolidine. It is therefore 3-methylpyrroline.

H. E. F. Notton.

Microchemical reactions of papaverine. M. Wagenaar (Pharm. Weekblad, 1927, 64, 1085—1089).—The precipitation of the alkaloid, methods of obtaining it crystalline, and the effect on it of the commoner alkaloid reagents are described. The mercuric iodide test is the most sensitive, a precipitate being obtained with as little as 0·1 mg. of the alkaloid, and in concentrations as low as 1 in 10,000; the precipitate is microcrystalline, but on cooling, after warming with dilute hydrochloric acid, separates again in characteristic four-sided crystals.

S. I. Levy.

Constitution of yohimbine. E. Winterstein and M. Walter (Helv. Chim. Acta, 1917, 10, 577—584).—Yohimbine is decomposed by soda–lime at 250° (cf. Barger and Field, J.C.S., 1915, 107, 1025) giving a dimethylindole, m. p. 55°, identical with that obtained by Warnat (this vol., 681) from yohimboaic acid, and a mixture of bases. Rapid distillation of small portions of yohimbine with zinc dust yields the same dimethylindole, whilst the following bases are separated as picrates after fractional distillation: (*a*) *iso*quinoline, (*b*) a base, $C_{13}H_{12}N_2$ (picrate, m. p. 268—270°; cf. Warnat, *loc. cit.*), and (*c*) a *base*, $C_{12}H_{10}N_2$ (*picrate*, m. p. 240—250°), probably formed from (*b*) by loss of a methyl group. The base (*b*) is identical in composition with the supposed dimethylquinoline of Barger and Field and is regarded as the dimethyl derivative of a condensed pyrrole-*iso*quinoline nucleus. The same fission products are obtained in high yield when yohimbine hydrochloride is distilled with 2·5 mols. of alkali in superheated steam at 300°.

H. E. F. Notton.

Behaviour of ψ-cocaine hydrogen *d*-tartrate and of cocaine hydrochloride towards reagents. M. Ferraris (Boll. Chim. Farm., 1927, 66, 577—580).—Towards the ordinary alkaloid reagents, psicaine and cocaine hydrochloride usually react similarly, but with mercuric chloride the former gives no precipitate and the latter a white precipitate. With silver nitrate a similar difference is observed. Cocaine, but not psicaine, blackens when triturated with mercurous chloride. When 0·01 g. of cocaine is heated with 2 drops of alcohol and a little powdered potassium hydroxide, the odour of ethyl benzoate is observed, whereas similar treatment of psicaine gives only a feeble and transitory aromatic odour. Certain other differences exist between the reactions of the two compounds, these being due mostly to the fact that one is a tartrate and the other a hydrochloride or to those conditions which determine the different effects of the two molecules on polarised light.

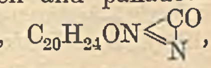
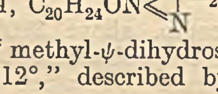
T. H. Pope.

Amine-oxides of alkaloids. II. M. Polonovski and M. Polonovski (Bull. Soc. chim., 1927, [iv], 41, 1186—1190).—*N*-Methylgranatoline, obtained by the reduction of ψ-pelletierine (Tanret, A., 1923, i, 832), reacts with hydrogen peroxide (30%) at the ordinary temperature to give N-*methylgranatoline oxide*, m. p. 218° (*hydrochloride*, m. p. 210°; *picrate*, m. p. 254°), which may be reduced to the parent substance by sulphur dioxide. Tropinone, best prepared by the oxidation of tropinal in concentrated sulphuric acid solution with potassium dichromate at 0°, yields similarly *tropinone oxide*, m. p. 98° (*hydrochloride*, m. p. 193°; *picrate*, m. p. 210°; *chloroaurate*, m. p. 176—177°). Hydrogen peroxide reacts vigorously with an acetone solution of scopoline to give *scopoline oxide*, m. p. 123° [decomp. 129°; *compound* containing water and hydrogen peroxide of crystallisation, $4C_8H_{13}O_3N,3H_2O_2,3H_2O$ (stable at 100°; decomposed by crystallisation from alcohol), m. p. 110—120°; *hydrochoride*, 175°; *hydrobromide*, m. p. 180—181° (decomp.); *picrate*, m. p. 200° (decomp.)]. Emetine yields amorphous *emetine oxide*, softening at 115°, $[\alpha]_D$ +44·3° in 95% alcohol (c=2·5).

G. A. C. Gough.

Amine-oxides of alkaloids. III. Action of acid chlorides and anhydrides. Preparation of nor-bases. M. Polonovski and M. Polonovski (Bull. Soc. chim., 1927, [iv], 41, 1190—1208).—The action of acetyl chloride or of acetic anhydride on the oxides of bases containing an *N*-methyl group results in the elimination of that group as formaldehyde with the formation of the corresponding nor-base. Benzoic anhydride reacts similarly in some cases. The oxide is liable to suffer complete decomposition unless dry materials are used and unless the vigorous reaction is controlled at the first stage. The reaction is completed by heating at 100° for 3 or 4 hrs. In this way the following compounds are prepared: acetylnortropidine (an oil); nortropidine (an oil; chloroaurate, m. p. 187°); acetylnortropinone (an oil); nortropinone (*hydrochloride*, m. p. 201°; *chloroaurate*, m. p. 168°); diacetylnortropanol (an oil); *N*-acetylnortropanol, m. p. 124°; nortropanol (hydrochloride, m. p. 285°; chloroaurate, m. p. 211°; chloroplatinate, m. p. 248—249°); *N*-acetylnor*apo*atropine, m. p. 113—114° [hydrochloride, 140° (darkening at 115°)]; diacetylnorhyoscyamine (*l*-*O*-acetyltropyl-*N*-acetylnortropanol); *N*-acetylnorscopolamine, m. p. 130°, $[\alpha]_D$ −25° in alcohol; *diacetylgranatoline*, m. p. 80°; *N*-acetylgranatoline, m. p. 120°; N-*acetylnornicotine* (an oil), $[\alpha]_D$ −13·6° in benzene.

G. A. C. Gough.

Strychnine and brucine. VI. Catalytic hydrogenation of strychnine and some derivatives. A. E. Oxford, W. H. Perkin, jun., and R. Robinson (J.C.S., 1927, 2389—2410).—The double linking of strychnine is reduced by hydrogen and palladous chloride, giving *dihydrostrychnine*,  $C_{20}H_{24}ON\!<\!\begin{matrix}CO\\ | \\ N\end{matrix}$, m. p. 220—222° [*methosulphate*, m. p. 322° (decomp.); *methiodide*, darkens slightly at 300—330°], which resists oxidation, but is reduced electrolytically or catalytically with formation of dihydrostrychnidine-*A*,  $C_{20}H_{24}ON\!<\!\begin{matrix}CH_2\\ | \\ N\end{matrix}$, m. p. 212—214°, identical with "methyl-ψ-dihydrostrychnidine, $C_{22}H_{28}ON_2$, m. p. 212°," described by Clemo, Perkin, and Robinson (this vol., 888) [dimethiodide, m. p. 285—290° (decomp.), and dimethochloride are identical with methyl*neo*dihydrostrychnidinium iodide and chloride respectively (*loc. cit.*)], and *hexahydrostrychnine*, $C_{20}H_{24}ON(CH_2{\cdot}OH){\vdots}NH$, m. p. 197—199° (*nitroso*- and *diacetyl* derivatives), also obtainable by catalytic reduction of tetrahydrostrychnine. Skita and Franck's "dihydrostrychnine," m. p. 209—210° (A., 1911, i, 1017), on the other hand, is stated to yield tetrahydrostrychnine, *i.e.*, $C_{20}H_{22}ON(CH_2{\cdot}OH){\vdots}NH$, by catalytic reduction. When dihydrostrychnidine methochloride is heated with methyl-alcoholic potassium hydroxide at 130° there are formed methoxymethyltetrahydrostrychnidine (cf. Clemo, Perkin, and Robinson, *loc. cit.*) and *methyldihydrostrychnidine* A, m. p. 178—180°.

*iso*Strychnine, m. p. 220°, yields an O-*acetyl* derivative, m. p. 133—134°, but no semicarbazone (cf. Oliveri-Mandalà and Comella, A., 1923, i, 1224) or phenylhydrazone was obtained. Catalytic reduction converts *iso*strychnine into *dihydro*iso*strychnine*, m. p. 244—246° (+3H₂O) or 249—251° (anhyd.) [*methosulphate*; *methiodide*, m. p. 320° (decomp.); O-*acetate*, m. p. 202—204°], obtained from dihydrostrychnine by heating with water at 165—185° or with methyl-alcoholic ammonia; it is prepared more easily by dissolving dihydrostrychnine in hot alcoholic sodium ethoxide and keeping the solution at 44—46° for 6 hrs. The strychnine–*iso*strychnine isomerism s thus proved to be independent of the double linking, which need not even be present. The isomerisation s possibly due to internal condensation between a ketonic carbonyl group and hydrogen atom adjacent to the ·CO·N⁚ group. *iso*Strychnic acid, m. p. 231° (decomp.), is not reduced by hydrogen and palladium, and it is therefore probable that the mol. of water it contains is constitutionally bound.

Electrolytic reduction of *iso*strychnine gives *isostrychnidine*, $C_{21}H_{24}ON_2$, m. p. 155—157° (+1·5H₂O) or 163—168° (+0·25H₂O) [*methosulphate*, m. p. 200—205° (decomp.)], which by the action of hydrogen and palladium yields *dihydro*iso*strychnidine*-b, $C_{21}H_{26}ON_2$, m. p. 151—153°, isomeric with *dihydro*iso*strychnidine*-a, m. p. 191—192° (+0·5H₂O), obtained by electrolytic reduction of dihydro*iso*strychnine.

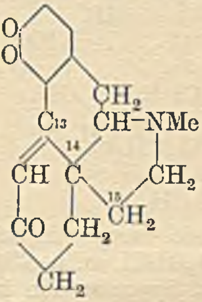
Strychnidine gives no *iso*strychnidine when heated with water, the product being *dioxyhydroxydihydrostrychnidine*, $C_{21}H_{26}O_4N_2$, m. p. 260° (decomp.; +4H₂O). *Dioxyhydroxyhexahydrostrychnine*, $C_{21}H_{28}O_5N_2$, has m. p. 201—203° (+2H₂O). Strychnidine couples with diazotised sulphanilic acid to form an azo-*compound*, from which by reduction with stannous chloride p-*aminostrychnidine*, decomp. above 330°, is obtained. This amine is diazotisable and gives azo-*dyes* with β-naphthol, H-acid, and J-acid. p-*Sulphobenzeneazomethylstrychnine* is described.

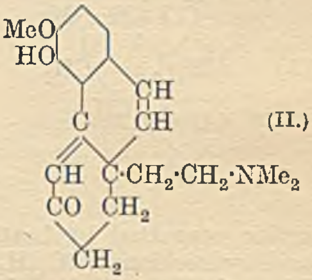
Benzoylation converts strychnic acid into a *mixed anhydride*, m. p. 215—218°.

C. Hollins.

Acid transformations of morphine alkaloids; constitution of thebainone. C. Schöpf and F. Borkowsky (Annalen, 1927, 458, 148—174).—Solutions of thebaine and of thebainone in concentrated hydrochloric acid (cf. Howard, A., 1884, 1201) probably contain products of similar constitution, since they have practically the same absorption spectrum. Thebainone and hydroxylamine give, in addition to the oxime, an additive *compound* (also +H₂O), m. p. 173—174°. The isolation from the product of hydrogenation of thebaine with palladium–calcium carbonate (cf. this vol., 472) of *dihydroepithebainoneoxime*, m. p. 228°, $[\alpha]_D^{20}$ −115·8° (the term epi- being used to denote stereoisomerism about C^{14}), which is isomeric but not identical with dihydrothebainoneoxime, $[\alpha]_D^{20}$ +6·6°, and with *thebainoloxime*, m. p. 217—218°, $[\alpha]_D^{18}$ +104·2°, renders the presence of a C^{15}—C^{13} linking in thebainone (Gulland and Robinson, J.C.S., 1923, **123**, 998) impossible. The following facts are adduced in favour of formula (I) for thebainone:

(I.)

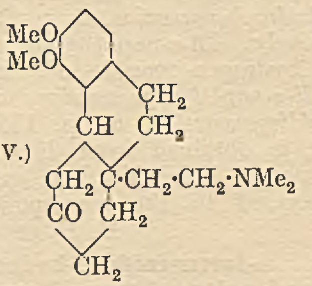


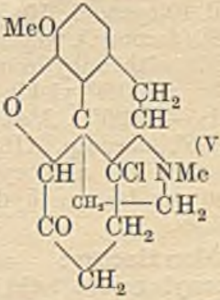


(II.)

(*a*) the absence of halochromy in acid solution of hydroxythebainone (Speyer, A., 1923, i, 127), (*b*) the impossibility of hydrogenating the double linking in thebainone, (*c*) the morphol degradation of thebainonemethine derivatives (cf. Knorr and Pschorr, A., 1905, i, 814, 920, 922), and (*d*) the impossibility of displacing the double linking in thebainonemethines into the $\Delta^{13(14)}$-position. Thus, *thebainonemethine* (II), m. p. 170—171° (*methiodide*, m. p. 252°; *oxime*, m. p. 210—211°), prepared from thebainone methiodide and aqueous sodium hydroxide is not isomerised by alkali or dilute acids; it is resinified by concentrated acid. It is hydrogenated to *dihydrothebainonemethine* (*hydriodide*, m. p. 258—259°). Attempts to confirm formula (I) by the preparation of stereoisomeric forms of dihydromethylthebainolmethine were unsuccessful. Methylthebainonemethine (III) is hydrogenated in presence of colloidal palladium to *dihydromethylthebainonemethine* (*methiodide*, m. p. 154—155°), which is reduced by sodium amalgam and alcohol to *dihydromethylthebainolmethine* (IV), oily (*methiodide*, m. p. 115—116°;

(IV.)

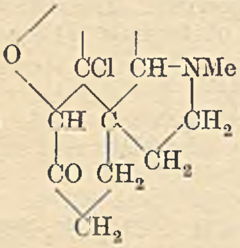


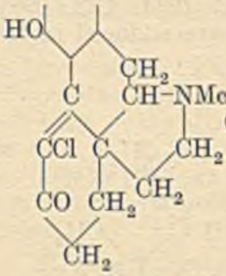


(V.)

methoperchlorate, m. p. 227—228°, $[\alpha]_D^{18}$ −40·7° or −46·6°). The same substance (IV) is obtained by hydrogenating *methylthebainolmethine* (*perchlorate*, m. p. 193—194°), which is prepared by reducing (III) with sodium amalgam and water, or by treating *methylthebainol methiodide*, m. p. 260° (cf. Hock, Diss., Munich, 1926), with alkali. (II) is reduced by sodium amalgam to *thebainolmethine*, m. p. 173—174°, which is readily hydrogenated in 10% acetic acid to *dihydrothebainolmethine*, m. p. 119—121°. Methylation of this last by Rodionov's method (A., 1926, 532) again yields the base (IV) (not identical with dihydromethyldihydrothebainonemethine; Cahn, A., 1926, 1264), identified as the methoperchlorate. Accordingly, thebaine is assumed to be transformed successively, on dissolution in cold concentrated hydrochloric acid, into the compounds (V), (VI), and (VII), the last being

(VI.)





(VII.)

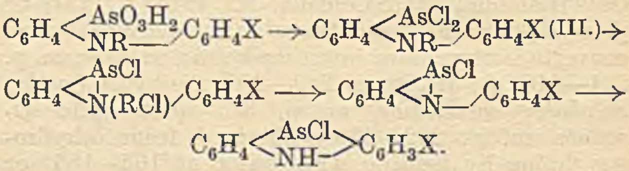
further converted by heating into morphothebaine [acid hydrochloride, $(C_{18}H_{19}O_3N)_2,3HCl$, m. p. 254—255°; cf. Howard, *loc. cit.*], and by reduction into thebainone. The transformations of codeinone into morphothebaine (cf. Cahn and Robinson, A., 1926, 745), of morphine into *apo*morphine, and of codeinone or thebaine into thebenine are explained along similar lines. The nomenclature of thebaine and thebainone derivatives is discussed. H. E. F. NOTTON.

Microchemical identification of morphine. M. WAGENAAR (Pharm. Weekblad, 1927, 64, 1119—1122).—A summary of the reactions suitable for the microchemical identification of the alkaloid, together with complete references to the literature, is given. The most delicate are those with mercuric bromide and iodide, which are positive at concentrations of 1 in 10,000. S. I. LEVY.

Organic arsenic compounds. Some cyanides and dicyanides. E. GRISCHKIEVITCH-TROCHIMOVSKI, L. MATEYAK, and ZABLOTSKI (Bull. Soc. chim., 1927, [iv], 41, 1323—1333).—Silver cyanide converts phenyldichloroarsine, α-naphthyldichloroarsine, and 10-chloro-5 : 10-dihydrophenarsazine, in benzene or toluene, into *phenyldicyanoarsine*, m. p. 78·5—79·5°, *α-naphthyldicyanoarsine*, m. p. 159—160° (decomp.), and 10-*cyano*-5 : 10-*dihydrophenarsazine*, m. p. 227—228° (decomp.), respectively. Di-α-naphthylarsenious oxide with anhydrous hydrogen cyanide in a sealed tube at 100° yields *di-α-naphthylcyanoarsine*, m. p. 191·5—192·5°. *Methyldicyanoarsine*, m. p. 115·5—116·5°, decomp. 118°, is obtained from dimethylcyanoarsine and cyanogen bromide. The cyano-compounds are hydrolysed to the corresponding oxides. H. BURTON.

Manufacture of 4-formamido-2-hydroxyphenylarsinic acid and salts. ÉTABL. POULENC FRÈRES and E. FOURNEAU.—See B., 1927, 892.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. V. General method of synthesis and determination of constitution. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1927, 2499—2516; cf. Burton and Gibson, this vol., 264).—Diphenylamine-*o*-arsinic acids are obtainable both from an aniline-*o*-arsinic acid and a bromobenzene, and from an *o*-bromophenylarsinic acid and an arylamine, the yields being dependent on the reactivity of the bromine atom, which increases in the order: bromobenzene, *o*-bromophenylarsinic acid, *o*-bromonitrobenzene. With the exception of the *N*-methyl compound, all the diphenylamine-*o*-arsinic acids may be converted into phenarsazinic acids by boiling with concentrated hydrochloric acid, or into 10-chloro-5 : 10-dihydrophenarsazines by reduction with sulphur dioxide and a little iodine in presence of alcoholic hydrochloric acid, the 10-chloro-compounds being oxidisable to the phenarsazinic acids (from which they may be regenerated by reduction). Ring-closure by reduction probably proceeds by way of the dichloroarsine, *e.g.*,



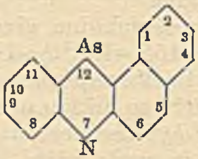
$$C_6H_4{<}\genfrac{}{}{0pt}{}{AsO_3H_2}{NR\text{——}}{>}C_6H_4X \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{AsCl_2}{NR\text{–}}{>}C_6H_4X\ (III.) \rightarrow$$

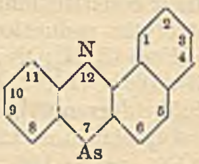
$$C_6H_4{<}\genfrac{}{}{0pt}{}{AsCl}{N(RCl)}{>}C_6H_4X \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{AsCl}{N\text{——}}{>}C_6H_4X \longrightarrow$$

$$C_6H_4{<}\genfrac{}{}{0pt}{}{AsCl}{NH\text{–}}{>}C_6H_3X.$$

When R=Me, a small amount of 10-chloro-8 : 10-dihydrophenarsazine is obtained. When X=*o*- or *p*-NO_2 and R=H, the decreased basicity of the nitrogen atom tends to prevent cyclisation. The intermediate dichloroarsine (III) is isolable only in the case where X=*o*-NO_2. The probable intermediate compound $C_6H_4X{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)Cl$, in the cyclisation by hydrochloric acid, appears transiently as an oil in most cases, but is not isolable. These reactions are also extended to the synthesis of benzophenarsazines (I) and *iso*benzophenarsazines (II).

(I)





(II.)

o-Bromophenylarsinic acid (prepared by an improved method) and bromobenzene condense with aniline and with *o*-aminophenylarsinic acid, respectively, to give *diphenylamine*-2-*arsinic acid*, m. p. 166° (slight decomp.), from which phenarsazinic acid hydrochloride, m. p. 203—205° (decomp.), and 10-chloro-5 : 10-dihydrophenarsine, m. p. 191°, are obtained. 4-*Methyldiphenylamine*-2′-*arsinic acid*, m. p. 160—165° (decomp.), prepared from *p*-toluidine or *p*-bromotoluene, behaves similarly; 2-*methylphenarsazinic acid hydrobromide*, m. p. 208—210° (decomp.), and 10-*bromo*-2-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 180° (decomp.), are described. 2-*Methyldiphenylamine*-2′-*arsinic acid*, m. p. 130—140°, prepared from *o*-toluidine, gives 4-*methylphenarsazinic acid*, m. p. 309—310° [*hydrochloride*, m. p. 199° (decomp.)], and 10-*chloro*- [m. p. 191° (decomp.)] and 10-*bromo*- [m. p. 190° (slight decomp.)] -4-*methyl*-5 : 10-*dihydrophenarsazines*. N-*Methyldiphenylamine*-2-*arsinic acid*, m. p. 182—184° (decomp.), obtained from methylaniline, is not cyclised by hydrochloric acid, but by the reduction method yields a small amount of impure 10-chloro-5 : 10-dihydrophenarsazine.

α-Naphthylamine condenses with *o*-bromophenylarsinic acid to form 2-α-*naphthylaminophenylarsinic acid*, m. p. 165°, which is converted into 7-*chloro*-7 : 12-*dihydro*iso*benzophenarsazine* (as II), m. p. 219°, and 7 : 12-*iso*benzophenarsazinic acid [*hydrochloride*, m. p. 232° (decomp.)]. β-Naphthylamine similarly gives 2-β-*naphthylaminophenylarsinic acid*, m. p. 181°, 12-chloro-7 : 12-dihydrobenzophenarsazine (as I), the 12-*bromo*-compound, m. p. 251—252° (decomp.), and 7 : 12-*benzophenarsazinic acid*, m. p. above 325° [*hydrochloride*, m. p. 234° (decomp.); *sodium*, *ammonium*, *barium*, *silver*, *mercuric*, *ferric*, *copper*, *cobalt*, and *calcium* salts described.]

The constitutions of several nitro- and amino-derivatives are confirmed by synthesis. 2-*Nitrodiphenylamine*-2′-*arsinic acid*, m. p. 238—240° (decomp.), prepared from *o*-bromonitrobenzene or from *o*-nitroaniline, gives 10-chloro-4-nitro-5 : 10-dihydrophenarsazine, m. p. 165° (Wieland and Rheinheimer, A., 1921, i, 371); 4-aminophenarsazinic acid is unaffected by nitrous acid at 5°. 3-*Nitrodiphenylamine*-2′-*arsinic acid*, m. p. 202°, from *m*-bromonitrobenzene, gives a single product of cyclisation, 10-*chloro*-3(or less probably 1)-*nitro*-5 : 10-*dihydrophenarsazine*, m. p. 258—259° (decomp.), which is oxidised to 3(or 1)-*nitrophenarsazinic acid*, not melted at 320° (*sodium* salt described); 10-*bromo*-3(or 1)-*nitro*-5 : 10-*dihydrophenarsazine* melts at 234° (decomp.). From 4-*nitrodiphenylamine*-2′-*arsinic acid*, m. p. 223° (decomp.), prepared from *p*-bromonitrobenzene, 10-*chloro*-2-*nitro*-5 : 10-*dihydrophenarsazine*, m. p. 276—278° (decomp.), is obtained, identical with the product of reduction of nitrated phenarsazinic acid (Burton and Gibson, A., 1926, 1162; Wieland and Rheinheimer, *loc. cit.*) in presence of hydrochloric acid; nitration of phenarsazinic acid therefore gives, as the more easily isolable product, the 2-nitro-compound.

C. Hollins.

Germanium. XVIII. Further organic compounds of germanium. W. R. Orndorff, D. L. Tabern, and L. M. Dennis (J. Amer. Chem. Soc., 1927, 49, 2512—2516; cf. A., 1926, 924).—Conversion of germanium tetraphenyl by bromine into triphenylgermanium bromide (m. p. 134°) takes place more readily in ethylene dibromide than in carbon tetrachloride solution (cf. Kraus and Foster, this vol., 268). *Triphenylgermanium chloride*, m. p. 117—118°, is obtained from triphenylgermanium oxide and hydrogen chloride in light petroleum, from the oxide and concentrated hydrochloric acid in boiling alcohol, or from a solution of triphenylgermanium bromide and hydrogen chloride. Diphenylgermanium dibromide could not be obtained by direct action of bromine on germanium tetraphenyl; direct hydrolysis of the reaction mixture yielded two *substances*, m. p. 147° and 210°, respectively, probably complex dehydration products of diphenylgermanic acid (cf. Morgan and Drew, A., 1925, i, 1197). *Triphenyl*-p-*tolylgermane*, m. p. 123—124°, is obtained from triphenylgermanium bromide and excess of magnesium *p*-tolyl bromide. *Triphenylanisylgermane*, m. p. 158—159°, and *triphenylethylgermane*, m. p. 75—76°, are obtained analogously. Treatment of triphenylgermanium bromide and *p*-bromodimethylaniline with sodium in boiling xylene affords *triphenyldimethylanilinogermane*, m. p. 140—141° [*hydrochloride*, m. p. 105—110° (decomp.)]. *Germanium tetrabenzyl*, m. p. 107—108°, obtained from magnesium benzyl chloride and germanium tetrachloride in ether–xylene, affords a *tetrasulphonic acid* (*barium* salt) when treated with 25% oleum at below 35°. Treatment of mercury diphenyl with germanium tetrachloride in xylene at 140° for 2 days, with subsequent hydrolysis, affords *phenylgermanic acid anhydride* $(GePhO)_2O$ (cf. Morgan and Drew, *loc. cit*). p-*Tolylgermanic acid anhydride* and *benzylgermanic acid anhydride* are obtained analogously, whilst *dimethylaminophenylgermanic acid anhydride* is obtained similarly from dimethylaniline and germanium tetrachloride at 100—110°. None of the above anhydrides has a definite m. p. *Germanium tetra*-n-*butyl*, b. p. 178—180°/733 mm., was prepared.

F. G. Willson.

Phosphorylation of proteins. C. Rimington (Compt. rend. Lab. Carlsberg, 1927, **17**, No. 2, 1—13).—Phosphorylation of proteins is readily effected by the slow addition of an ice-cold solution of phosphorus oxychloride in carbon tetrachloride to a rapidly stirred solution of the protein in the requisite quantity of dilute alkali, the reaction mixture being kept just alkaline by addition of 4*N*-sodium hydroxide and at a temperature below 5°. Caseinogen, serum-globulin, and dephosphorised casein (Rimington and Kay, A., 1926, 970) have been treated in this manner and the action of acid, alkaline, and enzyme hydrolysing agents on the products has been investigated. Phosphorised caseinogen contains 1·77% of phosphorus, the ratio P/N being 0·130, whilst for rephosphorised caseinogen the corresponding values are 1·75% and 0·124, respectively. Both products are coagulated by rennin. Phosphorised globulin contains 0·71% of phosphorus, the P/N ratio being 0·051. Under the action of pepsin and 0·25*N*-hydrochloric acid the phosphorised proteins slowly lose phosphorus as phosphoric acid, but 0·25*N*-sodium hydroxide at 37° liberates the whole of the phosphorus in 24 hrs. Trypsin causes a rapid separation of the whole of the phosphorus of phosphorised globulin in the form of an organic, acid-soluble substance, but liberates phosphoric acid from this compound only extremely slowly. Bone phosphatase, which liberates no phosphoric acid from the original phosphorised protein, rapidly liberates the whole of the phosphorus from this organic compound as phosphoric acid. The nature of the linking involved in proteins containing phosphorus is discussed, the author being of the opinion that a phosphoric ester of a hydroxyl group is formed.

J. W. Baker.

Phosphorus of caseinogen. I. Isolation of a phosphorus-containing peptone from tryptic digests of caseinogen. II. Constitution of phosphopeptone. C. Rimington (Biochem. J., 1927, **21**, 1179—1186, 1187—1193; cf. Rimington and Kay, A., 1926, 970; Rimington, this vol., 272, 581).—I. A peptone, $C_{37}H_{62}O_{33}N_9P_3$, named *phosphopeptone*, was isolated from tryptic digests of caseinogen in a yield corresponding with 50% of the organic phosphorus of the digest. The filtrate from a 38 hr. digest was precipitated with lead acetate and ammonia. The precipitate was then decomposed with hydrogen sulphide, and after removing the inorganic phosphorus the peptone was precipitated with uranium acetate. The *copper* and *barium* salts each containing nine equivalents of the metal and a *brucine* salt were prepared. The free acid has $[\alpha]^{15}_{5461}$ —80·53° and gives the biuret and ninhydrin reactions, but not the usual colour reactions for amino-acids. A primary colour reaction is also given with diazobenzenesulphonic acid, but there is no secondary colour after reduction. The peptide linkings of phosphopeptone are slowly attacked by trypsin, which also slowly liberates phosphorus as phosphoric acid.

II. Phosphopeptone was hydrolysed with hydrochloric acid and the resulting amino-acids were converted into their calcium salts. The concentrated salt solution was then treated with 97% alcohol, the precipitate dissolved in water and decomposed with oxalic acid, and converted into a copper salt which was found to be that of β-hydroxyglutamic acid. From the alcoholic solution of the calcium salts, α-amino-β-hydroxybutyric acid and serine were isolated. A hypothetical structural formula which is in agreement with the known chemical properties of the peptone is advanced. Posternak's work (this vol., 273, 581) is criticised. S. S. Zilva.

Racemisation. V. Action of acid and alkali on gelatin. P. A. Levene and L. W. Bass (J. Biol. Chem., 1927, 74, 715—725).—The average rotation of the mixture of amino-acids resulting from acid hydrolysis of gelatin was α_{5461} —0·23° to —0·38° (4 dm. tube); after preliminary treatment of the gelatin for 24 hrs. at 25° with 0·1, 1·0, and 3·0*N*-alkali, the corresponding rotations were —0·69°, —1·13°, and —0·2°, respectively. The results indicate that racemisation (principally of the *d*-amino-acids) is more complete in the dilute alkali, probably owing to the rapidity of hydrolysis in the concentrated alkali. The results agree with those of Dakin (A., 1913, i, 208).

C. R. Harington.

Constitution of the diazo-compounds of silk fibroin. A. Morel and P. Sisley (Bull. Soc. chim., 1927, [iv], 41, 1217—1224).—Fibroin, after treatment with nitrous acid at 10—12° for 24 hrs. in the absence of light, becomes yellow and couples slowly with certain amines and phenols with the production of bright colours, which, whilst fast to washing and light, are changed in tint by acids and alkalis. Many amines and phenols will not couple with the diazotised fibroin. The general properties of the colours are analogous to those of the azo-dyes, and it is suggested that the nitrous acid reacts with the tyrosine of the fibroin (Abderhalden, A., 1905, i, 75; 1922, i, 784) to produce an *o*-quinone-oxime which is reduced by further nitrous acid to form a diazonium nitrate. This view is supported (i) by the production of similar colours from tyrosine and (ii) by the preparation of phenolazo-β-naphthol from phenol, nitrous acid, and β-naphthol. According to this view diazotised fibroin, after reduction with stannous chloride, contains a free amino-group which accounts for its rapid diazotisation in contrast to the slow diazotisation of fibroin. G. A. C. Gough.

Hydrolysis of silk by 25% formic acid. N. D. Zelinski and K. P. Lavrovski (J. Russ. Phys. Chem. Soc., 1927, 59, 423—426).—The action of 25% formic acid on silk fibre, freed from gum, at 180°/10 atm. was investigated, to determine whether hydrolysis was complete, or whether, as in the action of 10% acid on proteins, very stable condensation products of the amino-acid were formed.

On treatment for 3 hrs., a 10% yield of tyrosine was obtained. No basic products of reduction, such as piperazine, but only small quantities of ammonia and methylamine, were obtained from the decomposition of the amino-acids. The solid separated from the aqueous solution on esterification in the presence of hydrochloric acid gave glycine ester hydrochloride, whilst from the mother-liquor, on further esterification, alanine ester, b. p. 49—50°, was obtained. Formic acid (25%) under similar conditions also hydrolysed pure glycine anhydride and so behaved like 4—5% solutions of mineral acids. M. Zvegintzov.

Osmometric method of determining the mol. wt. of proteins. G. Adair (J. Amer. Chem. Soc., 1927, 49, 2524—2525).—A reply to Svedberg and Nichols (this vol., 99), and a summary of arguments in support of results obtained by the osmometric method of determining mol. wt. of proteins (cf. Adair, A., 1926, 21; 1925, ii, 965). The provisional estimate of the average mass of the protein particles in serum is raised from 80,000 to 100,000. F. G. Willson.

Effect of radium radiation on pseudoglobulin. A. Fernau (Biochem. Z., 1927, 189, 172—174).—Pseudoglobulin on irradiation with radium is denatured as with serum- and egg-albumin (cf. A., 1926, 367), the coagulation temperature being first decreased and the globulin finally separating as a powder. The time of irradiation necessary for the commencement of precipitation is influenced both by the presence of salts and by the concentration of the solution, but pseudoglobulin solutions obtained by ordinary dialysis behaved similarly to those which were made completely salt-free by electrodialysis.

P. W. Clutterbuck.

Combination between acid dyes and proteins. R. A. Gortner (J. Biol. Chem., 1927, 74, 409—413).—A discussion of the results of Chapman, Greenberg, and Schmidt (this vol., 686). C. R. Harington.

Sulphur in proteins. III. Derivatives of *l*- and *i*-cystine. E. Abderhalden (J. Biol. Chem., 1927, 75, 195—197). R. A. Gortner (*ibid.*, 199—200). —Polemical (cf. Gortner and Hoffman, this vol., 581; Abderhalden, A., 1903, ii, 564).

C. R. Harington.

Halogenated proteins. VIII. Chlorogluten. A. J. J. Vandevelde (Rec. trav. chim., 1927, 46, 590—593; cf. A., 1925, i, 92; this vol., 474).—A solution of chlorine in carbon tetrachloride converts gluten into chlorogluten (N 10·6; Cl 23·2%), partly soluble in water and apparently a mixture; it is more resistant to reagents than other chlorinated proteins.

E. W. Wignall.

Micro-method for the determination of "hydrogen number." S. Ogawa (Sci. Rep. Tôhoku Imp. Univ., 1927, 16, 671—676).—Precise details of apparatus and experimental technique are given of a modification of Fokin's method (B., 1908, 878) of determining " hydrogen number " as a measure of unsaturation; it is possible to test 5—20 mg., depending on the degree of unsaturation, of various fatty materials. E. HOLMES.

Volumetric determination of alkoxy-groups. E. P. EATON and E. S. WEST (J. Biol. Chem., 1927, **75**, 283—288).—The compound is boiled with hydriodic acid and the alkyl iodide absorbed in pyridine at 80°; the pyridinium alkyl iodide is treated with excess of sulphuric acid and potassium iodate and the liberated iodine distilled into potassium iodide and titrated. The method is applicable to methoxyl and ethoxyl groups and to compounds containing sulphur.

C. R. HARINGTON.

Copper number for dextrose. C. A. AMICK (J. Physical Chem., 1927, **31**, 1441—1477).—The use of alkaline copper solutions is invalidated by the facts that the amount of oxidation depends on the alkalinity and concordant results differing greatly from series to series can be obtained according to conditions. Further, solutions made alkaline by carbonates give higher copper numbers than those made alkaline by alkali hydroxide. The volumetric method of Bertrand (A., 1907, ii, 136) is inaccurate because of adsorption of Fehling's solution by the asbestos mat or filter-paper used. The adsorbed material cannot be removed by washing but dissolves in the acidified iron alum solution used. Further, ferric salts catalyse the oxidation of the adsorbed tartrates by the permanganate. Iron salts, however, can be used when sodium fluoride is added to remove the excess of ferric iron by forming a complex, Na_3FeF_6, which is unstable in solutions of 2·5% acidity. Iron salts may also be used with sodium pyrophosphate if the acidity is kept low. In a new volumetric method, filtration is eliminated, and the cuprous oxide is oxidised by a phosphomolybdic reagent, the blue colour which is formed being discharged in the cold, by titration with permanganate. The reducing action of sugar is not due to carboxyl formation from the carbonyl group, as generally supposed. The results support the views of Nef for the formation, with subsequent fission, of enediols by the reducing sugars in alkaline solution.

L. S. THEOBALD.

Microchemical reactions for citric acid. M. WAGENAAR (Pharm. Weekblad, 1927, **64**, 1135—1138).—The formation of the anhydride and of the various salts does not afford satisfactory tests. Oxidation to acetone and conversion of this into iodoform can be effected, but malic and lactic acids give this compound also under the conditions employed. Oxidation in presence of hydrobromic acid yields pentabromoacetone, which can be brought to characteristic crystallisation by addition of ether; the corresponding iodine compound crystallises more readily, and is more suitable for the test. The reaction is not given by tartaric, succinic, lactic, malic, or oxalic acids. S. I. LEVY.

Characteristic colour reactions for lactic acid, methylglyoxal, and carbohydrates with carbazole and sulphuric acid. Z. DISCHE (Biochem. Z., 1927, **189**, 77—80).—The method of carrying out the carbazole reaction is described and tables indicate the colours obtained with a large number of aldehydes, ketones, hydroxy- and amino-acids, etc.

P. W. CLUTTERBUCK.

Colorimetric determination of *o*-dihydroxy-derivatives of benzene. H. SCHMALFUSS, K. SPITZER, and H. BRANDES (Biochem. Z., 1927, **189**, 226—228).—A method is described for the colorimetric determination of dihydroxybenzene derivatives, based on the colour obtained with ferric chloride, and applied to solutions of pyrocatechol, protocatechuic acid, protocatechualdehyde, adrenaline, and *l*-3 : 4-dihydroxyphenylalanine. The limits of the method are from $1{\cdot}12\times10^{-5}$ to $7\times10^{-7}M$ solutions and the error is ±3%. P. W. CLUTTERBUCK.

Evaluation of ethyleosin. W. C. HOLMES and J. T. SCANLAN (Stain Tech., 1927, **2**, 101—103).—Methods for the determination of eosin and ethyleosin in samples of the latter are described. The great difference in solubility of the two dyes in water makes this possible; at 26° 100 c.c. of water dissolve 44·2 g. of eosin and only 0·0312 g. of ethyleosin.

H. W. DUDLEY.

Extinction coefficients of dyes. R. W. FRENCH (Stain Tech., 1927, **2**, 124—125).—The extinction coefficients of seven acid and nine basic dyes are tabulated. H. W. DUDLEY.

Biochemistry.

Colloidal properties of the surface of the living cell. J. F. MCCLENDON (Fourth Colloid Symposium Monograph, 1926, 224—233).—Experiments on the conductivity of the corpuscle-interior of laked blood support the selective semipermeability of the colloidal cell surface. CHEMICAL ABSTRACTS.

Effect of certain dyes on blood *in vitro*. H. WALES, J. C. MUNCH, and E. W. SCHWARTZE (J. Pharm. Exp. Ther., 1927, **31**, 473—479).—The extinction coefficients of solutions of the following dyes in diluted blood have been determined in the range of the visible spectrum: guinea-green-B., light-green-S.F. yellowish, fast-green-F.C.F., indigotin, erythrosin, amaranth, ponceau-3R, orange-I, orange-II, naphthol-yellow-S., and tartrazine. Immediate readings show no diminution in intensity of the oxyhæmoglobin bands; on keeping, however, a diminution takes place and the band of reduced hæmoglobin appears (5450 Å.). Since in no case was a band at 4950 Å. detected it is concluded that no methæmoglobin was formed. E. A. LUNT.

Specific refraction of whole [plasma-]protein. K. RECKNAGEL (Arch. exp. Path. Pharm., 1927, **125**, 257—268).—The specific refractive index of the total plasma-protein shows marked variation even in one individual and is related to the specific viscosity, both values being dependent on the colloidal condition of the protein. W. O. KERMACK.

Quantitative micro-method for the fractionation of serum-proteins by electrodialysis. A. Tóth (Biochem. Z., 1927, 189, 270—293).—By using a centrifugable membrane for electrodialysis, the serum-protein can be separated immediately by centrifuging. The loss of protein during dialysis is usually less than 1% and never more than 2%. The changes of reaction, the separation of salts, and the formation of precipitate during electrodialysis were followed in parallel experiments, in one case with a combination of a chromed gelatin and collodion and in the other of a pair of collodion membranes. With the former pair, the reaction passed from that of the diluted serum to that of the isoelectric point of globulin, whilst with the latter pair the reaction was acid and then drew near to the isoelectric point of globulin. The decrease in electrolytes shows initially a rather steep and uniform fall, then a period of no further decrease, and finally a considerable decrease. The conductivity curve follows the same course with both pairs of membranes but the removal of electrolytes is quicker with the chromed gelatin–collodion pair. The precipitation curve is also of the same type for the chromed gelatin–collodion pair and reaches its maximum after 40 min., whereas with the pair of collodion membranes it remains steady where the conductivity curve shows its maximum, the high point being attained after 50 min. The course of electrodialysis is divided into three phases. In the first those electrolytes not combined or loosely combined with protein are removed and about 50% of the precipitation occurs, whilst in the second phase those crystalloids bound to the protein are removed, and in the third phase the conductivity again falls. The effect of age on the chromed gelatin membranes in respect to its nitrogen permeability is investigated with human sera. The pair of collodion membranes is recommended for quantitative investigation because of their easier preparation and their greater trustworthiness. P. W. Clutterbuck.

Preparation of serum-globulin and its definability. L. Reiner (Magyar Orvosi Arch., 1927, 28, 288—303).—Serum-euglobulin is not an additive product of protein and lipin. Globulin, which has a broad isoelectric zone, is not a homogeneous substance. Proteins with different isoelectric points cannot be isolated from so-called euglobulin.

Chemical Abstracts.

Normal bilirubin content of human sera. R. Sivó (Biochem. Z., 1927, 189, 159—161).—The normal bilirubin content of serum is 0·80—1·10 mg. % and values above 1·20 mg. % are regarded as pathological. The occurrence of a low bilirubin content in certain diseases could not be confirmed.

P. W. Clutterbuck.

Existence of lactacidogen in blood. (Mme.) A. Roche and J. Roche (Compt. rend., 1927, 185, 873—875).—Determinations of the lactic acid–phosphorus ratio for defibrinated dog's blood, diluted with twice its volume of sterile distilled water and maintained at 38—40°, indicate the presence of a hexosediphosphoric acid. The lactacidogen probably undergoes degradation by a phosphatase analogous to that found in muscle juices. J. Grant.

Reducing non-sugars and true sugar in human blood. M. Somogyi (J. Biol. Chem., 1927, 75, 33—43).—Fermentative removal of dextrose from blood is complete if, in the preparation for the precipitation of proteins by tungstic acid, the blood be diluted with a 10% aqueous suspension of washed yeast. The non-dextrose reducing substances of human blood amount almost constantly to 27 mg. per 100 c.c. (expressed as dextrose), whatever may be the total concentration of sugar, but are increased in amount in cases of nitrogen retention; they are unequally distributed between the red blood-corpuscles and the plasma, amounting to 47 mg. % in the former and 10 mg. % in the latter; part of the non-dextrose reducing power is due to ergothioneine.

C. R. Harington.

Preservation of blood for chemical analysis. F. F. Schwentker (Arch. Path. Lab. Med., 1927, 3, 410—413).—If the Lewis–Benedict method is employed, variably high results are obtained when sodium fluoride and thymol are used as preservatives.

Chemical Abstracts.

Concentration of urea in normal [human] blood. E. M. MacKay and L. L. MacKay (J. Clin. Invest., 1927, 4, 295—306).—The blood-urea varies between 11·0 and 48·0 mg. per 100 c.c., being higher in males than in females; there is a diurnal fluctuation. Chemical Abstracts.

Micro-determination of blood-sugar. Blood-sugars of insects. R. Blumenthal (Science, 1927, 65, 617—619).—The method of Folin and Wu is applied to the manipulation of 0·03 c.c. of material. The following average and extreme values for the blood-sugar (mg. per 100 c.c.) were obtained: *Romelea microptera* (nymph) 41·7, 34·2—49·4; *Melanoplus femur rubrum* 35·3, 30·6—41·9; *Melanoplus diffentialis* 36·5, 31·0—45·9; *Chortophaga viridifasciata* 34·0; *Encoptolophus sordidus* 36·4; *Popellia japonica* (larva) 63·0, 56·3—69·2. A. A. Eldridge.

Action of powdered metals on blood-catalase. G. Lio (Arch. Farm. sperim., 1927, 43, 218—224).—Finely-divided silver, nickel, copper, and cobalt have no action on hydrogen peroxide solution but gradually weaken and ultimately abolish the activity of blood-catalase. Powdered quartz is without influence in this direction. T. H. Pope.

Determination of calcium in whole blood. W. R. Caven and A. Cantarow (J. Lab. Clin. Med., 1926, 12, 76—77).—The calcium is determined volumetrically as oxalate, the blood being hæmolysed by distilled water. Chemical Abstracts.

Electrometric determination of iron in blood. J. F. King and F. H. Howard (J. Biol. Chem., 1927, 75, 27—32).—Blood was incinerated with sulphuric and perchloric acids and the solution of the residue titrated electrometrically with titanous sulphate against a standard solution of ferric sulphate by the method of King and Washburne (this vol., 24); with 5 c.c. of blood the error of the method is 0·2%.

C. R. Harington.

Manganese content of plants and animals. C. W. Lindow and W. H. Peterson (J. Biol. Chem., 1927, 75, 169—175).—Figures are given for the manganese content of numerous food materials of plant and animal origin. C. R. Harington.

Constituents of *Laganum* (*echinoidea*). I. M. Kotake (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 49—51).—Cholesterol is isolated from the ethereal extract of the dry, powdered horny covering of *Laganum*. The ethereal extract of the inner portion after hydrolysis yields more cholesterol and an unsaturated fatty acid which on reduction (without purification) with palladium-black and hydrogen in alcohol yields *dihydrolaganic acid*, $C_{20}H_{40}O_2$, m. p. 68·5—70° (*amide*, m. p. 104—105°), which is not identical with either stearic or arachic acids and probably contains a branched carbon chain.
J. W. Baker.

Nitrogenous extractives of ox liver. Y. Hiwatari (J. Biochem. [Japan], 1927, 7, 161—167).—An extract obtained from 14 kg. of ox liver yielded uric acid 5; guanine 0·7; adenine 1·5; xanthine 0·45; hypoxanthine 0·6; choline 3 g., and a small quantity of carnosine. Chemical Abstracts.

Determination of carnosine. F. M. Kuen (Biochem. Z., 1927, 189, 60—76).—Carnosine was determined by seven methods in the muscle of the ox, horse, pig, calf, and rabbit. Horse muscle contains 0·3% of carnosine when determined as the characteristic copper compound or after hydrolysis as histidine picrolonate, the value being practically constant for the different samples. Diazo-colorimetric and copper-colorimetric methods gave values which were too high. Frozen meat contained much less carnosine than fresh meat. Smoked flesh contains either no carnosine or histidine, or else only traces, but a substance is present which gives the diazo-reaction but is not precipitated by mercuric sulphate.
P. W. Clutterbuck.

Colloidal characteristics of muscle proteins. III. Physico-chemical constants for myogen. H. H. Weber (Biochem. Z., 1927, 189, 407—450).—Myogen solutions purified by electrodialysis contain 1—6% of myogen, only 5—10% of the total nitrogen of such solutions being present as other proteins (albumin). Pure myogen has *d* 1·35, and fresh electrodialysates in the absence of carbon dioxide have $[\alpha]_D$ +31°, but this increases threefold by acid ionisation. Hydrolysis of protein in very alkaline solution causes the concentration of hydroxyl ions obtained by electrotitration to appear 20% too high, and in very acid solutions the concentration of hydrogen ions 10% too low. The union of myogen with hydrogen and hydroxyl ions increases at a given p_{ah} (negative exponent of the hydrogen-ion activity) proportionally with the myogen concentration. The bound $H^{\cdot}$–p_{ah} curve (with 1 millimol. of myogen nitrogen) may be represented (apart from the isoelectric zone) by the dissociation curve of a univalent base with a dissociation constant at $K_B=3·5\times10^{-11}$ and a total acid-binding power of 115×10^{-3} millimol. $H^{\cdot}$, the base equivalent being 750. The bound OH'–p_{ah} curve (with 1 millimol. of myogen nitrogen) is described (apart from the isoelectric zone) by the addition of the dissociation curves of two univalent acids with dissociation constants $K_{a_1}=6·3\times10^{-9}$ and $K_{a_2}=10^{-11}$ and a total base-binding power of 17—89×10^{-3} millimol. OH′. The equivalent weight of the substance first dissociated is 5100 and the total base equivalent 815 (by electrotitration) and 1027 (by Willstätter's titration). For myogen chloride in pure hydrogen chloride solution, the activity, measured by the calomel electrode, shows an increase from 0·5 at p_{ah} 1·5 to 0·7 at p_{ah} 3, whilst in hydrogen chloride and *M*/30-sodium chloride it is only 0·4 at p_{ah} 3. The "non-dissolving space" (cf. Polányi, A., 1920, ii, 604) for 1 g. of acid-ionised myogen is only 2·7 cm., a figure much lower than the volume of myogen (disperse phase) as calculated from viscosity measurements (which at p_{ah} 1·5 is 12·4 cm.), and this discrepancy is of importance in view of Pauli's hydration theory of protein ions which depends on viscosity measurements. The alkaline ionisation of myogen at the p_{ah} of resting muscle is as high as the acid ionisation at p_{ah} 5·5, *i.e.*, at a p_{ah} almost never attained in muscle. Since myogen on account of its isoelectric point at p_{ah} 6·3 is the only muscle protein which is concerned in acid-swelling, the acid-swelling theory of contraction must be discarded. The total muscle myogen can neutralise only one fifth of the lactic acid arising in muscular fatigue, and since under these conditions one to two thirds of the lactic acid is neutralised by protein, a protein of much greater buffering power must be present (cf. A., 1925, i, 995).
P. W. Clutterbuck.

Lens protein and its fractions. A. C. Woods and E. L. Burky (J. Amer. Med. Assoc., 1927, 89, 102—110).—New methods of preparation yield a larger ratio of α- to β-crystallin. Serologically pure fractional antigens were obtained by a method utilising the isoelectric points of the crystallins.
Chemical Abstracts.

Isolation of a substance with carcinolytic properties from the reticulo-endothelial system. N. Waterman and L. de Kromme (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 499—501).—Normal blood-serum and normal organs contain a substance capable of dissolving cancer cells. This property disappears on the appearance of carcinoma, and it may be increased or diminished by *X*-rays according to the length of time of irradiation. Ether extracts of almost all organs possess a more or less lytic action, but the extracts of the lymphatic glands, spleen, and thymus are most active. The extraction is made with 10—15 times the volume of ether under a reflux condenser for 8 hrs. The ether is removed and the aqueous residue treated with excess of acetone. The white flocculent precipitate is washed with acetone, dried, ground with 96% alcohol, filtered, and the whitish-grey residue dried and shaken with a mixture of one part of phosphate buffer, p_H 7·7, with five parts of physiological sodium chloride solution, which dissolves the active matter. The lytic power of the product depends on the p_H of the environment. An acid reaction counteracts lysis, whilst an alkaline one promotes it. A lytic power of 81% has so far been obtained. The product contains neither tryptic nor lipolytic enzyme, and is free from protein. Its lytic power is affected by *X*-rays.
M. S. Burr.

Presence of acetaldehyde in cerebrospinal fluid. P. Thomas and E. Maftei (Bull. Sci.

Roumaine, 1927, 10, 16—20).—Small quantities of acetaldehyde have been detected in human cerebrospinal fluid. Cerebrospinal fluid is shown to contain neither decarboxylase nor an alcohol oxidase and so it is concluded that the acetaldehyde does not originate in the fluid itself, but in the blood. W. O. Kermack.

Chlorides of gastric contents in relation to free acidity. S. Miller and F. B. Smith (Lancet, 1927, i, 593—595).—The mean curves of the total chlorides in all grades of gastric acidity are similar in shape, and differ only in magnitude. The mean curves of the inorganic chlorides have the same general form and relation to time of digestion as those of the total chlorides, but agree more closely in magnitude. In hyperchlorhydria the inorganic chlorides tend to remain low, or rise only slightly.
A. A. Eldridge.

Relation of $p_{\rm H}$ to titratable acidity of milk. P. F. Sharp and T. J. McInerney (J. Biol. Chem., 1927, 75, 177—184).—In fresh milk the $p_{\rm H}$ varied from 6·0 to 7·73 and the titratable acidity from 0·05 to 0·5%, expressed as lactic acid; a curve is given by means of which the $p_{\rm H}$ can be deduced from the titratable acidity over the range of 0·1—0·5% of the latter. The relation between $p_{\rm H}$ and titratable acidity in sour milk is of a different character.
C. R. Harington.

Determination of calcium in human milk. C. S. Rothwell (J. Biol. Chem., 1927, 75, 23—26).—By treatment of the material with sodium chloride to make a concentration of 5% of the latter, the author's direct precipitation method (A., 1925, i, 1350) becomes applicable to human milk. C. R. Harington.

Chlorides and non-protein nitrogenous constituents of the sweat, urine, and blood as affected by heat and work. G. A. Talbert, E. E. Harris, J. R. Finkle, and S. H. Silvers (Amer. J. Physiol. Proc., 1926, 76, 185—186).—Sweat contained 3·2—6·5 mg. of chlorine, 0·338—1·625 mg. of nitrogen, 0·05—1·12 mg. of urea, and 0·04—0·211 mg. of ammonia per c.c. Generally, the chlorides and total nitrogen vary directly. A. A. Eldridge.

Physico-chemical properties of bilirubin in body-fluids. E. Forrai and R. Sivó (Biochem. Z., 1927, 189, 162—167).—Bilirubin, although readily ultrafiltrable, becomes completely unable to pass the ultrafilter in presence of colloids. Caffeine destroys the bilirubin–colloid union. P. W. Clutterbuck.

Instability of bilirubin and detection of bilirubin in urine. R. Sivó and E. Forrai (Biochem. Z., 1927, 189, 168—171).—Fresh urine must be used for the detection of bilirubin on account of the instability of bilirubin. Union with colloid (see preceding abstract) increases the stability of bilirubin.
P. W. Clutterbuck.

Relation of inorganic iron to nutritional anæmia. H. S. Mitchell and M. Vaughn (J. Biol. Chem., 1927, 75, 123—137; cf. A., 1926, 1269).—Whilst not all soluble iron salts are equally effective in the relief of nutritional anæmia, it remains true that no insoluble iron compound is satisfactory in this respect. No relationship could be observed between vitamin-*E* and the assimilation of iron.
C. R. Harington.

Blood-sugar curves in non-diabetic subjects. W. G. Lennox [with M. Bellinger] (J. Clin. Invest., 1927, 4, 331—352).—A progressive lowering of successive curves follows the ingestion or injection of dextrose; hence a single curve has little diagnostic significance. Chemical Abstracts.

Utilisation of protein, carbohydrate, and fat in hypoglycæmia in diabetics requiring insulin. Dextrose content of blood-plasma and corpuscles, and effect of insulin and dextrose on the acid–base balance of the blood. R. B. Gibson, L. Greer, and A. Barer (Amer. J. Physiol. Proc., 1926, 76, 188).—At high blood-sugar levels the metabolism is of the diabetic type; at hypoglycæmic levels the fat metabolism is augmented. Blood-sugar levels are incidental to, and not the cause of, the metabolic changes. Pre-operative administration of insulin and dextrose produces a shift of the acid-base balance further to the alkaline side.
A. A. Eldridge.

Fat metabolism in diabetes. I. Blood-lipins in experimental diabetes. W. R. Bloor, E. M. Gillette, and M. S. James (J. Biol. Chem., 1927, 75, 61—83).—Experimental diabetes, produced in dogs by removal of the greater part of the pancreas, resulted, whatever the nature of the diet, in an increase in the fasting concentration of lipins in the blood, and a still greater increase in the response of the blood-lipins to a fat meal. The variation was most marked in the fats and least in the lecithin; the increase in cholesterol was variable and usually less marked than that observed in human diabetics.
C. R. Harington.

Effect of the administration of sodium β-hydroxybutyrate on the glycosuria of phloridzin diabetes. N. Morris and S. Graham (Lancet, 1927, i, 1020—1021).—With dogs there was no appreciable rise in the D : N ratio. A. A. Eldridge.

Optical activity and reducing power of dextrose excreted by renal diabetics. E. J. Magers and R. B. Gibson (J. Biol. Chem., 1927, 75, 299—304).—The sugar excreted by renal diabetics was of the same character in the fasting condition and after ingestion of dextrose, and had, in all cases, the specific rotation of ordinary dextrose. C. R. Harington.

Epilepsy. Rational treatment by production of ketosis. F. B. Talbot, K. M. Metcalf, and M. E. Moriarty (Amer. J. Dis. Children, 1927, 33, 218—225).—In epileptic children treated by fasting or with ketogenic diet there is an increased blood-acetone concentration, and a marked excretion of acetone substances in the breath and urine. The alkaline reserve is lowered and the blood-sugar decreased.
Chemical Abstracts.

Changes in plasma-proteins of hæmatoporphyrin rabbits. M. Komatsu (J. Biochem. [Japan], 1927, 7, 1—17).—The albumin/globulin ratio in the plasma of hæmatoporphyrin rabbits exposed to sunlight is considerably diminished, owing to an increase in the globulin and a diminution of the albumin content. The rise in globulin content of the plasma runs more or less parallel to the developing anæmia, but it is not known whether the globulin owes its origin to the destruction of red blood-cells. There is a notable increase in the urobilin content of the urine of the hæmatoporphyrin rabbits. CHEMICAL ABSTRACTS.

Lævulose tolerance test for hepatic efficiency. G. KING (Lancet, 1927, i, 385—388).—Normally, the rise in blood-sugar after ingestion of 45 g. of lævulose is 8 mg. per 100 c.c.; there is a return to the fasting level in 1·5—2 hrs. In liver disease the reaction is atypical. A. A. ELDRIDGE.

Comparative sugar content of blood and of cerebrospinal fluid in various conditions. A. LEVINSON (Amer. J. Dis. Children, 1925, 30, 774—779).—No direct relation was observed in meningitis. Ingestion or injection of dextrose usually raised the cerebrospinal-fluid value, which is low in meningitis. CHEMICAL ABSTRACTS.

Blood as a physico-chemical system. VI. Terminal chronic nephritis. L. J. HENDERSON, A. V. BOCK, D. B. DILL, L. M. HURXTHAL, and C. VAN CAULAERT (J. Biol. Chem., 1927, 75, 305—313).—A nomographic representation is given of the condition of the blood immediately preceding death from chronic nephritis, the most conspicuous features being reduction in the hæmoglobin, increase in acidity, and a profound change in the distribution of electrolytes between red blood-corpuscles and plasma. C. R. HARINGTON.

Chemical aspects of the toxæmias of pregnancy. J. N. CRUICKSHANK (Glasgow Med. J., 1927, 26, 1—11).—In pre-eclamptic toxæmia there is no gross retention of nitrogen. The composition of the blood and urine characteristic of the later months of normal pregnancy is maintained in the toxæmias. The hydræmia characteristic of late pregnancy and the œdema of certain toxæmic cases are not related to the blood- or urine-chlorides. CHEMICAL ABSTRACTS.

Changes in oxygen capacity of rabbit hæmoglobin following splenectomy. B. B. STIMSON (J. Biol. Chem., 1927, 75, 95—99).—Splenectomy in rabbits was followed by a greater fall in oxygen capacity than in hæmoglobin content of the blood; no spectroscopic evidence of the presence of methæmoglobin could be obtained, but, after treatment with a reducing agent, the combining capacity of the blood for carbon monoxide was increased. The presence is therefore assumed of some oxidation product of hæmoglobin similar to, but not identical with, methæmoglobin. C. R. HARINGTON.

Respiratory metabolism following administration of various carbohydrates. H. J. DEUEL, jun. (J. Biol. Chem., 1927, 75, 367—391).—Ingestion of lævulose and sucrose leads to an immediate rise in the respiratory quotient; the rise is slightly slower with lactose and galactose, whilst with dextrose and maltose it is delayed for 45 min., and with starch for 1—2 hrs. The specific dynamic effects of all the carbohydrates were closely similar to one another, and approximated to the effects already observed in dogs. The maximum heat production occurred usually about 2 hrs. after ingestion of the carbohydrate and was not necessarily coincident with the highest respiratory quotient. C. R. HARINGTON.

Metabolism of dihydroxyacetone in normal and diabetic individuals. I. M. RABINOWITCH (J. Biol. Chem., 1927, 75, 45—60).—Further evidence is given in support of the previous suggestion (A., 1925, i, 1352; cf. also Kermack and others, A., 1926, 861) that, in the normal and diabetic individual, dihydroxyacetone can be oxidised directly, and, unless administered in large excess, is not converted into dextrose. The opposite conclusions of Campbell and others (A., 1926, 1272) are perhaps accounted for by technical errors in the determination of dihydroxyacetone. C. R. HARINGTON.

Distribution and recovery of dextrose injected into animals. O. FOLIN, H. C. TRIMBLE, and L. H. NEWMAN (J. Biol. Chem., 1927, 75, 263—281).—Dextrose injected intravenously into nephrectomised dogs disappears very rapidly from the blood-stream, but cannot be accounted for after 30 min. by the increase in the dextrose content of the muscles and the glycogen of the liver. Similar experiments with guinea-pigs showed, however, that by analysis of the whole animal 30 min. after the injection the whole of the dextrose could be accounted for; it was then found that such injections led at first to rapid accumulation of dextrose in the skin and glandular organs; in the course of 3—4 hrs. the dextrose content of these tissues and of the blood had returned to the normal, and there could then be detected the increase in the glycogen of the muscles and the liver as observed by other workers (cf. Cori and Cori, A., 1926, 1271). C. R. HARINGTON.

Behaviour of the glycæmic curve in the child during a prolonged fast. I and II. I. G. TOSI (Clin. pediatr., 1926, 8, 577—591, 592—603).—With infants on a tea–"saccharin" diet the minimal blood-sugar (0·05—0·06%; normal 0·06—0·10%) is attained in 24 hrs., with older children in 48 hrs. The decrease is followed by a rise which is apparently caused by the mobilisation of the glycogen reserves. Addition of fat to the diet does not essentially influence the glycæmic curve, but caseinogen does so. It is concluded that sugar can be formed from protein, but not from fat. CHEMICAL ABSTRACTS.

Sugar and cholesterol in the blood-serum in relation to fasting. R. E. SHOPE (J. Biol. Chem., 1927, 75, 101—113).—In man, the pig, the cat, and the guinea-pig, fasting causes a fall in the sugar and an increase in the free cholesterol and cholesterol esters of the blood; on resumption of food the reverse changes take place. In the rabbit, on the other hand, fasting is accompanied by an increase in the blood-sugar as well as in the cholesterol of the blood. The relationship between the sugar and cholesterol is regarded as indicating that the latter plays a part in the metabolism of fats. C. R. HARINGTON.

Effect of addition of alkali [to the diet] on alimentary hyperglycæmia during starvation. G. HIRSCH (Biochem. Z., 1927, 189, 451—459).—Administration to starving rabbits, dogs, and men of dextrose on the one hand and of the same amount of dextrose with alkali (sodium hydrogen carbonate and acetate) on the other showed that with alkali the specific dynamic action was decreased and the respiratory quotient increased, the blood-sugar curve was lower and after 4 hrs. hypoglycæmia intervened, and the increased sugar tolerance obtained by repeating the administration of sugar fell away.

P. W. Clutterbuck.

Lactate metabolism in infants. M. B. Brahdy (Amer. J. Dis. Children, 1927, **33**, 451—457).—The lactate ion does not influence the peripheral metabolism. Chemical Abstracts.

Ketosis in the rat. H. Levine and A. H. Smith (J. Biol. Chem., 1927, **75**, 1—22).—Variations in the fat, carbohydrate, or protein fractions of the diet of adult rats caused no corresponding fluctuations in excretion of ketones, nor could ketosis even be produced by sudden change from a diet rich in carbohydrate to one rich in fat. The mechanism of ketosis must therefore be different in man and in the rat, and the theory of Shaffer is not applicable to rats. Excretion of acetone substances in the rat was increased by injection of phloridzin or by addition of sodium carbonate to the diet rich in fat; under almost all conditions, β-hydroxybutyric acid represented about 70% of the total excretion of acetone substances. C. R. Harington.

Pasteurised and dried milk as source of calcium, phosphorus, and nitrogen. A. C. Willard and K. Blunt (J. Biol. Chem., 1927, **75**, 251—262).—Positive balances of calcium, phosphorus, and nitrogen were observed in children when these elements were supplied principally in the form of dried or pasteurised milk, the former being slightly the more satisfactory. C. R. Harington.

Purine metabolism. I. Distribution of uric acid in blood and lymph of the dog following intravenous injection of uric acid. A. A. Christman and H. C. Eckstein (J. Biol. Chem., 1927, **75**, 201—206).—Following intravenous injection of uric acid into dogs there was found a considerable increase in the uric acid content of the lymph obtained from the thoracic duct; this may account in part for the rapid disappearance of uric acid after injection, observed by Folin and others (J. Biol. Chem., 1924, **60**, 361). C. R. Harington.

Action of ammonium benzoate on the urine. J. M. Johnston (Edinburgh Med. J., 1927, **34**, 223—230).—When ammonium benzoate is fed to normal persons, there is diuresis with increase in the ammonia content; urines originally giving abnormal reactions due to drugs quickly revert to normal reaction. Hippuric acid output was first increased, and then unchanged benzoic acid appeared.

Chemical Abstracts.

Chemical changes during the life cycle of the tent caterpillar (*Malacosoma americana*, Fab.). I. Moisture and fat. II. Nitrogen and its relation to moisture and fat. W. Rudolfs (J. N.Y. Entomol. Soc., 1926, **34**, 249—256, 319—330).—The moisture content is lowest in the newly hatched larvæ and highest during the third to fifth larval instars. The fat content is lowest at hatching and highest when the larvæ have just pupated. The egg-mass contains 13% of nitrogen, and the growing larva 10·2% (average), decreasing from hatching to the last instar. The composition of the egg-mass was investigated in detail. Chemical Abstracts.

Intracellular oxidation-reduction potential. L. Rapkine and R. Wurmser (Proc. Roy. Soc., 1927, B, **102**, 128—137).—Micro-injection of indicators into the cells of the salivary glands of *Chironomus* or *Calliphora* larvæ or into the oocytes of the sea-urchin or of the star-fish shows that cytoplasm and nucleus are at p_H 7·2 and r_H 19—20. In the case of *Spirogyra* the p_H is 6 and r_H is 14—16. Injection of dextrose, lævulose, sodium succinate, and sodium pyruvate into the cells of the salivary gland of *Chironomus* does not change the r_H.

W. O. Kermack.

Effect of cold on animals. I. Chemical changes in the blood. S. Yamaguchi (J. Orient. Med., 1926, **5**, No. 6, 71).—When the body temperature of rabbits cannot be maintained, there is a decrease in the blood carbon dioxide, ammonia, urea, and amino-acids, and an increase in the dextrose, acetone, and lactic acid. Chemical Abstracts.

Behaviour of acetoacetic acid in the organism, compared with that of ethyl acetoacetate and ethyl sodioacetoacetate. E. Pace (Arch. Farm. sperim., 1927, **43**, 145—162).—In the frog, ethyl acetoacetate exerts a depressing action on the central nervous system, a dose of 0·05—0·06 g. causing temporary paralysis, and one of 0·1 g. death, with a frog weighing 20 g. Sodium acetoacetate produces in the frog nothing more than a slight torpor, even when 0·3 g. is administered to a frog of 20 g. The action of ethyl sodioacetoacetate on the frog is similar to, but less intense than, that of ethyl acetoacetate, 0·15 g. causing paralysis and 0·25 g. death. Although the elimination of these compounds from the organism occupies 24—36 hrs., the duration of the paralysis is only 2—5 hrs.

In the rabbit, ethyl acetoacetate has a weak depressing action and also induces albuminuria; the compound is completely decomposed in the organism, and the urine contains acetone and acetoacetic acid and a slightly increased proportion of ammonia, but no alcohol. Sodium acetoacetate produces no marked effects; it partly decomposes giving acetone and partly passes unchanged into the urine, which shows also increased excretion of ammonia. Ethyl sodioacetoacetate gives no acetone but is eliminated as sodium sodioacetoacetate, the alkyl group being completely oxidised in the organism; albuminuria and increase in the ammonia of the urine are also observed. T. H. Pope.

Pharmacological action of diaminoacetone. J. H. Wadia (J. Pharm. Exp. Ther., 1927, **31**, 481—483).—Diaminoacetone is pharmacologically almost inert. Following subcutaneous injection into the guinea-pig about 17% of the amount injected is excreted unchanged. E. A. Lunt.

Specific action of ketonic substances on respiration. K. Gollwitzer-Meier (Arch. exp. Path. Pharm., 1927, **125**, 278—286).—β-Hydroxybutyric acid and acetoacetic acid do not appear to influence respiration apart from their effect on the p_H of the blood. Acetone seems to have a specific stimulating action on the respiratory centre. W. O. Kermack.

Mechanism of the action of iodides on nitrogen metabolism. G. P. Grabfield, C. Gray, B. Flower, and E. Knapp (J. Clin. Invest., 1927, **4**, 323—329).—Increase (27%) in the nitrogen excretion of dogs follows the subcutaneous injection of sodium iodide without an increase in the sulphur excretion or change in the fluid intake and urine output.

Chemical Abstracts.

Blood-fat variations after iodine administration to rabbits. W. Büssem (Arch. exp. Path. Pharm., 1927, **126**, 63—76).—Intravenous injection into rabbits of large amounts of an iodine solution (Pregl's "septoiodine") results in considerable increases in the neutral blood-fat and the free blood-cholesterol. The increase in the latter is most marked a few hours after the injection and usually the value soon returns to the original level. An organic iodine preparation ("Jodisan-Bayer") gives similar results. Small doses of iodine injected intravenously cause a fall in the neutral blood-fat but a rise in the free blood-cholesterol. After the administration *per os* of a dose of thyroxine (0·6 mg.) there is a temporary small fall in the neutral fat and a corresponding rise in the free cholesterol of the blood. A. Wormall.

Detoxication of nitrites. E. Hesse (Arch. exp. Path. Pharm., 1927, **126**, 209—221).—Animals poisoned by sodium nitrite are protected by administration of a mixture of a suitable phenol and iron salt, such as orcinol and ferric chloride or guaiacol and Prussian-blue. This effect is due partly to the formation of an insoluble compound between the iron and the nitrosophenol which is produced and partly by the action of the phenol in inhibiting the production of methæmoglobin by the nitrite.

W. O. Kermack.

Fluid and chloride exchange between blood and cells after administration of theophylline. K. O. Möller (Arch. exp. Path. Pharm., 1927, **126**, 143—158).—Independently of its action on the kidneys theophylline causes water and chlorides to pass from the tissues into the blood.

W. O. Kermack.

Sulphate diuresis and combined sulphate–theophylline diuresis. K. O. Möller (Arch. exp. Path. Pharm., 1927, **126**, 159—179).—Intravenous administration of sodium sulphate has a marked diuretic action and lowers the concentration of chlorides in the blood. Simultaneous administration of theophylline and sodium sulphate causes a much more marked diuresis and a much larger excretion of chlorides than does either separately. The excretion of sodium sulphate administered intravenously is markedly increased by the administration of theophylline. W. O. Kermack.

Action of theophylline on the excretion of chlorides and water. K. O. Möller (Arch. exp. Path. Pharm., 1927, **126**, 180—203).—The essential action of theophylline on the kidneys is to cause an increase in the excretion of chlorides. This is accompanied by an increase in the excretion of water dependent on the amount of water present in the organism. W. O. Kermack.

Activity of heart-specific glucosides of the second order. P. Haupstein (Arch. exp. Path. Pharm., 1927, **126**, 121—128).—Glucosides acting on the heart are divided into two groups, the first containing the glucosides of *Digitalis purpurea*, whilst the second group contains all the others. The lethal doses for rabbits of *Adonis* glucoside I, *Adonis* glucoside II, scillarin, *Convallaria* glucoside, and "*g*-strophanthin" have been determined, using intravenous injection, slow and rapid intravenous infusion, subcutaneous injection, and introduction into the stomach. With intravenous injection it is found that the potency (reciprocal of the lethal dose) increases from *Adonis* glucoside I to "*g*-strophanthin" in the order given, and that the time between the injection and death decreases in the same order. The action of these drugs on the heart and the absorption of the glucosides after subcutaneous injection and oral administration are discussed.

A. Wormall.

Velocity of action of various narcotics. L. Lendle (Arch. exp. Path. Pharm., 1927, **125**, 287—300).—The rate of action of various narcotics has been determined by a new method. No relation appears to exist between the reaction time and the velocities of diffusion of these compounds *in vitro*.

W. O. Kermack.

Comparative pharmacology of certain trialkyl- and dialkyl-barbituric acids. A. W. Dox and A. M. Hjort (J. Pharm. Exp. Ther., 1927, **31**, 455—472).—A comparison has been made, mainly on mice, of numerous dialkyl and trialkyl derivatives of barbituric acid with particular reference to minimum anæsthetic dose and minimum lethal dose. Of the dialkyl derivatives studied 5-ethyl-5-*iso*butyl-, 5-ethyl-5-*n*-butyl-, 5-ethyl-5-*iso*amyl-, and 5-ethyl-5-hexyl-barbituric acids are most suitable as hypnotics, and of the trialkyl series studied only 1-methyl-5-ethyl-5-*iso*amylbarbituric acid is suitable.

E. A. Lunt.

Elimination and toxicology of veronal. G. Sensi (Annali Chim. Appl., 1927, **17**, 447—456).—Determinations made by the author's method (this vol., 173) show that from 70 to 85% of the veronal administered to dogs is eliminated in the urine. The extent of the elimination depends on the method of its introduction into the organism, and on the quantity and solubility of the compound administered, and also varies with different animals. Animal metabolism undoubtedly exerts a destructive action on veronal, and putrefaction of the organs results in gradual disappearance of the drug; the nature of the resultant products is unknown. These results contradict those of Ipsen (Wien. Med. Wochenschr., 74, 2025). In toxicological cases, veronal is best sought in the urine and kidneys. T. H. Pope.

Alkaloid trichloroacetates. Use of trichloroacetic acid in toxicology. II. Detection of alkaloids in viscera. M. G. Florence (Bull. Soc. chim., 1927, [iv], **41**, 1242—1244).—Small amounts of alkaloids in viscera and in other organic matter may be isolated by extraction with a 20% aqueous solution of trichloroacetic acid at 35°. The filtrate from the coagulated protein is extracted with light petroleum to remove neutral substances, basified, and re-extracted separately with different solvents to remove the alkaloids. A partial separation of the latter is obtained by this method. The method has been applied to the detection of alkaloids in milk, blood, and the viscera of poisoned animals; in some cases the recovery amounts to 91%. G. A. C. Gough.

Pharmacological action of certain quinine derivatives. W. E. Dixon and P. De (J. Pharm. Exp. Ther., 1927, **31**, 407—432).—Quitenine, *iso*propylhydrocupreine, benzoyl*iso*propylhydrocupreine, *iso*amylhydrocupreine, benzoyl*iso*amylhydrocupreine, eucupinotoxin, *iso*octylhydrocupreine, and allylhydrocupreine have been compared with quinine, with reference to their action on *Paramœcia*, ciliary movement, isolated plain and striated muscle, isolated frog's heart, red blood-corpuscles, and as local anæsthetics. The most toxic of the substances examined is eucupinotoxin, which causes acute œdema on intravenous injection. The local anæsthesia produced by these drugs is due to their action on the nerve endings.

E. A. Lunt.

Blood-gases in strychnine poisoning. W. Ludwig and H. Ebster (Arch. exp. Path. Pharm., 1927, **126**, 245—254).—Decrease of oxygen in the blood during strychnine poisoning is attributable to the paralysis of the respiratory system. Strychnine has no effect *in vitro* on the blood dissociation curves of oxygen or carbon dioxide. W. O. Kermack.

Action of ergotamine ("gynergen") on the blood-sugar level in rabbit and man. W. Seidel (Arch. exp. Path. Pharm., 1927, **125**, 269—277).—Administration of ergotamine tartrate lowers the blood-sugar but the duration of the hypoglycæmia is too short to be of therapeutic value in diabetes.

W. O. Kermack.

Physiological antagonism between calcium ions and ergotamine. R. Agnoli (Arch. exp. Path. Pharm., 1927, **126**, 222—234).—Ergotamine exercises an inhibitory action on the heart and the smooth muscle in the absence of calcium ions but this effect disappears in their presence.

W. O. Kermack.

Chemotherapy. II. Internal antisepsis by means of sulphato-compounds. M. Coplans and A. G. Green (J. Pharm. Exp. Ther., 1927, **31**, 433—443; cf. this vol., 172).—Preliminary experimental evidence is cited for the use of sulphato-green, sulphato-violet, and their leuco-compounds as internal antiseptics by virtue of the generation by hydrolysis, *in vivo*, from such substances of basic compounds with a bactericidal action. This is due to the relative instability of the sulphato-group in the side-chain of these compounds, in comparison with the stability of the sulphonic groups attached to the nucleus in the ordinary triphenylmethane series of acid-greens and acid-violets.

E. A. Lunt.

Action of caffeine on micro-organisms. G. B. Zanda (Arch. Farm. sperim., 1927, **43**, 277—288).—In the proportion of 1 g. per 100 c.c., caffeine prevents putrefaction of albumin solutions and destroys or inhibits the development of pathogenic organisms.

T. H. Pope.

Pharmacological action of some compounds related to camphor. I. J. Ischikawa (Arch. exp. Path. Pharm., 1927, **126**, 41—47).—ω-Aminopinane, ω-aminopinene, and *r*-homocamphenilone have very little antiseptic action against *B. coli*, but with Metschnikoff's *vibrio* the antiseptic value is more marked and is greatest in the case of ω-aminopinane. The effect of these substances on the isolated frog's heart has been determined. A. Wormall.

Germicidal effect of staining solutions. G. A. Eckfeldt and S. A. Koser (Stain Tech., 1927, **2**, 109—114).—Gentian-violet, crystal-violet, and carbol-fuchsin generally destroy the majority of non-spore-forming bacteria and yeasts in cover-slip preparations. Non-spore-forming organisms never survive the Gram staining process. Methylene-blue stains exert very little, if any, germicidal power and " Indian ink " is entirely without action.

H. W. Dudley.

Effect of neutral-red preparations on *Paramœcium caudatum*. C. N. Wilson (Stain Tech., 1927, **2**, 115—123).—Various commercial samples of this dye varied in physical properties and toxicity to *Paramœcium* owing to impurities. Neutral-red was toxic in a concentration of 1 : 100,000.

H. W. Dudley.

Influence of sodium acetate, borate, citrate, and phosphate on the activity of pancreatic amylase. H. C. Sherman, M. L. Caldwell, and J. E. Dale (J. Amer. Chem. Soc., 1927, **49**, 2596—2598).—In presence of 0·05*M*-sodium chloride and 0·004*M*-sodium borate, citrate, or phosphate, for ½ hr. periods at 40°, pancreatic amylase exerts its optimum activity at p_H 7·0—7·2. These activities are the same in presence of the citrate or phosphate, and slightly less in presence of borate or acetate, but this is probably due to a lowering of the buffering effect rather than to specificity of the acetate or borate ions. In presence of 0·05*M*-sodium chloride, the activity is independent of the concentration of the phosphate from 0·0005*M* to 0·05*M*, and of the borate from 0·001*M* to 0·01*M*, provided optimal p_H is maintained. Under the latter condition, the activity in starch solutions containing 0·05*M*-sodium chloride is unaffected by phosphate. It is concluded that acetate, borate, citrate, and phosphate have no marked specific effect on the enzyme.

F. G. Willson.

Human fructosediphosphatase. II. E. Forrai (Biochem. Z., 1927, **189**, 155—158).—Saline extracts of human liver, muscle, and kidney contain fructosediphosphatase, and after inactivation by heating are not reactivated by addition of insulin. Insulin has no effect on the hydrolysis *in vitro* of fructosediphosphoric acid by such extracts.

P. W. Clutterbuck.

Enzymic synthesis of protein. P. Rona and F. Chrometzka (Biochem. Z., 1927, **189**, 249—264).—The formation of sparingly soluble products by the action of pepsin on concentrated aqueous solutions of protein decomposition products at p_H 4—5 or by the action of trypsin at p_H 5·5 as reported by Wasteneys and Borsook (A., 1925, i, 97, 102, 472, 865) is completely confirmed, but the conclusion of the latter that this represents synthesis of protein is contested, the sparingly soluble products being formed in the case of pepsin by deamination and of trypsin by further hydrolysis of the substrate.

P. W. Clutterbuck.

Separation of trypsin and enterokinase by ultrafiltration. H. Bechhold and L. Keiner (Biochem. Z., 1927, **189**, 1—17).—Enterokinase is completely retained by a 4% acetic acid–collodion membrane, whilst trypsin still passes even a 10% membrane. Addition of the filtrate to the residue results in complete reactivation. The kinase particles must be greater than those of albumin or hæmoglobin, and about equal to those of glutin, whereas trypsin is extremely finely dispersed (semi-colloid). Neutralisation or making faintly alkaline with potassium hydroxide, but not with ammonia, increases the dispersion of the kinase. Kinase obtained by ultrafiltration contains proteins but is free from ash, carbohydrates, and protein decomposition products. The kinase and protein fraction is, by weight, 2·8% of the crude trypsin. Trypsin ultrafiltrates are proteolytically completely inactive, whereas the kinase fraction retains about 16% of the original activity and this "residual activity" cannot be reduced by exhaustive washing with water, 0·05*N*-ammonia solution, or with 0·01% hydrogen chloride solution. Separated trypsin is completely destroyed by keeping for 2·5 days, but the kinase and the trypsin which gives its residual activity retain their activity completely for at least 8 days. Addition of albumin inhibits tryptic activity and its removal by ultrafiltration leads to reactivation. Tryptic activity cannot be reduced by albumin, however, below the value of the residual activity (16%) and the residual activity of the kinase is not affected by addition of albumin. There is, therefore, no dynamic equilibrium between kinase and trypsin, but a part of the trypsin is free and removable by ultrafiltration, whilst 16% is bound to the kinase and cannot be detached either by ultrafiltration or by albumin. The inhibitory action of albumin is not due to any power to adsorb trypsin.

P. W. Clutterbuck.

Philothion. II. G. Rossi (Zymologica, 1927, 2, 105—115).—Experiment shows that the hydrogenation of sulphur by extracts of brewers' yeast, and of horse's liver and kidneys, at 40° (cf. Biochem. Terap. sperim., 1924, 351) does not take place if these extracts are previously heated at temperatures which enzymes are unable to withstand. The evolution of hydrogen sulphide observed by Abelous and Ribaut when such extracts, after being heated to boiling, act on sulphur at 40° (A., 1904, i, 704) either results from the insufficiency of the heating or represents the liberation of gas formed during the heating and adsorbed by the constituents of the extracts.

T. H. Pope.

Metabolism of yeast. O. Warburg (Biochem. Z., 1927, **189**, 350—353).—Commercial bakers' yeast respires 8—10 times as strongly as pure laboratory cultures, the respiration being a property not determined by the type of yeast but one arising during manufacture and decreasing again under other conditions of growth.

P. W. Clutterbuck.

Action of carbon monoxide and nitric oxide on respiration and fermentation. O. Warburg (Biochem. Z., 1927, **189**, 354—380).—Regarding iron as the respiratory enzyme, its distribution between oxygen and carbon monoxide is mathematically and experimentally investigated. It is shown that the mechanisms of fermentation and respiration are related processes. The disturbances of such distribution by respiration and irradiation are examined. The distribution of hæmoglobin between oxygen and carbon monoxide shows that hæmoglobin is related to but not identical with the respiratory enzyme. Cytochrome does not combine with carbon monoxide. Carbon monoxide inhibits the rate of multiplication of yeast cells and fermentation increases more slowly in carbon monoxide than in nitrogen, but with the same number of cells the rate is the same. Carbon monoxide does not inhibit formation of lactic acid or alcoholic fermentation. Nitric oxide forms a dissociating compound with the fermentation enzyme but with yeast cells it has also an irreversible side-reaction whereby cells are killed, the more quickly the higher the temperature. This side-reaction is not obtained with tumour cells (cf. A., 1926, 434, 1277).

P. W. Clutterbuck.

Biochemical conversion of oximinopyruvic acid into alanine. K. Maurer (Biochem. Z., **189**, 216—219).—Pyruvic acid oxime is reduced in a fermenting sugar solution to alanine, identified as the α-naphthylcarbimide and as the benzoyl derivative. A control experiment indicated that the alanine did not arise from yeast protein during autolysis.

P. W. Clutterbuck.

So-called co-enzyme of alcoholic fermentation. A. J. Kluyver and A. P. Struyk (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 569—575).—Theoretical. The so-called co-enzyme of zymase is considered to be a complex with a number of factors each essential to the alcoholic fermentation of hexoses by zymase: (1) with an introductory hydrogen acceptor such as acetaldehyde which, when Harden's technique (A., 1917, i, 501) is employed, will reactivate washed zymase, (2) with hexosephosphate which is the missing factor when Buchner and Haehn's technique (A., 1910, i, 648) is employed, (3) with antiprotease when Meyerhof's technique (A., 1919, i, 57) is employed. The restoration of the activity to inactivated zymase as prepared by Meyerhof and thought by him to be due to the existence of a widely distributed co-enzyme is due to the protective action exerted on the zymase by the preferential reaction of the proteolytic enzymes, always present, with smaller protein complexes than those usually associated with the zymase. Thus the partial hydrolysate from inactivated zymase acts as a co-enzyme for unhydrolysed inactivated zymase.

E. A. Lunt.

Modifications in the course of alcoholic fermentation by the action of the oscillating electromagnetic field on yeast. E. Benedetti (Atti R. Accad. Lincei, 1927, [vi], 5, 1029—1034).—The fermentative activity of yeast, exposed to the action of an oscillating electromagnetic field, is first diminished to a minimum, then increased, and again diminished to a second minimum.

T. H. Pope.

Poisonous action of quinine compounds on the power of fermentation of living yeast. P. Rona and H. W. Nicolai (Biochem. Z., 1927, **189**, 331—347).—A method is given for investigating separately the effect of the concentration of alkaloid and of the duration and p_H of the reaction on the poisoning of fermentation by quinine compounds. Poisoning was maximal after 30—60 min. The optimal poisoning effect was obtained at the p_H at which the alkaloidal base was set free. This p_H for vucine and eucupine is 4·4—5·3, and these substances, in distinction from quinine and optoquin, have considerable toxic action at this p_H. P. W. Clutterbuck.

Action of electric current on proteins and enzymes. V. Sadikov (Bull. Acad. Sci. U.R.S.S., 1927, 5—6, 385—396).—When an electric current is passed through dilute sodium hydroxide solution in which protein is suspended or dissolved, proteolysis appears to take place. Fats and polysaccharides are also decomposed under similar conditions. A whole animal, *e.g.*, a frog or mouse, immersed in sodium hydroxide solution through which a current is passed is largely dissolved. The effects of an electric current on bacteria, diphtheria toxin, and enzymes are also described. W. O. Kermack.

Chemical analysis of the tubercle bacillus. T. B. Johnson and R. D. Coghill (Amer. Rev. Tuberculosis, 1927, **15**, 494—499).—All cellular changes caused by autolysis must be minimised; heating is avoided, and fat is extracted with cold ether. Attempts to isolate a globulin fraction were unsuccessful. Most of the protein is soluble in 0·5% sodium hydroxide solution, although insoluble in water, but this fraction gives a low tuberculin reaction. The cold-water extracts contain a potent tuberculin. Chemical Abstracts.

Growth of the typhoid bacillus. A. Doskočil (Biochem. Z., 1927, **189**, 314—321).—Ammonium salts and amino-acids serve as a source of nitrogen for *B. typhosus* but amido- and imido-nitrogen (except of bile salts) is not generally accessible. Dextrose, lactic acid, the carbon chain of alanine, asparagine, and glutamic acid serve as a source of carbohydrate but not so the carbon chains of tyrosine, lysine, and glycine. The alanine chain probably passes through the stages of lactic, pyruvic, and glyoxylic acids. The bacillus is found in man to the greatest extent in the small intestine, blood, and gall-bladder. In late summer it thrives greatly in streams in virtue of the ammonium salts of organic acids arising from decaying vegetation. P. W. Clutterbuck.

Bacterial proteins. Presence of alcohol-soluble proteins in bacteria. K. Goadby (Proc. Roy. Soc., 1927, B, **102**, 137—142).—Bacteria suspended in sodium chloride solution (0·85%) when shaken with ether containing benzoyl chloride for 1—3 days are deprived of the carbohydrate material, which passes into the ethereal solution. The bacteria washed with acetone and dried are extracted at 37° with sodium chloride solution (0·85%) for 24 hrs., when some protein is removed. They are then suspended in 70% alcohol for 24 hrs. at 37°, which extracts a protein in the case of a large number of bacteria. The protein gives most of the usual protein reactions, and is similar to alcohol-soluble proteins from the seeds of cereals. W. O. Kermack.

Imitation of organic forms by means of sodium stearate. L. A. Herrera (Atti R. Accad. Lincei, 1927, [vi], 6, 18—22; cf. A., 1926, 244, 435; this vol., 279).—When added to a dilute solution of stearic acid in ordinary petrol, drops of 14% sodium hydroxide solution coloured with soap-black simulate a number of organisms, both in form and in their pulsations and changes of shape. The results are regarded as indicative of the importance of the fatty acids in morphogenesis. T. H. Pope.

Blood-sugar. VIII. Blood-sugar and -phosphorus curves. VI. Adrenaline. H. K. Barrenscheen, A. Eisler, and L. Popper (Biochem. Z., 1927, **189**, 119—124).—After subcutaneous and intravenous injection of adrenaline, the inorganic phosphate of blood and the urinary phosphate are decreased, the latter considerably, the effect being the reverse of that due to insulin (cf. A., 1926, 1270). P. W. Clutterbuck.

Diabetes and the action of insulin. XI. The organ secreting glycæmin. XII. Direct proof of the secretion of insulin by the pancreas. S. Dietrich (Arch. exp. Path. Pharm., 1927, **125**, 326—335, 336—342; cf. this vol., 795).—XI. The isolated frog's liver treated with ergotamine yields dextrose under the action of glycæmin but not of adrenaline. From this and other evidence it is concluded that the liver is the only source of glycæmin.

XII. After subcutaneous administration of dextrose or after vagus stimulation, insulin may be detected in the pancreatico-duodenal vein when it cannot be found in the carotid blood. W. O. Kermack.

Action of insulin. I. Inhibition of phosphate excretion by insulin. H. K. Barrenscheen and R. Berger (Biochem. Z., 1927, **189**, 302—307).—The power of the kidney of a mouse poisoned with insulin to hydrolyse sodium hexosediphosphate is considerably less than that of a normal mouse. This inhibition of kidney phosphatase possibly explains the decreased urinary phosphate excretion under the action of insulin. P. W. Clutterbuck.

Insulin and fructosephosphoric acid. E. Forrai (Biochem. Z., 1927, **189**, 150—154).—Insulin has no action on the hydrolysis, *in vitro*, of fructosediphosphoric acid by the enzymes of muscle pulp, blood, or liver, whilst, in rabbits, injection of fructosediphosphoric acid does not alleviate hypoglycæmic convulsions. P. W. Clutterbuck.

Insulin and fat metabolism. J. Hepner and O. Wagner (Biochem. Z., 1927, **189**, 322—330).—The effect of insulin on the liver-fat in rats, dogs, and guinea-pigs is investigated and the decrease in iodine value obtained under insulin is regarded as due to decreased desaturation of fat, it being assumed that fat transport from the periphery is inhibited by insulin. P. W. Clutterbuck.

Absence of hypoglycæmia after intraperitoneal administration of insulin to well-fed rabbits. F. M. Hoskins and F. F. Snyder (J. Biol. Chem.,

1927, 75, 147—155).—Intraperitoneal administration of insulin causes hypoglycæmia in fasting but not in well-fed rabbits. It is thought that the difference is due to the passage of the insulin through the liver when administered by the intraperitoneal route.
C. R. Harington.

Thyroxine in intermediate metabolism. A. Simon (Biochem. Z., 1927, 189, 265—269).—Addition of thyroxine to rabbit's liver pulp generally caused increased (11—247%), but sometimes decreased acetaldehyde formation, and glycogen determinations suggest that this change is due to the decomposition of carbohydrate. P. W. Clutterbuck.

Antimony trichloride as a possible quantitative reagent for vitamin-*A*. F. Wokes and S. G. Willimott (Analyst, 1927, 52, 515—524).—The reaction between antimony trichloride and cod-liver oil is a chemical one with a temperature coefficient of 2. It is probably of a condensation type and may be retarded by dehydration of the solvents. The conditions suggested for the test are: 2 c.c. of a decanted solution of antimony trichloride (recrystallised from chloroform) in anhydrous chloroform (concentration 26 or 27% wt./vol.) mixed in a ½ in. cell with a freshly-prepared solution of oil in chloroform (dried over calcium chloride), of such a concentration that 0·1—0·3 c.c. is used. The colour is read 30 sec. after mixing, in Lovibond blue units (the reading should be below 18) at 16°, a divergence of more than 1° requiring a correction. Since the blue colour rapidly changes to yellow, red, and reddish-brown, the time factor is important. D. G. Hewer.

Reaction of fatty extracts of certain organs with the antimony trichloride test for "vitamin-*A*." W. H. Wilson (Biochem J., 1927, 21, 1054—1058).—By this colour reaction it is shown that fatty extracts from the human liver may contain 25 times as much vitamin-*A* as a good sample of cod-liver oil. The intensity of the reaction varies within wide limits in different livers and may in some cases be no more than 1/250 of the maximum recorded. The substance responsible for the colour reaction is present in considerable amount in the liver at birth, but is not present in the placenta. The ether extract of livers of healthy animals slaughtered for food was found to contain from 6 to 12·5 times the amount of vitamin-*A* present in cod-liver oil. S. S. Zilva.

Vitamin-*A* of irradiated milk. G. C. Supplee and O. D. Dow (J. Biol. Chem., 1927, 75, 227—239).—Milk (dried or fresh) which has been irradiated with ultra-violet light in order to induce in it antirachitic activity, has neither suffered any loss of vitamin-*A* nor acquired toxic properties. C. R. Harington.

Separation of a substance from oils which inhibits destruction of vitamin-*A* by ferrous sulphate. H. W. Estill and E. V. McCollum (J. Biol. Chem., 1927, 75, 157—162).—On mixing a pyridine solution of lithium chloride with a light petroleum solution of cod-liver oil, a precipitate was obtained, which, on stirring with light petroleum, could be separated into a light and a heavy portion. Both fractions, after removal of lithium chloride, were free from vitamin-*A* and -*D*, but the light fraction, which is regarded as being perhaps vitamin-*E*, when added to the diet containing ferrous sulphate (J. Amer. Med. Assoc., 1927, 88, 1047) prevented the occurrence of ophthalmia. C. R. Harington.

Relation of inorganic dietary constituents to production of ophthalmia in rats. J. H. Jones (J. Biol. Chem., 1927, 75, 139—146).—The diet described by McCollum and others (J. Biol. Chem., 1922, 53, 313) leads to ophthalmia in rats only when it is made up at long intervals, and in this case the rapidity of appearance of the ophthalmia is proportional to the amount of ferrous sulphate in the diet; a catalytic effect of the latter salt on the oxidation of vitamin-*A* is therefore the probable explanation of the results. C. R. Harington.

Multiple nature of vitamin-*B*. H. C. Sherman and J. H. Axtmayer (J. Biol. Chem., 1927, 75, 207—212).—Autoclaving caused destruction of almost all the antineuritic activity of bakers' yeast; a mixture of such material with ground whole wheat gave, however, better growth than an equal amount of fresh yeast or of whole wheat. Vitamin-*B* is therefore divided into vitamin-*F* (heat-labile antineuritic) and vitamin-*G*, both factors being necessary for growth. On this basis, whole wheat is richer in vitamin-*F* than in vitamin-*G*, and the reverse is true of milk. C. R. Harington.

Extraction of vitamin-*B* from wheat germ. E. V. McCollum and H. D. Kruse (Amer. J. Hyg., 1926, 6, 197—200).—The efficiency of 95% alcohol containing 1% of various organic and inorganic acids or salts as an extractive for vitamin-*B* with minimal contamination by other substances was examined. The best results were obtained with alcohol containing tannic or gallic acid.
Chemical Abstracts.

Relation between the vitamin-*B* content of the ration eaten [by cows] and of the milk produced. S. I. Bechdel and H. E. Honeywell (J. Agric. Res., 1927, 35, 283—288).—Three cows were fed for more than 2 yrs., throughout their growth period, on a ration proved to be decidedly deficient in vitamin-*B* by experiments with rats. The milk from these cows, fed to rats as a supplement to a basal ration free from vitamin-*B*, was equal to milk from normally fed cows in supplying the deficiency. It would appear that cows, and possibly other ruminants, possess the power to synthesise vitamin-*B* and are not dependent on its presence in the ration eaten.
C. T. Gimingham.

Effect of administration of active iron compounds on the course of avitaminosis in pigeons. P. M. Suski (Biochem. Z., 1927, 188, 459—464).—In pigeons on a polished rice diet, a daily dose of 5 mg. of active iron oxide prevented loss in weight but did not retard death. A daily dose of 50 mg. of unirradiated or irradiated ferrous sulphate retarded the fall in weight and the irradiated material also retarded death. Active iron carbonate acted unfavourably on the course of avitaminosis (cf. this vol., 382). P. W. Clutterbuck.

Nutrition. VIII. Comparative vitamin-*B* value of foodstuffs. Cereals. I. R. H. A.

Plimmer, J. L. Rosedale, W. H. Raymond, and J. Lowndes (Biochem. J., 1927, 21, 1141—1161).—The estimations were carried out on pigeons by administering diets containing various quantities of the foodstuffs tested mixed with other ingredients (rice or flour and fish-meal) free from vitamin-*B*. The percentage of the foodstuffs necessary for maintenance was taken as a standard. The following substances were investigated and are arranged in order of activity: dried yeast, wheat germ, marmite, bakers' yeast, bran, middlings, whole wheat flour, rye (whole), millet, dari, maize (kibbled), barley (whole), buckwheat, whole oats, Sussex ground oats, and oatmeal. The last three were protective in diets containing 95% of the substance, whilst in the case of dried yeast 4% was sufficient. Maize germ and maize gluten contained little of the vitamin. The quantities of some of the above substances required to enable the birds to rear their young were also ascertained. These were higher than those required for maintenance.

S. S. Zilva.

Experiments with Jansen and Donath's antiberiberi vitamin. C. Eykman (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 376—382).—Investigations with pigeons and cocks demonstrate that the vitamin isolated by Jansen and Donath (this vol., 382) has the power to prevent and to cure polyneuritis gallinarum. H. F. Gillbe.

Synthesis of antineuritic vitamin by yeast. G. L. Peskett (Biochem. J., 1927, 21, 1102—1103).—Yeast grown on a synthetic medium containing very little antineuritic vitamin and under conditions excluding bacterial contamination produced considerably more of the vitamin than the amount present in the medium. Synthesis is thus definitely established (cf. Hawking, this vol., 796). S. S. Zilva.

Alkali reserve and p_H in avitaminosis-*C*. G. Mouriquand, A. Leulier, and P. Sédallian (Compt. rend., 1927, 185, 551—553).—In avitaminosis-*C* (guinea-pigs) no lowering of the blood-p_H occurs, whilst the fall in alkaline reserve is slow and appears only after the 27th day. The scorbutic lesions are not a function of the acidosis. The development of experimental scurvy takes place in two stages. In the first, the predystrophic, typical osteohæmorrhagic manifestations are seen, whilst in the second, the dystrophic, loss of weight takes place together with a fall in the blood-iron, the cholesterol of the suprarenals, and the alkaline reserve. The two phases appear to exist in other diseases besides scurvy.

W. Robson.

Antiscorbutic fraction of lemon juice. VI. E. Hoyle and S. S. Zilva (Biochem. J., 1927, 21, 1121—1127; cf. Daubney and Zilva, A., 1926, 871).—The concentrated antiscorbutic fraction from lemon juice does not contain any manganese, but contains traces of iron, phosphorus, and sulphur. These elements of the active fraction behave on dialysis like the active principle. S. S. Zilva.

Vitamin-*D*. I. Activation of cholesterol. A. Jendrassik and A. G. Keményffi (Biochem. Z., 1927, 189, 180—190).—The view that ergosterol is the activatable substance is confirmed, but the authors disagree with the suggestions that the activity of irradiated cholesterol is due to ergosterol present merely as an impurity, and also that removal of this impurity gives a cholesterol which is no longer activatable. The authors suggest that provitamin can be re-formed from that part of the cholesterol which contains so-called water of crystallisation. By withdrawing the last traces of water from cholesterol the provitamin present is destroyed and the possibility of re-formation is lost, and the characteristic provitamin absorption bands between 280 and 300 μμ disappear. Fractionation of irradiated cholesterol with ethyl alcohol shows that cholesterol is only partly activated, but after removal of the active material an inactive substance is left which can always, under suitable conditions, be reactivated. The bromination experiments of Windaus could not be confirmed, reduction of the bromination product always giving an activatable cholesterol. The difference is supposed to be due to the fact that the authors, after bromination and reduction, treated their cholesterol with water to make possible the re-formation of provitamin. Windaus' result that boiling cholesterol with animal charcoal completely removes the activatable substance is confirmed.

P. W. Clutterbuck.

Antirachitic value of irradiated cholesterol and phytosterol. VIII. Activation of sterol fractions by ultra-violet irradiation. A. F. Hess and R. J. Anderson (J. Biol. Chem., 1927, 74, 651—657).—α-Sitosterol (when freshly prepared) was rendered strongly antirachitic by irradiation with ultraviolet light, whilst β- and γ-sitosterols, which had been purified by bromination and subsequent reduction, could not be so activated. C. R. Harington.

Photochemical production of vitamin-*D* from ergosterol. O. Rosenheim and T. A. Webster (Lancet, 1927, ii, 622—625).—The lowest protective dose of irradiated ergosterol (vitamin-*D*) for the rat is 0·0001—0·00005 mg. per day. The maximum activity was produced within 30 min. by the radiations of the mercury vapour lamp and remained constant up to 4 hrs.' irradiation, although decomposition of the ergosterol proceeded throughout this period. Probably, after a short initial period, the formation and destruction of the vitamin take place at the same rate, so that the activity remains constant until the ergosterol is exhausted. Ergosterol is activated by sunlight; this is significant in connexion with the known curative effect of sunlight in rickets.

H. W. Dudley.

Relation of vitamin-*E* to iron assimilation. N. Simmonds, J. E. Becker, and E. V. McCollum (J. Amer. Med. Assoc., 1927, 88, 1047—1050).—The death of rat-fœtuses by deficiency in vitamin-*E* is due to a crisis in their assimilation of iron. Ferrous sulphate (0·2% of the diet) is harmful, but not ferric citrate or wheat-germ oil. Liver contains much iron, and liver fats contain much vitamin-*E*.

Chemical Abstracts.

Manifestations of life in fruit and foliage and their detection by means of the potentiometer. F. Scurti and D. Cortese (Annali Chim. Appl., 1927, 17, 407—414).—All fruits, foliage, and vegetables contain well-defined electrical systems, which may be measured with the electrometer by immersing two platinum electrodes in two different tissues of the same plant or of the same organ. In such systems the *P.D.* varies greatly with the tissues connected, and any tissue may act as either positive or negative pole. The electrical potential is always greatest with the fresh material. T. H. Pope.

Chemical composition of plants in relation to photoperiodic changes. G. T. Nightingale (Wisconsin Agric. Exp. Sta. Res. Bull., 1927, No. 74, 1—63).—Tomato and salvia plants may store nitrate for subsequent conversion into other nitrogen compounds. Hemicellulose is utilised as a source of sugar. When there is no external supply of nitrogen or opportunity for carbohydrate synthesis, and reserve carbohydrates are depleted, there is decomposition of protein and increase in amino-acids, amide-nitrogen, and proteose-nitrogen. Salvia, unlike tomato, is limited in the assimilation of nitrate by a 7 hr. day, even although carbohydrate is available. Carbohydrates accumulated in the short-day plants. Plants subjected to a short photo-period gained more in total nitrogen than those subjected to a long photo-period. Chemical Abstracts.

Photosynthesis of naturally occurring compounds. I. E. C. C. Baly, J. B. Davies, M. R. Johnson, and H. Shanassy. **II.** E. C. C. Baly, W. E. Stephen, and N. R. Hood. **III.** E. C. C. Baly and J. B. Davies.—See this vol., 1040, 1041.

Photochemical formation of peroxides during oxygen transport by chlorophyll. H. Gaffron (Ber., 1927, 60, [*B*], 2229—2238).—Attempts to isolate peroxides of fluorescent dyes which are active in promoting transport of oxygen have been unsuccessful. Acceptor peroxides are, however, produced during the photo-oxidation of aliphatic amines in the presence of chlorophyll. If a solution of chlorophyll in amylamine is exposed to light and then placed in the dark, the quantity of peroxidic oxygen is approximately equal to the amount of molecular oxygen absorbed. This oxygen is quantitatively evolved when a catalyst, such as manganese dioxide, is added to the darkened solution; it can be determined quantitatively by the iodometric method. Photochemical action depends greatly on the solvent used, increasing more than one hundredfold when solutions in acetone or pyridine are used in place of aqueous solutions; the absorption of oxygen ultimately reaches 2 mols. for each mol. of primary or secondary amine. Tertiary and aromatic amines are more stable after illumination; a proportion of the oxygen is evolved spontaneously when the solution is placed in the dark, but this can be reduced to 2—3% by dilution of *iso*amylamine with dioxan. Addition of a molecular proportion of water to *iso*amylamine causes only one half of the absorbed oxygen to be subsequently removable; further addition of water up to 50% has no further effect and the peroxide produced is completely stable (hence probably hydrogen peroxide). In di*iso*butylamine and in ethylamine dissolved in dioxan photo-oxidation proceeds much more slowly and 65% and 50% of the absorbed oxygen respectively is subsequently recoverable as such. H. Wren.

Aspect of the biochemistry of sugars. P. A. Levene (Nature, 1927, 120, 621).—Polemical against Robinson (this vol., 960). A. A. Eldridge.

Biochemistry of the sugars. R. Robinson (Nature, 1927, 120, 656).—A reply to Levene (see preceding abstract). A. A. Eldridge.

Correlation of chemical composition with hardiness in brambles. R. V. Lott (Missouri Agric. Exp. Sta. Res. Bull., 1926, No. 92, 1—22).—The hardiness is related to the percentage of bound water, as determined by the dilatometer method. The correlation coefficient between the bound water and pectin is 0·67±0·06, and between the protein-nitrogen and bound water 0·60±0·07.
Chemical Abstracts.

Hydrogen-ion concentration of plant tissues. I. Method. J. Small. **II. Flowering and other stems.** M. W. Rea and J. Small (Protoplasma, 1926, 1, 324—333, 334—344).—I. A microcolorimetric indicator method is described.

II. The plant families are classified according to the reaction of the tissue of the young flowering stem.
Chemical Abstracts.

Adaptability of the quinol electrode to the determination of p_H in expressed plant saps. M. Domontovich (Nauch. Agron. Zhur., 1925, 2, 700—712).—The results are in fair agreement with those obtained with the hydrogen electrode.
Chemical Abstracts.

Influence of reaction of culture medium on growth of strawberry plants. L. S. Morris and J. W. Crist (Mich. Agric. Exp. Sta. Tech. Bull., 1927, No. 77, 1—16).—The range for survival is p_H 4·0—8·0, for satisfactory growth 5·0—7·0, for optimal growth 5·7—6·0. Absorption of iron and aluminium was greater from the more acid solutions.
Chemical Abstracts.

Antagonistic influence of hydrogen and calcium on the development of *Saprolegnia*. M. F. Lilienshtern (Trav. Soc. Nat. Leningrad, 1925, 55, No. 3, 3—16).—Calcium (1—2% at p_H 3·6; 0·2% at p_H 4·6) neutralises the limiting influence of hydrogen ions. Chemical Abstracts.

Essential nature of aluminium and silicon for plant growth. A. L. Sommer (Univ. Calif. Pub. Agric. Sci., 1926, 5, 57—81).—Addition of aluminium (1 in 10^6) to culture solutions somewhat increased the yield of seed with peas, and the growth and yield of seed with millet. Addition of gelatinous silicic acid improved the growth of rice and millet.
Chemical Abstracts.

Action of rare-earth [and other] elements on plants. (Signa.) M. Arena (Rend. Acad. Sci. fis. mat. Napoli, 1927, [iii], 33, 37—39).—Small quantities of salts of uranium, zirconium, beryllium, cerium, tungsten, and rubidium stimulate the growth of roots in slips of *Alternanthera spathulata* in Pfeffer's solution. Ammonium molybdate has a feeble action, and vanadium oxychloride poisons the plant.
E. W. Wignall.

Effect of nutrient conditions on activity of oxidase and catalase. B. D. Ezell and J. W. Crist (Mich. Agric. Exp. Sta. Tech. Bull., 1927, No. 78, 1—24).—For lettuce, radish, and spinach, the correlation between catalase activity and growth was better than that between oxidase activity and growth, both being negative. CHEMICAL ABSTRACTS.

Influence of age on the composition of the wood of the maritime pine. M. H. PATY (Chim. et Ind., 1927, **18**, 204—210).—In a study of the variation of the composition of wood with the age of the tree, the three classes of compounds considered were pentosans, lignin, and celluloses. The first were determined by conversion into furfuraldehyde (and methylfurfuraldehyde) by hydrolysis, lignin by extraction of the wood with dilute sulphuric acid, total cellulose by chlorination. Pentosans and methylpentosans were found to reach a maximum at 5 years (10%) and then decrease slowly. Lignin showed a very slight continuous increase. α-Cellulose and total cellulose increased rapidly up to 20 years, then slowly. The content of oleoresins increased slowly but never exceeded 2%. The effect of tapping and of air-drying after cutting was also studied.

C. IRWIN.

Fruit-spur composition in relation to fruit-bud formation. G. F. POTTER and H. R. KRAYBILL (Proc. Amer. Soc. Hort. Sci., 1925, **22**, 146—150).—Similar carbohydrate : nitrogen relations in spurs are not always accompanied by similar degrees of fruit-bud formation. CHEMICAL ABSTRACTS.

Evolution of tannin in fruits. Kaki. E. BOTTINI (Annali Chim. Appl., 1927, **17**, 415—425).—The fruits of *Diospyros lycopersicon* and *D. kirakaki* contain considerable proportions of tannin and acids, and a small amount of reducing sugars, but no pectin. As the fruits mature, the tannin disappears almost entirely, the acids diminish in quantity, and appreciable amounts of sugars and of pectin are formed. The presence of ozone in the air favours the oxidation of the tannin and the formation of carbohydrates, but does not affect the organic acids, the pectin, or the colouring material. Formaldehyde, on the other hand, produces no change in the proportions of any of these constituents. A low temperature (1—2°) does not prevent the disappearance of the tannin or organic acids, but modifies sensibly the ripening process, diminishing the proportions of reducing sugars and of pectin. The results are explainable on the assumption that the gradual disappearance of the tannin during ripening is the result of the joint action of a condensing enzyme, which determines the formation of colouring matter, and an oxidising enzyme, which, as in the respiratory process, transforms the tannin into carbon dioxide and water.

T. H. POPE.

Decomposition of hexoses in plants. I. Zymase apparatus of seed. V. ZALESKI [with O. PISARSHEVSKI]. **II. Condition and activity of the zymase apparatus in seed.** V. ZALESKI [with L. NOTKINA] (Biochem. Z., 1927, **189**, 39—48, 101—113).—I. The view of Bodnár (cf. A., 1926, 438, 439) that pea-zymase requires for its activity the presence of an activator is confirmed. Boiled extract of peas, however, can be replaced by boiled extract of yeast or muscle, and extracts of yeast, pea, and muscle all accelerate alcoholic fermentation of pea-meal. The activator plays no rôle in the formation of hexosephosphates nor can it be replaced by any usual hydrogen donator or acceptor. Assumption of the existence of a zymase zymogen is unnecessary, the stimulatory action of oxygen on the alcoholic fermentation of pea-meal depending not on the conversion of zymogen into active zymase but on the liberation of the activator.

II. Further evidence is given in support of the authors' view that the increase of the activity of zymase during the first stages of germination of peas is due not to an increased formation of zymase nor to the oxidative conversion of zymogen into zymase, but to the formation of an activator which is also an unknown activator of the alcoholic fermentation of carbohydrates. P. W. CLUTTERBUCK.

Enzyme content of resting wheat grains. A. OPARIN and N. POSPELOVA (Biochem. Z., 1927, **189**, 18—25).—The enzyme content of resting seeds depends on the kind of seed and differs for each year of harvesting. Seeds which have lost their power to germinate still contain some catalase, peroxidase, and amylase. The annual variation in catalase content runs parallel with the variations in germinating power.

P. W. CLUTTERBUCK.

Galactoaraban of lupin seeds. A. HEIDUSCHKA and H. TETTENBORN (Biochem. Z., 1927, **189**, 203—207).—Potassium galactoaraban, $C_{16}H_{28}O_{14}$,KOH is prepared from seeds of *Lupinus luteus* by the method of Schulze, Steiger, and Maxwell (A., 1890, 283). Various preparations always gave the same specific rotation, mean $[\alpha]^{20}_{D}$ $+76{\cdot}98\pm1{\cdot}83°$, and the same *copper* salt, $C_{16}H_{28}O_{14}$,$CuSO_4$. Galactoaraban, when boiled with hydrochloric acid, gave considerable amounts of furfuraldehyde. Galactoaraban, $C_{16}H_{28}O_{14}$, appears to contain one molecule of galactose and two molecules of pentose.

P. W. CLUTTERBUCK.

Blackening of the pods of the broom, *Sarothamnus scoparius*, Wimm. H. SCHMALFUSS, H. BARTHMEYER, and H. BRANDES (Biochem. Z., 1927, **189**, 229—232).—The melanogen of *Sarothamnus scoparius*, Wimm. is identified as a pyrocatechol derivative. The pods blacken when sufficient oxygen penetrates the epidermis and chlorophyll-containing layer in which the melanogen is found, and this occurs either during drying of the pods or after injury of their cuticle. P. W. CLUTTERBUCK.

North American Sarraceniaceæ. Review. Nectar. J. S. HEPBURN. **Pitcher liquor.** F. M. JONES and J. S. HEPBURN. **Enzymes of the pitcher liquor. Chemistry of pitcher liquor.** J. S. HEPBURN and F. M. JONES. **Bacteriology of pitcher liquor.** J. S. HEPBURN and E. Q. ST. JOHN. **Absorption of nutrients in the pitchers.** J. S. HEPBURN, E. Q. ST. JOHN, and F. M. JONES. **Composition of tissues.** J. S. HEPBURN and E. Q. ST. JOHN. **Bibliography.** J. S. HEPBURN (Trans. Wagner Free Inst. Sci., 1927, **11**, 3—30, 31—33, 35—48, 49—68, 69—73, 75—83, 85—86, 87—91, 93—95).—The nectar of *Darlingtonia californica* and *Sarracenia flava* contains *d*-lævulose, and of *S. minor*, *S. sledgei*, *S. drummondii*, and *S. purpurea* a reducing sugar. The reaction towards litmus and p_H values of the pitcher liquor were investigated, and the behaviour of the proteases present was examined. The pitcher liquor did not contain reducing sugar, but hydrogen sulphide was sometimes present. The bacteria present in the open pitchers were able to use amino-acids, amides, and ammonium salts of organic acids as their sole source of carbon and nitrogen. The following data for the chemical composition of the pitchers (leaves) and rhizomes are recorded: moisture, crude fat, crude protein, crude fibre, ash (soluble and insoluble) and its alkalinity, and nitrogen-free extractives. CHEMICAL ABSTRACTS.

Production of nitrites by *Verticillium* in pure culture. J. DUFRÉNOY (Bull. Soc. Chim. biol., 1927, 9, 935—936).—Nitrite was detected in a culture medium, originally containing nitrate but no nitrite, after *Verticillium* (isolated in pure culture from apricot, plum, or cherry tree) had been grown on it for 15 days. W. O. KERMACK.

Isolation of the oil and alkaloids of stavesacre seed (*Delphinium staphisagria*). L. N. MARKWOOD (J. Amer. Pharm. Assoc., 1927, 16, 928—932).—Extraction of the seeds of *D. staphisagria* with light petroleum yields the alkaloid, delphinine, and an oil having d_4^{20} 0·891, n^{20} 1·462, acid value 92·8, iodine value (Hanus) 80·2, saponification value 190·0, acetyl value 12·8, and unsaponifiable matter 2·92%. The purification and crystallographic examination of the alkaloid are described. E. H. SHARPLES.

Ether-soluble substances of cabbage leaf cytoplasm. IV. Diglyceridephosphoric acid. H. J. CHANNON and A. C. CHIBNALL (Biochem. J., 1927, 21, 1112—1120; cf. this vol., 386).—From the products of hydrolysis of the diglyceridephosphoric acid with barium hydroxide an ether-insoluble fraction of lead salts was obtained which behaved like a mixture of salts from about equal parts of stearic and palmitic acids. The ether-soluble fraction of the lead salts from the unsaturated acids yielded hexabromostearic and tetrabromostearic acids on bromination, showing the presence of linolenic and linoleic acids in the original mixed fatty acids. Small quantities of oleic acid may have been present; arachidonic acid was absent. The greater part of the acids formed on hydrolysis were found in the unsaturated acid fraction. The name *phosphatidic acid* is assigned to the diglyceridephosphoric acid. S. S. ZILVA.

Glutelins. II. Glutelin of rice (*Oryza sativa*). D. B. JONES and F. A. CSONKA (J. Biol. Chem., 1927, 74, 427—431).—Rice endosperm differs from wheat endosperm (this vol., 799) in containing only one glutelin, which was prepared by extracting the rice with 0·2% sodium hydroxide and treating the extract with ammonium sulphate to 3% saturation. The preparation so obtained shows a higher content of nitrogen and certain differences in the nitrogen distribution as compared with the preparations of other workers. C. R. HARINGTON.

Glutelins. III. Glutelin of oats (*Avena sativa*). F. A. CSONKA (J. Biol. Chem., 1927, 75, 189—194).—Oat flour was extracted with 0·2% sodium hydroxide and the filtrate treated with ammonium sulphate to 10% saturation; the crude glutelin was purified by repeated dissolution in dilute sodium hydroxide and precipitation with alcohol and ammonium sulphate, the final yield being 1·9% of the flour; the material had its isoelectric point at p_H 6·45 and contained total N 17·53%, of which 13·46% was amide-N, 1·99% cystine-N, 15·30% arginine-N, 3·49% histidine-N, and 5·45% lysine-N. C. R. HARINGTON.

Globulins of rice (*Oryza sativa*). D. B. JONES and C. E. F. GERSDORFF (J. Biol. Chem., 1927, 74, 415—426).—Rice endosperm, on extraction with 5% sodium chloride, yielded 0·09% of a globulin coagulating at 74° and 0·07% of a second globulin coagulating at 90°. The residue from the sodium chloride extraction, on treatment with dilute sodium hydroxide, gave 2·4% of a glutelin. From rice bran there was obtained 2·88% of globulin, 0·13% of albumin, and no glutelin. Figures are given for the nitrogen distribution of the various proteins. C. R. HARINGTON.

Proteins of sesame seed, *Sesamum indicum*. D. B. JONES and C. E. F. GERSDORFF (J. Biol. Chem., 1927, 75, 213—225).—Fat-free sesame seeds were extracted with 10% sodium chloride solution. On heating the extract at 68° a precipitate was obtained, containing about 40% of ash (magnesium, sodium, potassium, and phosphorus); there were further isolated an α-globulin, coagulation temperature 95°, which could be crystallised from 2% sodium chloride, and a smaller amount of a β-globulin, coagulation temperature 84°. Figures are given for the nitrogen distribution of the various fractions. C. R. HARINGTON.

Nitrogenous components from the fruit of *Citrus grandis*, Osbeck, form. Buntan Hayat. Y. HIWATARI (J. Biochem. [Japan], 1927, 7, 169—173).—From 27 kg. of macerated juice sacs of the *Citrus* fruit of Buntan were obtained: 2·2 g. of glycine-betaine, 8·5 g. of stachydrine, and 0·2 g. of putrescine. CHEMICAL ABSTRACTS.

Nitrogenous constituents of maize pollen. C. G. VINSON (J. Agric. Res., 1927, 35, 261—278).—The nitrogenous compounds extractable from finely-ground maize pollen by dilute sodium hydroxide solution have been studied. The pollen contains very little, if any, globulin. A substance resembling glutelin was precipitated on neutralisation of the alkaline extract with sulphuric acid, and constituted 9·9% of the air-dry pollen. The following substances were detected in the filtrate from the glutelin fraction, after extraction with ether and hydrolysis: adenine, arginine, lysine, tyrosine, choline, and β-hydroxyglutamic acid. Aspartic and glutamic acids were not present. Proteolytic enzymes were not found, but carbohydrases and a pectase were present. A compound believed to be a flavone or flavonol was also isolated. The use of Neuberg's reagent for precipitating amino-nitrogen compounds proved unsatisfactory. C. T. GIMINGHAM.

Phosphorus compounds of plants. II. Solubility of phosphorus compounds of barley flour. S. MINKOVSKA (Bull. Acad. Polonaise, 1926, *B*, 1007—1039; cf. Koehler, this vol., 798).—The results obtained in the extraction of phosphorus compounds from barley flour by water, and by hydrochloric acid, acetic acid, and sodium hydroxide solutions agree with those obtained by Koehler with maize. The amounts of total soluble phosphoric acid and inorganic phosphate extracted are determined principally by the final reaction of the extract. Barley flour contains enzymes which can rapidly liberate inorganic phosphoric acid from organic phosphorus compounds. The optimum reaction for these enzymes is p_H 5·4—4·7. On long keeping, dry barley flour shows an increase in inorganic phosphoric acid. Freshly-prepared barley flour contains 0·076% inorganic P_2O_5, 0·59% phytic P_2O_5, and 0·20% P_2O_5 in other organic combinations. G. W. Robinson.

Phosphorus compounds of plants. III. Solubility of phosphorus compounds of oat flour and ability of phytic acid to combine with protein substances of flour. S. Lindenbaum (Bull. Acad. Polonaise, 1926, *B*, 1041—1098).—The results obtained for oat flour resemble those obtained by Minkovska (cf. preceding abstract) for barley flour. The optimum reaction for the enzyme in oat flour transforming organic into inorganic phosphoric acid is p_H 5·75—4·9. Oat flour contains 0·084% mineral P_2O_5, 0·573% phytic P_2O_5, and 0·133% P_2O_5 in other organic combinations. Oat flour contains certain substances one of which is a protein with isoelectric point at p_H 5·8—6·8. In media on the acid side of its isoelectric point this compound forms an insoluble compound with phytic acid. G. W. Robinson.

Phosphorus compounds of plants. IV. Phosphorus compounds of the mycelium of *Aspergillus niger*. W. Vorbrodt (Bull. Acad. Polonaise, 1926, *B*, 1099—1108).—A preliminary note. The results obtained by extracting the mycelium of *Aspergillus niger* with varying concentrations of hydrochloric acid, acetic acid, and sodium hydroxide resemble those obtained by other workers for maize, barley, and oat flour (cf. preceding abstracts).

G. W. Robinson.

Distribution of potassium and sodium in plants. G. André and E. Demoussy (Bull. Soc. Chim. biol., 1927, 9, 861—866).—See this vol., 798.

Absorption of potassium salts by the root system of plants. K. Lemanczyk (Bull. Acad. Polonaise, 1926, *B*, 1109—1155).—Experiments on the absorption of potassium salts from nutrient solutions by the roots of barley plants are described. Absorption is considered to consist of two phases, viz., equivalent absorption, including absorption of salt molecules as such, and ionic absorption. The former phase predominates. Changes in the reaction of the nutrient solution are due to the second type of absorption. In ionic absorption, the exchange is between potassium ions in the solution and calcium and magnesium ions in the root-cells, and between the anions of the solution and hydrogen carbonate ions in the root-cells. Time–concentration curves show a periodicity, due to the interference of absorption and swelling. Absorption from solutions of electrolytes is influenced by the nature of the electrolytes, by the ratio of the concentrations of equally charged ions, and by the antagonistic action of ions.

G. W. Robinson.

Alleged occurrence of creatine and creatinine in soil and in plants. W. Linneweh (Z. Biol., 1927, 86, 345—350).—A series of substances giving the same colour reactions as creatinine is tabulated. The formation of a crystalline salt with zinc chloride is not conclusive without analysis, since betaine gives a similar salt. The formula of betaine–zinc chloride is not, as given by Liebreich, $(C_5H_{11}O_2N)_2,ZnCl_2$, but $(C_5H_{11}O_2N)_2,3ZnCl_2,H_2O$. Moreover, the nitrogen contents of arginine monopicrate and creatinine picrate agree within the limits of experimental error. The occurrence of creatine or creatinine in soil, in plants, and in bacterial cultures is not proven.

W. Robson.

Electrodialysis in biochemistry. Technical processes. J. Reitstötter.—See B., 1927, 849.

Determination of carbon dioxide and oxygen by the Haldane apparatus with automatic mixing. G. Gmeiner (Biochem. Z., 1927, 188, 285—289).—The raising and lowering of the mercury container of the Haldane apparatus are effected by attaching it to a rotating lever, the excursion being regulated by the distance of the container from the axis of rotation. P. W. Clutterbuck.

Gasometric micro-determination of iodate and sulphate. Determination of total base in blood-serum. D. D. Van Slyke, A. Hiller, and K. C. Berthelsen (J. Biol. Chem., 1927, 84, 659—675).—The solution of sulphates is shaken for 1 hr. with barium iodate; the resulting solution of iodates is transferred to the apparatus of Van Slyke and Neill (A., 1924, ii, 872), treated with excess of hydrazine, and the nitrogen evolved is measured. An empirical correction is applied for the incompleteness of the reaction between barium iodate and the soluble sulphates. The method is applicable to the determination of total base in 0·1 c.c. of blood-serum with an error of 0·8%, after preparation of the material by the method of Stadie and Ross (A., 1926, 100).

C. R. Harington.

Electrolytic determination of sodium plus potassium. J. L. Stoddard (J. Biol. Chem., 1927, 74, 677—688).—Biological material is incinerated by the method of Fiske (A., 1922, ii, 408). The resulting solution is subjected to electrolysis in a special apparatus with mercury electrodes; the sodium and potassium amalgam formed is determined by titration, a positive correction of 1·2% being applied to the results. C. R. Harington.

Determination of cyanogenetic glucosides. L. R. Bishop (Biochem. J., 1927, 21, 1162—1167).—A satisfactory method is described which is based on the decomposition of most of the glucoside by heating the leaf in water and decomposition of the remainder by added emulsin. The liberated hydrocyanic acid is aspirated, absorbed by potassium hydroxide, and titrated with silver nitrate.

S. S. Zilva.