BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1928.

General, Physical, and Inorganic Chemistry.

The aurora and its spectrum. J. C. McLennan (Proc. Roy. Soc., 1928, A, 120, 327—357).—Wave-lengths of the band heads in the band spectrum of nitrogen are given and compared with those of the aurora. The green auroral line λ 5577·341 Å. is shown to be due to the excitation of oxygen in the presence of rare gases, and could be caused by electrons given off by the sun and entering our atmosphere. The line was produced in an apparatus which is described and its Zeeman effect observed longitudinally. From this it is concluded that the green line has its origin in atomic oxygen and is due to a transition between low metastable energy states, being represented by $\nu={}^1D_2-{}^1S_0$. The intensity of the light of the night sky has been measured at various times of the night, and it has been shown that there is a variation in the intensity of that green light which gives rise to the auroral line. It shows a maximum about $1\frac{1}{2}$ hrs. after midnight. The height of the ozone layer has also been measured.

J. L. Buchan.

Spectrum of singly-ionised carbon (C II). A. Fowler and E. W. H. Selwyn (Proc. Roy. Soc., 1928, A, 120, 312—326; cf. A., 1924, ii, 285).—Methods for the production and observation of the spectrum are described. Most of the C II terms can be considered as arising from the addition of an electron in various orbits to a C III core. The lines have been classified and lists are given showing those of C II between λ 7236 and 2137 and also between λ 1760 and 534. Certain lines between λ 2137 and 1894, possibly due to C II or C III, are recorded.

J. L. Buchan.

Variations in the fine structure of H_α. G. E. Harrison (Proc. Physical Soc., 1928, 40, 300—306).—The intensity changes taking place in the fine structure of H_α with alteration of the bore of the discharge tube at constant gas pressures and current densities were examined. The large variations in the electric field surrounding an emitting particle are held to account for the observed changes in the intensity distribution, which amounted to 100%. The doublet separation appeared to be independent of these changes, the mean value obtained being 0·304 cm.$^{-1}$

C. J. Smithells.

Structure of the induction spectra of the rare gases; arc spectra of argon, krypton, and xenon. A. T. Williams (Proc. Physical Soc., 1928, 40, 312—315).—The value of the excitation by induction method to separate different orders of the spectra of the rare gases is emphasised. The arc spectra of argon, krypton, and xenon are examined, constant separations and groups of lines being deduced from Bloch and Dejardin's results. The regions occupied by different series are established and also the correspondence between theoretical terms and Meissner's terms in the arc spectrum of argon.

C. J. Smithells.

Regularities exhibited between certain multiplets for elements in the second long period. R. C. Gibbs and H. E. White (Proc. Nat. Acad. Sci., 1928, 14, 559—564).—The regular displacement of multiple levels and of multiplets which holds for iso-electronic systems in the first long series has been found to hold also for elements in the second long period. In this period the strong lines in the spectra are due to electron transitions $5p$ to $5s$ in the presence of 0, 1, 2, 3 . . . 10 $4d$ electrons. In each case a single line was chosen from all those radiated in order to represent the position in the spectrum of each electron transition. The transition chosen was that taking place between two levels involving the highest R, L, and J values. The diagram between radiated frequency and atomic number shows marked similarity to that for the first long period.

A. J. Mee.

Degree of association of sodium vapour. D. S. Villars (Proc. Nat. Acad. Sci., 1928, 14, 508—511).—By photographing the absorption spectrum of an alloy of sodium and potassium and obtaining the positions of the sodium bands, the convergence frequencies for the excited and unexcited states were determined. Using these values, the heat of dissociation of diatomic sodium was found to be 26·8 g.-cal. By means of the Sackur–Tetrode equation, the degree of association is calculated for various temperatures. Sodium vapour is very largely diatomic, especially at the lower temperatures. This conclusion does not agree with previous work.

A. J. Mee.

Broadening of spectral lines by the Doppler effect. G. Polvani (Nuovo Cim., 1927, 4, 365—370; Chem. Zentr., 1928, i, 1936).—At the absolute zero spectral lines should have a finite width.

A. A. Eldridge.

Dissociation energy of nitrogen. G. Herzberg (Nature, 1928, 122, 505—506).—It is shown that, in agreement with Gaviola's result (this vol., 1075), the dissociation energy of the neutral nitrogen molecule is probably about 9 volts; hence Sponer's interpretation of the afterglow requires modification.

A. A. Eldridge.

Interpretation of the atmospheric oxygen bands. Electronic levels of the oxygen mole-

cule. R. S. Mulliken (Nature, 1928, **122**, 505).—The upper, ^1S, level of the atmospheric oxygen bands, at 1·62 volts above the ^3S normal level, is identified with the predicted ^1S level. The low absorption coefficient for the transition $^3S \longrightarrow {}^1S$ is in agreement with the expected metastability of the ^1S level. A ^1D level of O_2 should exist between the ^3S and ^1S levels, and a new system of atmospheric absorption bands in the infra-red corresponding with the transition $^3S \longrightarrow {}^1D$ may be found.

A. A. Eldridge.

Wave-lengths in the secondary spectrum of hydrogen. H. G. Gale, G. S. Monk, and K. O. Lee (Astrophys. J., 1928, 67, 89—113).—Wave-lengths of 3064 lines between 3394 and 8902 Å. have been measured with precision. A. A. Eldridge.

Width of the *D* absorption lines in sodium vapour. A. S. Fairley (Astrophys. J., 1928, **67**, 113—122).—Between 180° and 380° the mean width varies from 0·11 to 3·78 Å. (for D_1) and 0·09 to 3·12 Å. (for D_2). For lines wider than 0·25 Å. the results support Stewart's view that the width can be ascribed to "radiation resistance." It is indicated that the Fraunhofer *D*-lines are due to only about 4×10^{14} non-ionised sodium atoms in a column 1 cm. square above the photosphere.

A. A. Eldridge.

Effect of pressure on the spectrum of the iron arc. H. D. Babcock (Astrophys. J., 1928, 67, 240—261).—The pressure effect for 130 lines in the arc spectrum of iron between 3895 and 6678 Å. has been measured for pressures below 1 atm. Empirical expressions make it possible to predict the pressure effect for both terms and lines. No connexion between term displacements and azimuthal or inner quantum numbers was observed. Theories attributing the pressure effect to coupling forces between adjacent similar atoms are rejected.

A. A. Eldridge.

Normal state of helium. J. C. Slater (Physical Rev., 1928, [ii], **32**, 349—360).—An approximate wave function for normal helium is calculated, and the charge density obtained agrees well with Hartree's independent result. The calculated diamagnetism of normal helium agrees with the observed value. The repulsive forces between two helium atoms and the van der Waals attractive forces are determined, and thence the "molecular diameter" is calculated. Approximately correct values are deduced for the density and the b. p. of the liquid. R. A. Morton.

Origin of the helium spectrum. L. S. Ornstein and H. C. Burger (Physica, 1928, 8, 111—118).—The intensity of the helium spectrum, excited in a capillary by a hot or cold cathode, was studied. Curves show the intensity of $^3P^3S$ as a function of pressure and current density. At sufficiently low pressures the triplet spectrum would probably be absent. At higher pressures the duration of the mean free path of an excited atom will become of the order of the radiation period, 10^{-8} sec.

Chemical Abstracts.

Band spectra in the extreme ultra-violet excited by active nitrogen. H. P. Knauss (Physical Rev., 1928, [ii], **32**, 417—426).—Gaseous hydrogen, oxygen, nitrogen, carbon monoxide, or nitric oxide was mixed with glowing nitrogen activated by means of an oscillatory discharge. The two oxides showed bands in the region (1000—2500 Å.) accessible to a vacuum spectrograph. In addition to the β and γ bands of nitric oxide characteristic of the afterglow, a new system (δ band) was found with the same final levels, *i.e.*, levels associated with the normal electronic state of the molecule. The initial level is an electronic state with zero vibration (level *C*) and the 0—0 δ-band is at 1915·7 Å. (6·44 volts). A few bands of the fourth positive group of carbon monoxide were obtained in the afterglow. The total energy of the levels affected was 8·2—9·0 volts. The conclusion is reached that the excitation of spectra in the afterglow is caused by a nitrogen molecule in one of a series of metastable states carrying the corresponding energy. The experiments support the view that atoms of nitrogen combine to form an excited molecule responsible first for the emission of α bands and later for the excitation of other spectra.

R. A. Morton.

Electronic states and band spectrum structure in diatomic molecules. VII. $^2P \longrightarrow {}^2S$ and $^2S \longrightarrow {}^2P$ transitions. R. S. Mulliken (Physical Rev., 1928, [ii], 32, 388—416; cf. this vol., 105).—The empirical structure types for $^2P \longrightarrow {}^2S$ and $^2S \longrightarrow {}^2P$ bands are discussed. The arrangement of the rotational levels in the ^2P state changes continuously with the parameter $\Delta E/B$ (ΔE=electronic doublet separation), the changes accounting largely for observed variations in band structure. Examples are given, and it is shown that the views of Hill and Van Vleck are supported. A consistent notation is applied to the branches of MgH, CaH, OH, ZnH, CdH, HgH, and NO bands, and has already been used for BO and CH λ 3900. The detailed discussion of band structure, missing lines, and intensity relationships indicates close agreement between the later formulæ and the experimental data. R. A. Morton.

Fluorescence and absorption of a mixture of mercury and zinc vapours. J. G. Winans (Physical Rev., 1928, [ii], **32**, 427—434).—Shorter rays than 2000 Å. (aluminium spark) excite vapour distilling from slightly amalgamated zinc, the first triplet of the sharp series of zinc being emitted. Neither the non-distilling vapour nor that distilling from pure zinc is excited. The same kind of mercury–zinc mixture shows continuous absorption from <1850 to 2050 Å. in distilling but not in stagnant vapour. The stagnant vapour and the zinc vapour show, in addition to the absorption lines of zinc, three bands, two of which correspond with absorption bands in cadmium. The absorption spectrum of mercury differs from that of the amalgam. The fluorescence is emitted by 2^3S zinc atoms produced possibly through absorption by HgZn molecules and dissociation into excited zinc and normal mercury atoms, or else through collisions of the second kind between normal zinc atoms and excited HgZn molecules. R. A. Morton.

Absorption bands in the spectra of mixtures of metallic vapours. R. K. Waring (Physical Rev., 1928, [ii], **32**, 435—442).—At a given temperature, the amount of thallium in the vapour state is increased by adding mercury vapour, indicating that thallium–mercury molecules are formed. A number of absorption bands are attributed to HgTl, but the resolving power was not sufficient to disclose structure. Asymmetric broadening of atomic thallium lines and the 2288 Å. line of cadmium, due to mercury vapour, has been observed; this may be due either to a superimposed molecular band or to transfer of kinetic energy by collisions. Mixtures of indium and cadmium vapours at 400°, 500°, and 800° show absorption bands due to InCd molecules. The short wave-length limits are given. The degree of resolution used disclosed traces of structure. R. A. Morton.

Polarisation of resonance radiation in mercury. H. F. Olson (Physical Rev., 1928, [ii], 32, 443—446).—The line $1^1S_0-2^3P_1$ of mercury excited by plane polarised light shows incomplete polarisation with and without a weak field parallel to the electric vector. The initial polarisation depends on the relative intensities of the hyperfine structure lines in the exciting light. A successful interpretation of data is supplied on the basis of a semi-classical model. The damping constant is found to be $1{\cdot}02(\pm0{\cdot}02)\times10^7$ sec.$^{-1}$ R. A. Morton.

Comparison of measurements of critical potentials of mercury vapour. J. C. Morris, jun. (Physical Rev., 1928, [ii], 32, 447—455).—A special tube has been designed for comparing the different methods for determining the critical potentials of mercury vapour. For critical potentials other than those of ionisation the Hertz method is the best: of the 13 critical potentials below ionisation, 10 have spectroscopic significance, whilst 3 are probably due to mercury molecules. The partial current method (Franck and Hertz) gave concordant results but less resolution, whilst the method of Franck and Einsporn gave results indicating that it serves to detect photoelectric effects and not metastable atoms. Compton's method gave satisfaction. Three ultra-ionising potentials at 10·65, 11·34, and 11·78 volts occur, but an attempt to test the molecular origin of these high ionising potentials failed. R. A. Morton.

Spark spectra of mercury vapour. J. Valasek (J. Opt. Soc. Amer., 1928, 17, 102—106).—The critical potentials necessary for the excitation of the E_3 spectrum of mercury vapour (cf. Bloch and Bloch, A., 1924, ii, 78) have been found to be 108 and 118 volts. W. E. Downey.

Time interval between the appearance of spectral lines in the spectra of alkali and alkaline-earth metals. G. L. Locher (J. Opt. Soc. Amer., 1928, 17, 91—101).—Using the method of Beams (A., 1926, 1069), the time intervals between the appearance in spark discharge spectra for fifty lines of the above metals have been found to vary between zero and 2×10^{-8} sec. W. E. Downey.

Second spark spectrum of cadmium, Cd III. J. C. McLennan, A. B. McLay, and M. F. Crawford (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 45—54).—The spark spectrum of cadmium in air has been measured between 2250 and 1850 Å., and in hydrogen between 1850 and 1450 Å. The chief wave-lengths correspond with a d^9p-d^9s transition in Cd^{++}. A new multiplet $^2P(d^{10}s)-^2D(d^9s^2)$ has been discovered. C. W. Gibby.

Arc spectrum of germanium. C. Richter (Z. wiss. Phot., 1928, 25, 380—393; cf. this vol., 99).—The arc lines of the spectrum of germanium have been schematically arranged in relation to five ground terms. The strongest lines show satellites. The Zeeman effect of a number of lines has been examined. W. E. Downey.

Regularities in the spark spectrum of hafnium (Hf II). W. F. Meggers and B. F. Scribner (J. Opt. Soc. Amer., 1928, 17, 83—90).—The wave-lengths of some 1500 hafnium lines have been accurately measured. Attempts to classify Hf I lines have not been successful, but 206 lines ascribed to Hf II have been arranged. W. E. Downey.

Structure of the first spark spectrum of silver, Ag II. J. C. McLennan and A. B. McLay (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 1—13; cf. Beals, A., 1926, 1071).—The spectrum Ag II is similar to Cu II and Zn II, and is in agreement with the structure predicted by the Hund theory. The deep-lying $^2D(d^9s^2)$ term of Ag I has been separated, and the screening constants for orbits of the 4_3 type have been calculated. C. W. Gibby.

First spark spectrum of gold, Au II. J. C. McLennan and A. B. McLay (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 103—115).—The first spark spectrum of gold has been measured from 2225 to 1390 Å. The $^{3,1}D(d^9s)$, $^{3,1}F,D,P(d^9p)$, and $^{3,1}D(d^9,s)$ terms of Au II corresponding with those most easily recognised in Cu II and Ag II have been identified. C. W. Gibby.

Influence of argon on the spectrum of sulphur. J. C. McLennan, R. Ruedy, and L. Howlett (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 79—86).—The influence of argon on the spectrum of sulphur from sulphur dioxide has been investigated. At low pressures the spark lines are suppressed and the arc lines enhanced. Similar results were obtained with an electrodeless discharge. With increasing current in the primary the intensity of the argon lines reached a maximum, whilst that of the sulphur lines increased steadily. C. W. Gibby.

Spark spectra of [sulphur and of] selenium and tellurium. L. Bloch and E. Bloch (Compt. rend., 1928, 187, 562—564).—Extension of earlier experiments (A., 1927, 1117) led to the identification of three successive degrees of excitation of tellurium, Te II (3374·10—2304·29), Te III (3365·17—2239·50), and Te IV (3345·93—2226·07), corresponding with singly-, doubly-, and triply-ionised atoms, respectively, the arc spectrum being designated Te I. No new rays were found on repetition of experiments with sulphur, but an additional selenium spectrum, Se IV (3360·36—2446·96), was identified. The wave-lengths of the new rays are given. J. Grant.

Absorption in excited krypton and xenon and the spectra of the inert gas type I. J. C. McLennan and R. Ruedy (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 15—26).—In krypton the component of shorter wave-length of pairs of constant frequency-difference is absorbed, these lines representing the transition $^3P_2-p$. The unabsorbed component originates in the $^1P_1$ level. Separation occurs between the $^3P_1$ and $^1P_1$ levels (4930) for a few lines; also the $^3P_2{}^1P_1$ separation for the strongest ultraviolet lines. Intercombination lines between triplet and singlet systems occur in all the rare gases except helium. The Na^+ spark lines in the violet correspond with the red neon lines $2p_j-S_i$. C. W. Gibby.

Fine structure of the scattered radiation from graphite. B. Davis and D. P. Mitchell (Physical Rev., 1928, [ii], 32, 331—335).—Experiments with a double *X*-ray spectrometer on the "undisplaced" scattered radiation from graphite indicate that the broadening of the spectral line is due to fine structure and a small displacement. Using a molybdenum target, four lines were observed: (*a*) the undisplaced line Mo-$K\alpha_1$ scattered from the whole atom; (*b*), (*c*), and (*d*) displaced 0·0012, 0·002, and 0·0113 Å., respectively, from $K\alpha_1$, in the direction of longer wave-lengths. The line (*d*) agrees with $h\nu'=h\nu-Ve$, where Ve is the energy level (287 volts) of the carbon atom. The relation does not hold for (*b*) and (*c*). No evidence of scattered radiation was obtained on the short-wave side of the Mo-$K\alpha_1$ position.

R. A. Morton.

At. wt. of silver. O. Hönigschmid (Z. Elektrochem., 1928, 34, 625—627).—The determinations in the Munich laboratories gave (N=14·008) Ag=107·880, 107·879 (A., 1927, 806). Recent experiments on the ratio barium perchlorate/barium chloride/silver give Ag=107·880 (O=16).

S. K. Tweedy.

Progression relation in the molecular spectrum of oxygen occurring in the liquid and in the gas at high pressure. O. R. Wulf (Proc. Nat. Acad. Sci., 1928, 14, 609—613).—In gaseous oxygen at moderate and high pressures, and also in liquid oxygen, several investigators have observed a number of bands in the visible and ultra-violet up to 2400 Å., where continuous absorption begins. These are shown to constitute a progression of bands and are quite distinct from the Schumann–Runge system and the atmospheric bands. The intensity of the bands increases rapidly to shorter wave-lengths for any one length of light path and concentration of oxygen. The behaviour observed may be explained by supposing that polymerised molecules of oxygen, O_4, decompose into normal ozone molecules and either excited or unexcited oxygen atoms. The effect of dissociation into a normal oxygen atom and an excited ozone molecule cannot be calculated, since nothing is known about the electronic levels of the O_3 molecule.

M. S. Burr.

Time lag in the emission of spectral lines excited in a vacuum. H. Nagaoka and T. Futagami (Proc. Imp. Acad. Tokyo, 1928, 4, 361—363).—Previous work on the retardation of the emission of spectral lines has been extended by photographing the spectra on a moving photographic film. In the oscillatory discharge from copper and aluminium at diminished pressures it is found that although the spark lines are emitted immediately there is a lag of at least 10^{-5} sec. before the arc lines appear. As the emission of the arc lines proceeds their intensity first increases to a maximum and then gradually fades away. Many of the lines show much stronger reversal in air than in a vacuum. It is suggested that whilst the emission of spark lines is a consequence of the discharge process, some time must elapse before the evacuated space contains a sufficient number of electrons for the excitation of the arc lines. The change in intensity is attributed to the recombination and subsequent re-excitation of the ionised atoms.

A. E. Mitchell.

Relative intensities of the Stark effect components of the Balmer H_β and H_γ lines. H. Mark and R. Wierl (Naturwiss., 1928, 16, 725—726).—The intensities of Stark effect components calculated according to Schrödinger's wave mechanics are in numerous instances the reverse of those found by Stark. For H_β and H_γ, Stark's data have been confirmed by maintaining the canal rays parallel to the lines of force of the resolving field; if, however, the canal rays proceed vertically to this direction, the conditions being otherwise unchanged, the results are in agreement with Schrödinger's theory. R. A. Morton.

Absorption coefficient of slow electrons in mercury vapour. T. J. Jones (Physical Rev., 1928, [ii], 32, 459—466).—The absorption coefficient α in mercury vapour for electrons with energies of 0·5—400 volts has been determined by two methods. In the first, a homogeneous electron beam was obtained by bending electrons through a series of slits suitably arranged in a magnetic field, whilst the second method gave a fairly homogeneous beam without the use of a magnetic field. The values of α obtained by the two methods agree fairly well. The absorption coefficient increases continually as the electron energy decreases to 0·5 volt. No evidence was obtained for the sharp decrease in α for electrons slower than 3 volts as reported by Beuthe (this vol., 213). The results agree fairly well with those of Maxwell (A., 1926, 989) over the whole range of electron energies and with those of Brode (A., 1925, ii, 1020) at the lower energies. R. A. Morton.

Oscillations in ionised gases. I. Langmuir (Proc. Nat. Acad. Sci., 1928, 14, 627—637).—Theoretical. Electrons accelerated from a hot cathode, and originally forming a beam of cathode rays with uniform translational motion, rapidly acquire a random or temperature motion (A., 1926, 3; this vol., 342). This scattering appears to be due to oscillations of the electrodes of less than 0·2 volt and frequencies up to $1{\cdot}2\times10^9$. The oscillations must be regarded as compressional electric waves, probably analogous to sound waves. The mathematical theory of these oscillations in the "plasma," or neutral regions containing approximately equal numbers of ions and electrons, is discussed.

M. S. Burr.

Element of time in the photo-electric effect. E. O. Lawrence and J. W. Beams (Physical Rev., 1928, [ii], 32, 478—485).—The time variation of the photo-electric emission from a metal surface illuminated by light flashes of 10^{-8} sec. duration has been studied. Photo-electric emission begins in less than

3×10^{-9} sec. after the beginning of the illumination of a potassium hydride surface. The time during which the photo-electric emission persists after cessation of irradiation is less than 10^{-8} sec. A wave travelling along a wire resulting from the sudden change of potential of one end by a spark discharge is so steep that the time necessary for about half the wave front to pass a point 6 m. along the wire is $4\cdot5\times10^{-9}$ sec. The short flashes of light were obtained by the Kerr cell electro-optical shutter (Proc. Nat. Acad. Sci., 1927, **13**, 207), the speed of operation of which has now been determined. R. A. MORTON.

Scattering of positive ions from a platinum surface. R. W. GURNEY (Physical Rev., 1928, [ii], **32**, 467—477).—The velocity distribution, angle distribution, and critical energy of potassium, cæsium, and lithium ions scattered from a platinum surface have been determined. R. A. MORTON.

Condition of radium salts after storage in sealed glass tubes. A. G. FRANCIS and A. T. PARSONS (Nature, 1928, **122**, 571).—Considerable quantities of radium salts (*e.g.*, 171·8 and 54·9 mg. of radium as 92% chloride and 50% bromide, respectively), sealed in glass tubes, can be safely kept unopened for at least 7 years, provided the drying has been thorough. Labels or other foreign materials should not be attached directly to the glass of tubes containing radium, and the tubes should be stored out of contact with organic matter.

A. A. ELDRIDGE.

γ-Rays from potassium salts. W. KOLHÖRSTER (Naturwiss., 1928, **16**, 28; Chem. Zentr., 1928, i, 1746).—Measurements of γ-radiation at Stassfurt are recorded. A. A. ELDRIDGE.

Ionisation curve of pure oxygen for α-rays from polonium. T. ONODA (J. Phys. Radium, 1928, [vi], **9**, 185—186).—The ionisation curve of pure oxygen for α-rays from polonium has been determined. The gas used was prepared by an electrolytic method. From the curve the extrapolated range of the rays was found to be 3·63±0·01 cm. at 15° and 760 mm., whilst at 0° and 760 mm. it was found to be 3·49±0·01 mm. The range in air under the first conditions of temperature and pressure was 3·87±0·01 cm., so that the stopping power of the oxygen molecule relative to air is 1·066±0·01. A. J. MEE.

Attempt to accelerate the rate of radioactive transformation. H. HERSZFINKIEL and L. WERTENSTEIN (Nature, 1928, **122**, 504).—The unexpected apparent stability of uranium atoms under bombardment by radium α-rays might be due to the formation of an atom of uranium-II, and not of uranium-X_1; the period of uranium-II, however, is too long to permit its detection, although with thorium the product formed after one α- and two β-transformations would be radiothorium with a period of only 2·02 years. On bombardment of thorium dioxide with radon α-rays, however, no change in α-ray activity was observed. It is computed that the upper limit of the probability of an α-ray collision producing an explosion of this type in the α-satellite is less than 1 in 8×10^{6}.

A. A. ELDRIDGE.

Apparent evidence of polarisation in a beam of β-rays. R. T. COX, C. G. MCILWRAITH, and B. KURRELMEYER (Proc. Nat. Acad. Sci., 1928, **14**, 544—549).—An experiment is described in which β-particles are twice scattered at right angles and then enter a Geiger counter. The relative numbers entering are noted as the angle between the initial and final segments of the path is varied. Readings were taken for angles between 90° and 270°. The results show a marked asymmetry which can be explained most easily on the assumption that there is a true polarisation due to the double scattering of asymmetrical electrons. A. J. MEE.

Existence of meso-products in the disintegration series of actinium. J. VON WESZELSZKY and L. IMRE (Z. anorg. Chem., 1928, **175**, 141—160).—A quantitative separation of radioactinium from the other disintegration products of actinium is shown to be effected by heating the oxide mixture containing the actinium in radioactive equilibrium with its disintegration products in a current of dry chlorine saturated with the vapour of sulphur chloride, whereby radioactinium chloride alone sublimes. It may be further purified by precipitation with ammonia or hydrogen peroxide after addition of a small quantity of thorium nitrate to the chloride solution. The activity of the purified product rises to a maximum in about 14 days, whereas according to the Geiger–Nuttall theory maximum activity should not be reached until the twentieth day. It is shown that this variation from the theory is not due to the presence of an inactive product which further disintegrates into a very active product, nor to the greater homogeneity of the volatilised radioactinium as compared with that obtained by other methods, and the suggestion is made that the anomalies found in this series are of a similar nature to those found in other parts of the periodic system where the atomic weights do not increase with the atomic number.

A. R. POWELL.

Angular scattering of electrons in hydrogen and helium. G. P. HARNWELL (Proc. Nat. Acad. Sci., 1928, **14**, 564—569).—Experiments were made to determine the possibility of selective angular scattering of electrons in atomic hydrogen in order to extend the work on scattering by crystals, and to test the observations of Dymond on the scattering of electrons by helium. The apparatus is described in detail. It was found that there were no favoured angles for scattering from hydrogen or from helium. Dymond's experiments were repeated, but his results could not be reproduced. A. J. MEE.

Isotopes of neon. T. R. HOGNESS and H. M. KVALNES (Nature, 1928, **122**, 441).—The existence of Ne^{21} is confirmed. Atmospheric neon is estimated to be composed of Ne^{22} 10, Ne^{21} 2, Ne^{20} 88%.

A. A. ELDRIDGE.

Polarisation of the resonance radiation from degenerate systems. F. C. HOYT (Physical Rev., 1928, [ii], **32**, 377—387).—The polarisation of radiation excited by light in resonance with the principal absorption frequency of a gas has been discussed on the basis of wave mechanics. Calculation of the electric moment of the perturbed atom on the Schrödinger density hypothesis shows that when the incident light is linearly polarised the radiation has the same degree of polarisation as though the atom were in a weak magnetic field parallel to the electric vector of the light. With circular polarisation this fictitious field is perpendicular to the plane of polarisation. Heisenberg's rule, deduced from the correspondence principle, is confirmed. R. A. MORTON.

Quantum theory of electronic impacts. J. R. OPPENHEIMER (Physical Rev., 1928, [ii], 32, 361—376).—Earlier mathematical treatment of electronic collisions has erroneously neglected terms in the solution corresponding with an interchange of the colliding electron with one of those in the atom. The corrected first-order cross-section for elastic collisions with atomic hydrogen and helium has been calculated by Dirac's method. Using Born's method for hydrogen, the complete solution indicates that the elastic cross-section becomes infinite, for low velocities with the reciprocal of the velocity. For hydrogen, the first-order cross-section is a monotonically increasing function; for atoms with completely paired electrons the monotonic increase is broken by a minimum at velocities corresponding with about 1 volt, and the higher the azimuthal quantum number of the paired valency electrons the more marked is the minimum and the lower the voltage at which it occurs. R. A. MORTON.

Recent theories of the atom. W. F. G. SWANN (J. Opt. Soc. Amer., 1928, 17, 163—197).—A lecture.

Wave mechanics and radioactive disintegration. R. W. GURNEY and E. U. CONDON (Nature, 1928, 122, 439).—Radioactive disintegration is regarded as a natural consequence of the laws of quantum mechanics. A. A. ELDRIDGE.

Interpretation of Dirac's theory of the electron. G. BREIT (Proc. Nat. Acad. Sci., 1928, 14, 553—559).—Mathematical. Dirac's matrix-operators in wave-mechanics, α_1, α_2, and α_3, have not yet been given any physical significance. It is shown that α_1, α_2, and α_3 can be regarded as operational matrix-representations of the velocity-vector $\dot{x}/c$, $\dot{y}/c$, $\dot{z}/c$, in the same way as the Pauli matrix-operators, s_x, s_y, s_z, represent the spin of the electron. A. J. MEE.

Properties of salt-like compounds and atomic structure. II. Influence of deformation of the electron sheaths. K. FAJANS (Z. Krist., 1928, 66, 321—354; Chem. Zentr., 1928, i, 2046).

The self-consistent field and the structure of atoms. J. C. SLATER (Physical Rev., 1928, [ii], 32, 339—348).—Hartree's method (this vol., 216, 933) for the solution of problems in atomic structure has been examined in relation to Schrödinger's equation. Term values calculated by Hartree require correction because (*a*) electron distributions are not really spherical, (*b*) the resonant interactions between electrons are not allowed for, and (*c*) polarisation energy is neglected. The sizes of the corrections are of the same order as the errors occurring in Hartree's numerical examples. R. A. MORTON.

Fluorescence of fluorspars excited by light of different wave-lengths. H. NISI and K. MIYAMOTO (Proc. Imp. Acad. Tokyo, 1928, 4, 357—360).—Fluorspars are found to be divisible into three classes according as they show both red and blue fluorescence, only blue fluorescence, or no appreciable fluorescence. The fluorescence spectrum of a specimen of the first class was found to comprise two main groups of lines. One group excited by wave-lengths in the region of 2300 Å. comprises lines in the red and yellow usually accompanied by others in the blue and green portions of the spectrum. The other group is excited by wave-lengths in the region of 2800 Å. The red and yellow lines of the 2300 Å. group are identified with samarium phosphor lines and it is suggested that those of the 2800 Å. group with the blue and green lines are due to europium and terbium phosphors. It is also suggested that the fluorescence phenomenon is due to the presence of traces of rare-earth phosphors. A. E. MITCHELL.

Raman effect in highly viscous liquids. S. VENKATESWARAN (Nature, 1928, 122, 506).—Experiments with glycerol and mixtures of glycerol with water indicate that the transformation of the monochromatic incident radiation into general or white radiation is closely connected with the special state of molecular aggregation which gives rise to a high viscosity. A. A. ELDRIDGE.

Wave-length shifts in scattered light. W. H. MARTIN (Nature, 1928, 122, 506—507).

Scattering of light by particles of metallic oxides dispersed in dry air. T. C. NUGENT and H. P. WALMSLEY (Proc. Physical Soc., 1928, 40, 269—280).—The changes with time in the brightness of the Tyndall light from clouds of the oxides of zinc, copper, cadmium, and arsenic were measured, and can be accounted for by supposing that the particles disappear by aggregation and sedimentation. The curves obtained fluctuate in a similar way to the ionisation currents from the same cloud, suggesting that aggregation produces unstable complex particles which periodically break up in large numbers. A series of clouds vaporised from various masses, m, of arsenic trioxide gave values for the initial brightness of the Tyndall beam approximately proportional to $m^{2/3}$. In certain clouds the rapid fluctuations in brightness appear to form groups which succeed one another at intervals given by $t=Ar^n$, where A and r are constants and n is an integer. C. J. SMITHELLS.

Wave-lengths in the nitrogen peroxide absorption spectrum. L. C. K. CARWILE (Astrophys. J. 1928, 67, 184).—Wave-lengths from 3978·67 to 6323·22 Å. in the absorption spectrum of nitrogen peroxide have been measured and the results published privately (University of Virginia, U.S.A.). A. A. ELDRIDGE.

Infra-red absorption spectra of the halogen derivatives of methane. M. A. EASLEY, L. FENNER, and B. J. SPENCE (Astrophys. J., 1928, 67, 185—194).—Infra-red absorption spectra (0·8—3 μ) of methyl iodide, methylene chloride, bromide, iodide, and iodobromide, chloroform, bromoform, carbon tetrachloride and tetrabromide, and trichlorobromomethane were studied. Bands were not observed with compounds containing no hydrogen. A. A. ELDRIDGE.

Absorption spectra of water and ice, with reference to the spectra of the major planets. J. C. McLennan, R. Ruedy, and A. C. Burton (Proc. Roy. Soc., 1928, **A**, **120**, 296—302).—The absorption spectra of water and of ice have been photographed using long columns, and the bands obtained compared with those in the spectra of Uranus, Saturn, Neptune, and Jupiter. The strong band at 7200—7260 Å. given by these planets has been shown to be similar to that given by liquid water, whilst the band at 5430 Å. remains unidentified. The absorption of ice is different from that of water, the intensities being shifted towards longer wave-lengths. J. L. Buchan.

Light absorption and coloration of alkali halides. K. Przibram (Naturwiss., 1928, **16**, 27—28; Chem. Zentr., 1928, i, 1747).—The absorption maxima in the visible region of coloured alkali halides are in the order fluoride, chloride, bromide, iodide, and sodium, potassium, cæsium, rubidium for displacement towards the long wave-length side. The lability of the coloration increases in the order sodium, potassium, cæsium, rubidium chloride.

A. A. Eldridge.

Luminescence of solid nitrogen under cathode-ray bombardment. J. C. McLennan, H. J. C. Ireton, and E. W. Samson (Proc. Roy. Soc., 1928, **A**, **120**, 303—311).—An apparatus for producing the luminescence emitted by solid nitrogen bombarded with high-speed electrons is described, and the spectrum of this luminescence has been photographed from 2000 to 8600 Å. The usual bands N_1, N_2, and N_4 are found and also bands at 6400 (probably N_3), 8535, 6725, and 6187 Å. Other bands are found at shorter wave-lengths and are tabulated. At the temperature of liquid hydrogen the bands N_1, N_2, and N_4 are all phosphorescence bands, but N_1 is thermoluminescent at a slightly higher temperature. Curves are given showing the rates of decay of the bands, each stage of which can be represented by an equation of the same form. The probable cause of the luminescence is discussed. J. L. Buchan.

Photo-electric emission of water and of aqueous solutions. L. Counson and A. Molle (Arch. Sci. phys. nat., 1928, **10**, 213—242).—Purified water is found to be photo-electric towards light of the region 2000—1300 Å. This effect is not due to accidental impurities on the surface of the water. Solutions of alkali halides are less photo-electric than pure water. Solutions of salts containing oxygen are more photo-electric than pure water. W. E. Downey.

Decomposition of ammonia by high-speed electrons. J. C. McLennan and G. Greenwood. —See this vol., 1197.

Chemical reactions of carbon monoxide and hydrogen after collision with electrons. A. Caress and E. K. Rideal.—See this vol., 1198.

Influence of disaggregation on the fluorescence of complex natural substances. H. Pringsheim and O. Gerngross (Ber., 1928, **61**, [*B*], 2009—2011).—The powdered polysaccharide is placed on non-fluorescent, porous plates and examined in filtered, ultra-violet light. Gelatin preparations are observed in solution or as films on glass plates. Disaggregation of lichenin, cellulose, glycogen, amylopectin, starch-amylose, inulin, inulin acetate, and gelatin appears to cause marked increase in fluorescent power.

H. Wren.

Relationships between absorption spectrum and chemical constitution of azo dyes. II. Influence of position isomerism on the absorption spectrum of nitro-derivatives of benzeneazophenol, -*o*-cresol, and -*m*-cresol. W. R. Brode (Ber., 1928, **61**, [*B*], 1722—1731).—Determinations have been made of the absorption spectra of the nine possible mononitro-derivatives of benzeneazo-phenol, -*o*-cresol, and -*m*-cresol containing the nitro-group in the non-hydroxylated nucleus between 400 and 1300 f. in alcoholic and aqueous sodium hydroxide solution. The results, together with observations on the corresponding methyl compounds (to be published later), show that increase in mol. wt. is usually accompanied by decrease in the frequency of the absorption bands. Substitution of a nitro-group in the *p*′-position causes marked increase in intensity of the first main band and slight decrease of that of the second band. The frequency of the main band is displaced towards lower values in comparison with the isomeric compounds substituted in the *o*′- or *m*′-position. Introduction of a nitro-group in the *o*′-position, compared with the relationships of the *m*′-substituted isomerides, induces a general decrease in the intensity of absorption without altering the frequency of the bands. A subsidiary band on the side of higher frequency of the main band is shown by *o*′- and *m*′-substituted derivatives of benzeneazophenol. The main absorption band of all these compounds in aqueous sodium hydroxide appears to be formed of two components, although actually more than two are present. The equilibrium which appears to exist between the two components or bands depends on the position of the substituting group in the molecule. The same general effect is experienced with nitro- and methyl derivatives. Substitution in the *o*′-position causes an increase in intensity in the component of less frequency and a corresponding decrease in that of greater frequency. Substitution in *m*- or *o*′-position causes a weakening in the component of lower frequency; if a substituent is also present in the *o*′-position, a diminution of the sum of the intensities of both bands is induced. Introduction of a substituent in the *m*′-position does not cause a marked difference in the spectrum from that of the unsubstituted compound. Substitution in the *p*′-position causes a very decided increase in the intensity of the main band, a diminution in that of the second band, and a lowering of frequency of the middle of the main band. Mononitro-derivatives of benzeneazophenol in aqueous sodium hydroxide show the same general duplex structure and the same equilibrium in the second absorption band as in the first or main band, thus showing that the former is a harmonic of the latter and similarly influenced by position or substitution effects.

o-*Nitrobenzeneazo*-o-*cresol*, m. p. 105°, m-*nitrobenzeneazo*-o-*cresol*, m. p. 132—133°, o-*nitrobenzene*-

azo-m-*cresol*, m. p. 162°, and m-*nitrobenzeneazo*-m-*cresol*, m. p. 164—166°, are incidentally described.
H. WREN.

Structural relationships of silicates. B. GOSSNER (Ber., 1928, 61, [*B*], 1634—1638).—Röntgen-spectrographic measurements of numerous silicates disclose the following regularities. A general structure with a definite number of oxygen atoms and definite sum of the numbers of other atoms can recur in spite of considerable variation in the nature of the latter. Such similar general structure is accompanied by a close similarity in volume and in length of the side of the elementary parallelepiped. Silicates are thus shown to be related to one another in a manner unsuspected from goniometric measurement. Data are recorded for the three groups (I) babingtonite, $CaFeSi_2O_6,SiO_2$, anorthite, $CaSi_2O_5,Al_2O_3$, and epididymite, $BeSi_2O_5,SiO_3NaH$; (ii) beryl, $3BeSi_2O_5,Al_2O_3$, and cordierite, $Mg_3Si_5O_{12},2Al_2O_3$; (iii) diopside, $MgCaSi_2O_6$, and tremolite, $Mg_3CaSi_4O_{12}$. H. WREN.

Dielectric constant and electric moment of carbon monoxide, carbonyl sulphide, carbon disulphide, and hydrogen sulphide. C. T. ZAHN and J. B. MILES, jun. (Physical Rev., 1928, [ii], 32, 497—504).—Debye's equation $(\varepsilon-1)vT=AT+B$, in which ε is the dielectric constant, v is the specific volume referred to the ideal volume at S.T.P., T is absolute temperature, and A and B are constants, applies well to the above gases. Values for A and B are given and from the relation $\mu^2=1{\cdot}198\times10^{-36}B$, the electric moment μ is calculated, giving the values: carbon monoxide, 0·10; carbon disulphide, 0·326; carbonyl sulphide, 0·650; and hydrogen sulphide 0·931 in c.g.s. e.s. units $\times10^{18}$. Data by other workers and discrepancies are discussed. It seems likely that carbon disulphide and carbonyl sulphide, like carbon dioxide, possess a rectilinear structure.
R. A. MORTON.

Experimental proof of "negative dispersion." H. KOPFERMANN and R. LADENBURG (Nature, 1928, 122, 438—439).

Ionising potentials of methane, ethane, ethylene, and acetylene. J. C. MORRIS, jun. (Physical Rev., 1928, [ii], 32, 456—458).—The ionisation potentials of the pure gases determined in an ionisation tube of the Mackay type, calibrated against mercury and helium, are: methane 14·4, ethane 12·8, ethylene 12·2, acetylene 12·3 volts, correct within 0·2 volt.
R. A. MORTON.

Structure of thin films. XII. Cholesterol and its effect in admixture with other substances. N. K. ADAM and G. JESSOP (Proc. Roy. Soc., 1928, A, 120, 473—482; cf. this vol., 937).—The action of cholesterol on unimolecular films of fatty acids and of other substances on water or dilute hydrochloric acid has previously been studied. It is found that the presence of cholesterol contracts the film, and curves are given showing this effect on films of myristic and oleic acids, nonylphenol, and ethyl palmitate. A similar effect is given by cholesteryl formate and acetate. The effect is less on vapour-expanded films than on liquid-expanded films. From measurements of the surface vapour pressures of these films it is concluded that the contraction given by cholesterol is probably not due to its attraction of the smaller molecules. The effect of other large molecules has also been studied, and similar results have been obtained, so it is thought that the large molecules offer a mechanical obstruction to the tilting of the small molecules, thus preventing them from covering so large an area. J. L. BUCHAN.

Height of ozone in the upper atmosphere. F. W. P. GÖTZ and G. M. B. DOBSON.—See this vol., 1209.

Internal field of polarisation [of the molecules of a substance under the action of an external field]. R. DE MALLEMANN (Compt. rend., 1928, 187, 536—538).—Mathematical. In the case of a regular assembly of molecules, such as a cubic crystal, the field is zero. The field in the case of a fluid is essentially due to the irregularity of the molecular arrangement. W. E. DOWNEY.

Method for determining the Kerr constant of poor insulating materials by means of alternating electric fields. W. ILBERG (Physikal. Z., 1928, 29, 670—676).—An improved method for determining the Kerr constant is described and applied to nitrobenzene. The constant is given for a range of wave-lengths in the visible and a dispersion curve constructed. The results are in agreement with Havelock's formula. R. A. MORTON.

Liquid crystals. L. S. ORNSTEIN (Physikal. Z., 1928, 29, 668—670).—Largely explanatory. The tendency of liquid crystalline substances to form parallel "swarms" can be explained equally well by the aggregate swarm hypothesis and by the crystal hypothesis. R. A. MORTON.

Rotation dispersion and spatial configuration in complex salts of cobalt and of rhodium containing ethylenediamine and *trans*-1 : 2-diamino*cyclo*pentane. F. M. JAEGER and H. B. BLUMENDAL (Z. anorg. Chem., 1928, 175, 161—230).—Reduction with metallic sodium of an absolute-alcoholic solution of *cyclo*pentanedionedioxime affords r-trans-1 : 2-*diaminocyclopentane* as a colourless liquid, b. p. 170°, with a faint ammoniacal odour [*diacetyl* derivative, monoclinic prisms, m. p. 219—220° (corr.)]. The *r*-base may be resolved into its optical antipodes by fractional crystallisation of the hydrogen *d*- or *l*-tartrate. The *l*-base has b. p. 166° (corr.), d_4^{15} 0·9463, and $[\alpha]_{5463}^{15}$ −64° [*diacetyl* derivative, m. p. 248° (corr.); *chloride*, $[\alpha]_D^{15}$ −22°; *sulphate*, $[\alpha]_D^{15}$ −12°; *hydrogen* d-*tartrate*, m. p. 143°, $[\alpha]_D^{15}$ +10·5°]. On boiling a solution of cobalt chloride and hydrogen peroxide or a solution of sodium chlororhodite with the racemic base co-ordination complexes of the triethylenediamine type, $[M(C_5H_{12}N_2)_3]X_3$, are obtained, which can be resolved into their optical antipodes by means of *d*- or *l*-tartaric acid. The cobalt and the rhodium salts with the same direction of rotation have similar spatial configurations, the dextrorotatory ions containing 3 mols. of the *l*-base and the lævorotatory ions 3 mols. of the *d*-base; no compounds with 2 mols. of one base and 1 mol. of the other could be prepared. The following salts of the *r*-cobalt base were prepared: *chloride*, $[Co(C_5H_{12}N_2)_3]Cl_3,3H_2O$, triclinic blood-red prisms;

iodide ($1H_2O$), yellowish-brown precipitate; *nitrate* (anhyd.), red needles; *perchlorate* (anhyd.), red needles, and *chlorate* ($3H_2O$), blood-red monoclinic prisms. The following salts of the corresponding *r*-rhodium base have also been prepared: *chloride* ($2H_2O$), triclinic prisms; *bromide* ($1H_2O$), fine needles; *iodide* ($1H_2O$); *nitrate* ($2H_2O$); *chlorate* ($2H_2O$), monoclinic prismatic tablets; *perchlorate* (anhyd.), long, hair-like needles; *sulphate* and *nitrite*. The perchlorates of the *r*-cobalt and rhodium bases spontaneously decompose into their optical antipodes, the former above −1·5° and the latter above 48°. The optically active perchlorates of both bases crystallise with $12H_2O$, the chlorides with $4H_2O$, and the chlorates with $12H_2O$, all in the pentagonal icositetrahedral class of the cubic system; the nitrates and chlorides also crystallise with $3H_2O$ in hexagonal bipyramids and the perchlorates in rhombic crystals with $1H_2O$. The molecular dispersion of all the above salts is extraordinarily great; in the case of the cobalt salts it is three times as great as that of the corresponding triethylenediamine compounds for light of short wave-length and up to ten times as great for light of long wave-length, whilst in the case of the rhodium compounds the diamino*cyclo*pentane derivatives have seven to eight times as great a molecular dispersion as the corresponding ethylenediamine derivatives. Digestion of dichlorodiethylenediamine-cobaltic chloride with *r*-, *l*-, or *d*-*trans*-1 : 2-diamino*cyclo*pentane affords a new series of co-ordination complexes of the type $[Co\ en_2\ (C_5H_{12}N_2)]Cl_3$, the racemate of which is resolvable by means of *d*- or *l*-tartaric acid into two optical antipodes $[Co\ en_2\ l\text{-}(C_5H_{12}N_2)]_DCl_3$ and $[Co\ en_2\ d\text{-}(C_5H_{12}N_2)]_LCl_3$. The following salts derived from the *r*-base are described: *diethylenediamine*-r-trans-1 : 2-*diamino*-cyclo*pentanecobaltic chloride* ($3H_2O$), *bromide* ($1H_2O$), and *iodide* (anhyd.), *nitrate* ($1H_2O$), and *perchlorate* ($4H_2O$). The values of [α] for the d- and l-*bromides* ($+2H_2O$) from the resolution of the *r*-bromide are as follows $[\alpha]^{18}_{4357}$ ±835°, $[\alpha]^{18}_{5185}$ ±0°, $[\alpha]^{18}_{5320}$ ±162°, $[\alpha]^{18}_{5875}$ ±0°, and $[\alpha]^{18}_{6564}$ ±87·5°. The complexes derived from the *d*- and *l*-bases in the above way are partly racemic, optically active compounds which can be resolved into components which are not mirror images of one another, as they have formulæ of the type: $[Co\ en_2\ l\text{-}(C_5H_{12}N_2)]_DX_3$ and $[Co\ en_2\ l\text{-}(C_5H_{12}N_2)]_LX_3$. By treating cobalt chloride with diamino*cyclo*pentane and hydrogen peroxide and heating the solution with hydrochloric acid, bright green crystals of trans-*dichlorodi*-trans-1 : 2-*diamino*cyclo*pentanecobaltic chloride*, $[Cl_2(C_5H_{12}N_2)_2Co]Cl,2H_2O$, are obtained; this salt, when boiled with water, is converted into the *cis*-form (anhyd.). Attempts to convert these compounds into the corresponding ethylenediaminedi-*trans*-diamino*cyclo*pentane compounds failed, decomposition taking place into the triethylenediamine and tri-*trans*-diamino*cyclo*pentane compounds. Compounds derived from 2 mols. of one optical isomeride and 1 mol. of the other were also unstable, decomposing as follows:

$3[Co(d\text{-}C_5H_{12}N_2)_2l\text{-}C_5H_{12}N_2]X_3 = [Co(d\text{-}C_5H_{12}N_2)_3]X_3 + 2[Co(l\text{-}C_5H_{12}N_2)_3]X_3$. A. R. POWELL.

Present position of the strain theory. W. HÜCKEL (Fortschr. Chem. Phys. u. physikal. Chem., 1928, 19, 1—101; Chem. Zentr., 1928, i, 2037).—A critical discussion. A. A. ELDRIDGE.

Vacuum grating spectrograph for ultra-violet and soft X-rays. J. THIBAUD (J. Opt. Soc. Amer., 1928, 17, 145—154).—A vacuum grating spectrograph using the tangential incidence method is described. It has been used to measure various soft X-rays of wave-lengths varying from 17·7 Å. ($L\alpha$ of iron) to 65 Å. (M of molybdenum). Absorption spectra of carbon, nitrogen, and oxygen have been obtained. W. E. DOWNEY.

Effect of chemical combination on the structure of the K absorption limit. B. DAVIS and H. PURKS (Physical Rev., 1928, [ii], 32, 336—338).—The structure and shift of position in the K absorption limits of silver, molybdenum, and copper and the compounds Ag_2S, Ag_2O, MoO_3, MoS_2, and Mo_2O_3 have been determined by means of the double X-ray spectrometer. The width for a pure element decreases with increasing atomic number. In the compounds, the absorption limit is broadened, but little displacement occurs. There is marked evidence of fine structure in Mo_2O_3. Apparently the readjustment of energy which occurs with chemical combination extends throughout the whole atomic system and is not confined to the outer layers of the atom. The position and form of the K limit of molybdenum are independent of temperature. R. A. MORTON.

Velocity distribution of photo-electrons produced by soft X-rays. E. RUDBERG (Proc. Roy. Soc., 1928, A, 120, 385—422).—An apparatus for studying the velocity of photo-electrons produced by soft X-rays on solid conductors is described. Curves showing the variation of photo-electric current with magnetic field strength are given for silver, copper, aluminium, and carbon, two curves for each, one before and the other after heating in a vacuum at 400°. From the shape of the curves it is concluded that the emission is made up of two parts: (1) a group of electrons of the low energy corresponding with only a few volts, and (2) a group of fast electrons of between 200 and 280 volts. Baking the electrode, *i.e.*, removing the adsorbed gas, reduces the emission, but this influence is confined to the low-velocity electrons. Curves are also given showing the distribution of energy over the field. The nature of the two groups in the emission is discussed. It is also suggested that some of the conclusions reached from experiments on soft X-rays should be modified.

J. L. BUCHAN.

Reflexion and refraction of electrons by a crystal of nickel. C. J. DAVISSON and L. H. GERMER (Proc. Nat. Acad. Sci., 1928, 14, 619—627).—The analogy between the reflexion of a homogeneous beam of electrons from a crystal face, previously observed (this vol., 683), and X-ray reflexion is discussed. The Bragg formula for the intensity maximum of X-rays does not, however, hold in the case of electrons at speeds due to bombarding potentials at least up to 600 volts. It is probable that the analogue of a given electron beam is the adjacent X-ray beam of shorter wave-length. This leads to values of the refractive index greater than unity. This is in agreement with the view that electron refraction in the optical sense is a property of the crystal. Refraction in the case of electrons does not appear to arise from the same cause as for *X*-rays and light rays, since the trend of what may be regarded as the normal dispersion curve of nickel for the former is opposite to that of the normal dispersion curves of materials for the latter. M. S. Burr.

Diffraction of cathode rays by mica. S. Kikuchi (Proc. Imp. Acad. Tokyo, 1928, **4**, 354—356).—An explanation is offered of the diffraction patterns obtained when a beam of cathode rays is passed through mica plates of different thickness (*ibid.*, 271). An electron in passing through a mica plate of appreciable thickness will be scattered more than once, so that during its passage through the plate a cathode-ray beam will become progressively more divergent. The energy losses must be small in comparison with the total energy, so that there will be no appreciable change in wave-length, the effect being the production of a point source of homogeneous rays in the crystal itself. Then if in the crystal there is a net plane of strong reflecting power this will reflect regularly all the rays giving rise to the reflexion and absorption lines observed (*loc. cit.*). Variation of the angle of incidence of the ray to this net reflecting plane and of the thickness of the crystal will then produce all the diffraction patterns observed. A. E. Mitchell.

Spectrum and state of polarisation of fluorescent *X*-rays. A. H. Compton (Proc. Nat. Acad. Sci., 1928, **14**, 549—553).—The spectrum of the fluorescent *X*-rays from silver, excited by *X*-rays from a tungsten target, shows the complete absence of any continuous spectrum. Absorption measurements indicate that the line radiation constitutes more than 99% of the total radiation, the results being in agreement with the work of Sadler. The relative intensity and positions of the spectrum lines are approximately the same in the fluorescent as in the primary *X*-rays. By using the method of Hagenow and Compton, the polarisation of fluorescent *X*-rays was tested. The fluorescent *X*-rays from silver are unpolarised, with a probable error of 0·5%. A. J. Mee.

Polarisation of characteristic radiation. J. A. Bearden (Proc. Nat. Acad. Sci., 1928, **14**, 539—542).—An apparatus is described for finding the extent of polarisation of characteristic *X*-rays. Characteristic *X*-radiation is probably unpolarised, a result in agreement with the usual ideas on *X*-ray production, and with Compton's work on the polarisation of fluorescent radiation. A. J. Mee.

Spectrum of *X*-rays from the back of a tungsten target. E. Lorenz (Proc. Nat. Acad. Sci., 1928, **14**, 582—588).—The spectral distribution of radiation from the back of a tungsten target was investigated in order to gain information about the electrons producing it. A special tube was designed in order to obtain radiation of sufficient intensity. Five voltages varying from 22,400 to 82,500 were used. The spectrum was obtained by measuring for each voltage the ionisation currents as a function of the crystal angle, an ordinary Bragg spectrometer with a calcite crystal, and an ionisation chamber containing methyl iodide being used. The spectrum appears to be produced at high voltages mainly by secondary electrons. No secondary electrons, however, appear from the *N* levels when the voltage across the *X*-ray tube is 22,400 volts, and neither *N* nor *M* electrons when the voltage is 83,350. In order to explain this it is necessary to assume that there is practically no absorption of primary electrons in any level in the tungsten anode if the energy of the primary electrons exceeds that of the level by about 40 times. The probability of absorption in any level is thus a function of the voltage across the tube, reaching a maximum and then decreasing to zero for energies of primary electrons which exceed the energy of the level by about 40 times. It is therefore to be expected that the intensity of any characteristic series due to the knocking out of electrons from an atom will also be a function of the voltage of the tube, increasing at first, and then decreasing. A. J. Mee.

Destruction of single crystals of aluminium by rolling. T. Sakao (Mem. Coll. Sci. Kyōtō, 1928, **11**, 279—282).—Single-crystal sheets of aluminium were reduced 10% in thickness by rolling in small steps, and Laue patterns obtained after each pass. From the progressive distortion of the Laue spots it appears that a rotation of the crystal fragments takes place about an axis parallel to the direction of rolling, irrespective of the orientation of the original crystal. C. J. Smithells.

Crystallographic orientation of electrolytically deposited metals [copper and nickel]. G. Tammann and H. Straumanis (Z. anorg. Chem., 1928, **175**, 131—140).—On a polished copper cathode the crystals of electrolytically deposited copper (from sulphate solutions) are small and their orientation bears no relation to that of the base metal. But if the surface of the cathode is previously etched with nitric acid, ammonia and hydrogen peroxide, or ammonium persulphate, the electrolytically deposited metal grows in the same orientation as the crystals of the base metal, provided that only a low current density is employed. This growth takes place only when the deposition of the copper is a primary reaction; copper deposits formed by a secondary reaction, *e.g.*, by electrolysis of cyanide solutions, have an irregularly oriented structure. From ammoniacal solutions nickel is deposited on coarsely crystallised, etched nickel cathodes in a finely crystalline form which bears no crystallographic relation to the cathode. A similar behaviour is shown by nickel deposited from sulphate solutions on etched copper cathodes and by copper deposited on etched nickel cathodes. The deposition of copper on etched spheres of single-crystal copper is illustrated diagrammatically; on the cube poles octahedral nodules are formed, on the octahedral poles tetrahedral nodules, and on the dodecahedral poles prismatically arranged ridges, and the field between the various poles can be divided into regularly shaped zones according to the structure of the deposit thereon. The value of these indications in determining the orientation of crystals in a metal sheet is discussed. A. R. Powell.

***X*-Ray analysis of copper–tin alloys.** A. Westgren and G. Phragmén (Z. anorg. Chem., 1928, **175**, 80—89; cf. A., 1926, 1084).—X-Ray analysis of alloys of the copper–tin system by the powder method has, in general, confirmed recent work on the equilibria in this system. The maximum solid solubility of tin in copper is 15%, the parameter of the α-lattice increasing from 3·608 to 3·693 Å. by the gradual addition of tin. The β-phase, stable only at high temperatures, has a body-centred cubic lattice (a=2·972 Å. with 5% Sn) in which the tin and copper atoms are irregularly distributed at the lattice points. The γ-phase has a face-centred cubic lattice (a=17·91 Å.) the elementary cube of which contains 416 atoms; the phase is homogeneous when the composition corresponds with $Cu_{31}Sn_8$. The concentration of valency electrons in this formula is the same as in those ascribed to the compounds which Bradley and Thewlis (A., 1926, 1084) investigated in the copper–zinc and copper–aluminium systems, viz., Cu_5Zn_8 and Cu_9Al_4. The ε-phase has an hexagonal structure with the densest sphere packing, the constants for which increase from a=2·747, c=4·319 Å. to a=2·755, c=4·319 Å. (c/a=1·572—1·568) with increasing tin concentration; the tin and copper atoms in this phase also are irregularly distributed at the lattice points, hence the formula Cu_3Sn generally ascribed to ε is not admissible. Alloys containing more than 60% Sn have the nickel arsenide lattice with a=4·190, c=5·086 Å. The tetragonal tin lattice has a base of 5·818 Å. and a height to top of the prism of 3·174 Å. A. R. Powell.

X-Ray analysis of silver–cadmium alloys. H. Åstrand and A. Westgren (Z. anorg. Chem., 1928, **175**, 90—96).—The work of Natta and Freri (this vol., 223) is confirmed and amplified. The parameter of the α-face-centred cubic lattice increases from 4·078 to 4·170 with increase of cadmium from 0 to 44 at.-%. The β-phase contains 49—51 at.-% Cd; the body-centred cubic lattice contains only 2 atoms in the elementary cube (a=3·327 Å.). The region of pure γ extends from 57 to 66 at.-% Cd; the body-centred cubic lattice contains 52 atoms in the elementary cube (a=9·935—9·980 Å.). The γ-phase contains 69—83 at.-% Cd and consists of an hexagonal lattice of densest packing (c/a=1·582—1·559). Above 400° the β-phase undergoes a polymorphic change to β′, the lattice of which resembles that of ε (c/a=1·615). The change point in the cooling curve found by Petrenko and Fedorov (A., 1911, ii, 281) at 200° is not due to a change of phase. A. R. Powell.

Fibrous structure in metals deposited by the difference of electrolytic solution pressures. S. Tsuboi (Mem. Coll. Sci. Kyōtō, 1928, **11**, 271—277).—Silver deposited on copper from silver nitrate solutions forms flat, acicular crystals which have a fibrous structure. The fibre axis lies in the [110] direction, and makes an angle of 30° with the acicular axis, the direction of growth being nearly parallel to the [112] direction. The (111) plane is nearly parallel to the flat surface of the crystal in most of the fibres. C. J. Smithells.

Recrystallisation of aluminium. K. Tanaka (Mem. Coll. Sci. Kyōtō, 1928, **11**, 229—232).—The orientations of 192 single crystals of aluminium were determined and the crystals then extended 4—20% and annealed for 5 hrs. at 600°. No relation between the orientation of the grains formed on recrystallisation and that of the original crystal could be found. C. J. Smithells.

Arrangement of micro-crystals in the banded "supposed aragonite (Arareishi)." H. Fukushima (Mem. Coll. Sci. Kyōtō, 1928, **11**, 223—227).—X-Ray analysis shows that the banded mineral "arareishi," previously supposed to be aragonite, consists of calcite crystals, the principal axes of which are perpendicular to the surfaces of the layers. C. J. Smithells.

X-Ray analysis of copper–magnesium alloys. A. Runqvist, H. Arnfelt, and A. Westgren (Z. anorg. Chem., 1928, **175**, 43—48).—Röntgenographic examination of alloys of the copper–magnesium series proves the existence of two compounds only, namely, Cu_2Mg and $CuMg_2$. The former has a face-centred cubic lattice containing 24 atoms in the elementary cube; the parameter varies from 7·021 to 7·036 Å. within the homogeneous region, which extends at the most through only 1 at.-%. The second compound has a face-centred rhombic lattice the parameters of which are as follows: a=5·273, b=9·05, c=18·21 Å., the axial ratios being 0·295 : 0·497 : 1; the elementary parallelepiped contains 48 atoms. A re-measurement of the constants of the lattice of very pure magnesium gave a=3·203, c=5·196 Å., whence c/a=1·622. A. R. Powell.

Laue photograph taken with convergent X-rays. T. Fujiwara (Mem. Coll. Sci. Kyōtō, 1928, **11**, 283—301).—Some of the spots in the Laue pattern from a tungsten crystal, obtained by using white radiation from a molybdenum target, show the spectrum of the K radiation of molybdenum, from which the orientation of the crystal can be determined. By using a convergent beam of white X-rays the sharpness of the Laue spots is destroyed but the chance of obtaining the spectrum lines is increased. The method is developed for determining the reflecting planes and orientation of the crystal. C. J. Smithells.

Examination of the micro-crystals of calcium carbonate in molluscan shells by means of X-rays. I. J. Tsutsumi (Mem. Coll. Sci. Kyōtō, 1928, **11**, 217—221).—The shell of *Atrina japonica* consists of three layers, the middle or prismatic one having a columnar structure. This layer is shown by X-ray analysis to consist of calcite crystals the principal axes of which coincide with those of the columns. C. J. Smithells.

Crystal structure of carbamide and the molecular symmetry of thiocarbamide. S. B. Hendricks (J. Amer. Chem. Soc., 1928, **50**, 2455—2464).—The unit of the carbamide structure contains 2 mols. and has d_{001} 4·77 Å. and d_{100} 5·73 Å. The space-group is V_d^3; the oxygen atoms are probably at (0, $\frac{1}{2}$, 0·57), ($\frac{1}{2}$, 0, —0·57), the carbon atoms at (0, $\frac{1}{2}$, 0·32), ($\frac{1}{2}$, 0, —0·32), and the nitrogen atoms at (0·13, $\frac{1}{2}$—0·13, 0·20), ($\frac{1}{2}$—0·13, —0·13, —0·20), (—0·13, 0·13+$\frac{1}{2}$, 0·20), and (0·13+$\frac{1}{2}$, 0·13, —0·20).

Thiocarbamide has a simple orthorhombic lattice; the unit contains 4 mols. and has d_{001} 8·57 A.,

d_{010} 7·68 Å., and d_{100} 5·50 Å., the suffixes referring to the crystallographic axes. The space-group is V_h^{16}, the sulphur and carbon atoms being at (0, u, v), ($\frac{1}{2}$, $\frac{1}{2}-u$, v), (0, $u+\frac{1}{2}$, $\frac{1}{2}-v$), and ($\frac{1}{2}$, u, $v+\frac{1}{2}$), and the nitrogen atoms occupying the general positions. The crystallographic evidence favours a symmetrical formula for thiocarbamide. S. K. TWEEDY.

Crystal structure of topaz. L. PAULING (Proc. Nat. Acad. Sci., 1928, **14**, 603—606).—With the help of the co-ordination theory of ionic crystals a structure for topax has been predicted which agrees satisfactorily with the experimental X-ray data obtained by Leonhardt (Z. Krist., 1924, **59**, 216). The fundamental polyhedra for topaz are assumed to be an octahedron of oxygen and fluorine anions about each aluminium ion and a tetrahedron of oxygen ions about each silicon ion. The anion–anion distance determining the length of a polyhedron edge is taken to be 2·72 Å. throughout (A., 1927, 399). Assuming the polyhedra to be regular, the edges of the unit structure are d_{100} 4·72, d_{010} 8·88, and d_{001} 8·16 Å. The unit contains 4 mols. of $Al_2SiO_4F_2$. Each aluminium octahedron shares two edges with adjoining octahedra, and the four corners occupied by oxygen ions, and defining these edges, are shared with tetrahedra. The other two corners, occupied by fluorine ions, are shared with octahedra. The oxygen ions, although crystallographically of three kinds, are, from the point of view of the co-ordination theory, alike, for each is attached to two aluminium octahedra and one silicon tetrahedron. Each fluorine ion is shared between two octahedra. The arrangement of the oxygen and fluorine ions is that of double hexagonal close packing. It is probable that a consideration of the effect of deformation will give values for the edges of the unit of structure in still better agreement with those observed. M. S. BURR.

Constitution of tungsten carbides. K. BECKER (Z. Elektrochem., 1928, **34**, 640—642).—The carbides were prepared by burning a tungsten wire in a mixture of hydrogen with suitable quantities of acetylene or methane. The conductivities of such carburetted wires are recorded. The carbide stable above 2400° (Skaupy, this vol., 381) is a modification (β-form) of the carbide W_2C; it forms crystals which break down noisily to a crystalline powder above the transition point. This form may be supercooled to the ordinary temperature, but if pulverised it changes into α-W_2C. X-Ray photographs show that the α-variety forms hexagonal closest-packed crystals, the structure being of the cadmium iodide type. The carbon atoms are at (0, 0, 0) and the tungsten atoms at ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}+p$) and ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{4}-p$), where p=0·02 approximately. The X-ray data for the carbide WC agree with those of Westgren and Phragmén (A., 1926, 1084). In these carbides the domain of the carbon atom is the same as in diamond. The mean coefficients of linear expansion of the carbides were determined in two axial directions by X-ray methods; the carbide W_2C exhibits greater anisotropy than the carbide WC. S. K. TWEEDY.

Structure of acetylene. J. K. MORSE (Proc. Nat. Acad. Sci., 1928, **14**, 645—649).—Regarding acetylene as an ethane molecule from which four hydrogen atoms have been removed, the co-ordinates of the dynamic isomerides of acetylene, in terms of R, the radius of the carbon atom, have been determined as previously for ethane (this vol., 351) and methane (this vol., 461), and the moments of inertia of these structures compared with the moments of inertia obtained from band-spectra analysis (Levin and Meyer, this vol., 570). The value obtained by the latter method is $2{\cdot}4\times10^{-39}$ g. cm., which is in close agreement with that calculated for the largest number of dynamic isomerides. The method of investigation employed appears to be of wide application. In connexion with acetylene itself it might prove a convenient starting point for (1) the interpretation of X-ray diffraction effects from solid acetylene and the determination of the lattice structure, (2) the study of the relative abundance of the various dynamic isomerides by an analysis of the effect of temperature on the intensities of these bands, and (3) a study of the possible electron configurations in the acetylene molecule and the physical effects to be expected from them. M. S. BURR.

X-Ray investigation of long-chain compounds. A. MÜLLER (Proc. Roy. Soc., 1928, **A**, **120**, 437—459; cf. A., 1927, 503).—The hydrocarbon from supa oil, believed to be triacontane by Robertson and others (cf. B., 1927, 172), is now shown by determination of crystal structure to be the *hydrocarbon* $C_{29}H_{60}$, the $C_{30}H_{62}$ hydrocarbon having been synthesised and examined alongside for comparison. The dimensions of the unit cell are a=7·45, b=4·97, c=77·2 Å., and the angles between its faces are all 90°. The other constants have been determined and are summarised. J. L. BUCHAN.

Crystal structure of monomethylammonium chlorostannate and chloroplatinate. R. W. G. WYCKOFF (Amer. J. Sci., 1928, [v], **16**, 349—359).—The atomic arrangement of monomethylammonium chlorostannate, $(NH_3Me)_2SnCl_6$, is a distortion of the fluorspar structure. The unit cell contains a single molecule; α=50° 14′, a_0=8·42 Å. Monomethylammonium bromostannate and chloroplatinate have similar structures. In the latter α=48° 46′, a_0=8·31 Å. C. W. GIBBY.

Crystal structure of solid methane. J. C. MCLENNAN and W. G. PLUMMER (Nature, 1928, **122**, 571—572).—In an X-ray "powder" investigation of methane at a temperature between those of liquid air and liquid hydrogen, only a cubic form was observed, the structure being based on a face-centred lattice; the unit cell of edge 6·35 Å. contained 4 mols. of methane, whence $d_{calc.}$ is 0·413. A. A. ELDRIDGE.

Crystal structure of cinnabar and covellite. B. GOSSNER and F. MUSSGNUG (Zentr. Min. Geol., 1927, *A*, 410—413; Chem. Zentr., 1928, i, 2049).—Cinnabar has a 4·17, c 9·50 Å.; space-group D_3^4 or D_3^6. Covellite, CuS, has a 3·81, c 16·46 Å.; space-group D_{6h}^4, with six molecules in the unit cell. A. A. ELDRIDGE.

Crystal structure of pyrargyrite. B. GOSSNER and F. MUSSGNUG (Zentr. Min. Geol., 1928, *A*, 65—73; Chem. Zentr., 1928, i, 2049—2050).—Rhombohedral pyrargyrite, Ag_3SbS_3, has r 7·07 Å., α 104° 1′; space-group C^6_{3r}. The unit cell contains two molecules. The positions of the atoms are discussed.

A. A. ELDRIDGE.

Structure of β-corundum. C. GOTTFRIED (Z. Krist., 1928, **66**, 393—398; Chem. Zentr., 1928, i, 2050).—The unit cell, containing 12 mols., has a 5·63, c 22·63 Å.; space-group D^4_{6h}.

A. A. ELDRIDGE.

Crystal structure of pentaerythritol. A. NEHMITZ (Z. Krist., 1928, **66**, 408—416; Chem. Zentr., 1928, i, 2050).—Evidence is adduced for the view that pentaerythritol has no polar axis; hence the space-group is S^2_4.

A. A. ELDRIDGE.

Crystal structure of pentaerythritol tetra-acetate and tetranitrate. A. GERSTÄCKER, H. MÖLLER, and A. REIS (Z. Krist., 1928, **66**, 355—392; Chem. Zentr., 1928, i, 2050).—Pentaerythritol tetra-acetate has a 12·18, c 5·58 Å., with two molecules in the unit cell; space-group C^3_{4h}; the tetranitrate has a 9·38, c 6·09 Å., with two molecules in the unit cell; space-group V^4_d.

A. A. ELDRIDGE.

X-Ray study of some triclinic-pinacoidal crystals. A. GERSTÄCKER, H. MÖLLER, and A. REIS (Z. Krist., 1928, **66**, 421—433; Chem. Zentr., 1928, i, 2047).—r-Tartaric acid monohydrate has (100) 8·3, (001) 4·95, (111) 11·2 Å.; anhydrous, (100) 14·6, (010) 9·6, (001) 4·9 Å. Malonic acid has (010) 11·2, (001) 5·2, $(\bar{1}10)$ 5·3 Å. Potassium persulphate has (100) 7·4, (010) 6·55, (001) 7·4, (101) 5·11 Å.

A. A. ELDRIDGE.

Structure of triclinic-pinacoidal crystals and racemate formation. A. REIS (Z. Krist., 1928, **66**, 417—420; Chem. Zentr., 1928, i, 2047).—A discussion.

A. A. ELDRIDGE.

Form of organically deposited calcium carbonate, and influence of the medium. F. ULRICH (Z. Krist., 1928, **66**, 513—515; Chem. Zentr., 1928, i, 2072).—The calcium carbonate deposited at 15—22° by *Cyanophyceæ* from nutrient solutions containing calcium is rhombohedral, the habit varying with the concentration of the agar-agar.

A. A. ELDRIDGE.

Crystal structures of the alkaline-earth metals. G. L. CLARK, A. J. KING, and J. F. HYDE (Proc. Nat. Acad. Sci., 1928, **14**, 617—618).—Calcium, strontium, and barium, of a purity greater than 99·9%, have been prepared, and the crystal structures examined by the Hull powder method of X-ray spectrography. The results are in full agreement with those of Hull (Physical Rev., 1921, **17**, 42). Barium crystallises in the cubic system with a unit cell of two atoms and constant 5·04 Å., forming a body-centred cubic lattice; $d_{\text{calc.}}$ 3·52. Sharp spectra could not be obtained for strontium. At the most only seven ill-defined diffraction lines were observed. Simon and Vohsen (this vol., 694), from the results of crystal analyses, assign a face-centred cubic lattice to strontium, with the constant 6·03 Å., but consider that a hexagonal modification may be possible at high temperatures. Two of the seven lines might be made to agree with the structure given by Simon and Vohsen. The fact that strontium is a transition step between calcium and barium may account for its anomalous behaviour. It is predicted that radium probably crystallises as a body-centred cubic lattice.

M. S. BURR.

Light figures of copper and iron. G. TAMMANN and A. A. BOTSCHWAR (Z. anorg. Chem., 1928, **175**, 121—130).—When a fine ray of light is passed through a pin-hole in a piece of photographic paper on to an etching pit in a deeply etched crystal surface of copper or iron a light figure is reflected on to the paper in a form characteristic of the orientation of the crystal and of the angle of incidence of the light. When the incident ray is perpendicular to the reflecting surface an octahedral plane produces a figure composed of three intersecting lines of equal length at an angle of 120° to one another, a cube plane gives a "webbed" cross and a rhombic dodecahedral plane a straight line. The value of light figures in determining the orientation of the crystal faces on a metal surface is illustrated with reference to a copper single-crystal sphere deeply etched with ammonium persulphate.

A. R. POWELL.

Etching phenomena on copper single crystals. G. TAMMANN and F. SARTORIUS (Z. anorg. Chem., 1928, **175**, 97—120).—When a single-crystal copper sphere is etched with a suitable reagent, small, bright surfaces of regular shape joined by bright lines appear regularly disposed over the surface of the sphere. The bright lines form the boundaries of a series of circular planes intersecting at the centre of the sphere. Along two of these circles in planes at right angles to one another are arranged alternately cube faces and rhombic dodecahedral faces. If one of the cube faces is considered as the north pole, another will be at the south pole and four others arranged equidistantly round the equator, whilst one of the twelve dodecahedron faces will be midway between every pair of cube faces and one of the eight octahedron faces in the middle of the four quadrants of each hemisphere. If the sphere is etched with ammonium persulphate twenty-four (201) faces will also appear regularly oriented over the surface, whereas etching with ammoniacal persulphate develops only the octahedron faces together with bright lines joining these to the points at which the cube faces normally appear. Etching with nitric acid and mercurous nitrate produces a diamond network of bands joining the (111) to the (100) poles, and etching with 50% nitric acid containing 0·5% of silver nitrate develops the octahedron poles and lines joining them to one another. The rate of dissolution of the metal is greatest at the bright spots in the etching figures developed by the attack of the solvent. If a single-crystal cylindrical rod is allowed to remain for some hours in a solution of ammonium persulphate the cylinder becomes a twelve-sided prism, the indices of the sides being (two opposing sides having the same index) successively (111), (052), (353), $\bar{9}$91), (301), and $(\bar{3}1\bar{2})$, the length of the sides and hence their rate of dissolution increasing in the order given. The changes in reflexion of etched copper spheres and the shapes of the etching figures developed by different reagents are discussed at some length.

A. R. POWELL.

Electrons and symmetry. P. Vinassa (Nuovo Cim., 1927, 4, 981—998; Chem. Zentr., 1928, i, 1931—1932).—An application of the view that electron arrangement obeys the laws of crystallographic symmetry to considerations of valency, polyatomicity, photographic phenomena, and phosphorescence. A. A. Eldridge.

Theory of crystal growth. I. N. Stranski (Z. physikal. Chem., 1928, **136**, 259—278).—It is assumed that the surface layer of a crystal is essentially similar to the inner layers and that units in the surface take up mean positions forming a continuation of the inner lattice, and, further, that these positions correspond with minimum energy values. On this basis it is possible to express quantitatively the growth or dissolution of a crystal in terms of the work necessary to remove to infinity from their mean positions of rest the various units of the surface layer. Calculations made for a crystal of the sodium chloride type are in fair accord with experimental results. F. G. Tryhorn.

Structure of quenched carbon steel. G. Kurdumov and E. Kaminsky (Nature, 1928, **122**, 475—476).—*X*-Ray examination of quenched carbon steels containing 0·64—1·44% C shows that the tetragonal structure exists not only at the surface but also at a depth of 5 mm. The length of the *c* axis increases, whilst that of the *a* axis diminishes, with increasing carbon content. In steel containing 1·03% C the ratio *c/a* is constant (1·041—1·045) for initial temperatures of 900°, 1100°, and 1300°; in steel containing 0·91% C the diminution of the ratio commences at 850°. Inhomogeneity of the tetragonal structure causes diffusibility of the lines of the *X*-ray photograms. Austenite was present in all specimens. Honda's β-martensite is probably a mixture of tetragonal crystals with different small ratios of the axes. Sekito's results (cf. B., 1928, 713) are criticised. A. A. Eldridge.

Existence of an isomorphism, forbidden by the strict structure theory, of crystals of hexammine, aquopentammine, and diaquotetrammine complexes of high elements of symmetry. O. Hassel (Norsk. geol. Tidsskr., 1927, 9, No. 1, 6 pp.; Chem. Zentr., 1928, i, 1360).—It is considered that crystallographically equivalent positions in crystals of complex cobalt compounds are not always occupied by chemically identical groups. The lattice structure of the compounds $[Co(NH_3)_6SO_4]Br$, $[Co(NH_3)_6]SO_4I$, $[Co(NH_3)_5H_2O]SO_4I$, $[Co(NH_3)_5H_2O]SO_4Br$, the corresponding chromium compounds, and compounds in which the sulphur was substituted by selenium or chromium is discussed. A. A. Eldridge.

Crystals of 5-methylamino-3-methylhydantoyl-5-methylamide. J. J. P. Valeton (Z. Krist., 1928, **66**, 516; Chem. Zentr., 1928, i, 2075).—The crystals, m. p. 187°, are triclinic holohedral. $a : b : c =$ 1·2493 : 1 : 1·0012, α 90° 38′, β 93° 52′, γ 107° 39′. A. A. Eldridge.

Theory of the meso-structure of organic compounds. I. Kotŭkov (Bull. Siberian Inst. Tech., 1927, **48**, No. 1, 35 pp.; Chem. Zentr., 1928, i, 1944—1945).—The strength of linkings is considered to change quite gradually in the series methane, hexahydrobenzene, benzene, ethylene, acetylene; the stronger is the affinity claim of one carbon atom for others, the smaller is the affinity remaining for the neighbouring hydrogen atom. If the carbon–hydrogen linking is weak, the hydrogen possesses a residual affinity called “ mesovalency.” The view is applied to the explanation of *cis–trans*-isomerism, ease of hydrolysis, polymorphism, etc. A. A. Eldridge.

Magnetic susceptibility of sodium and potassium. C. T. Lane and E. S. Bieler (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 117—123; cf. McLennan, Ruedy, and Cohen, A., 1927, 1017).—The magnetic susceptibilities of sodium and potassium are found to be $0·67 \times 10^{-6}$ and $0·60 \times 10^{-6}$, respectively. The metals were distilled three times, and the iron content was too small to affect the accuracy of the results. C. W. Gibby.

Mol. wt. of saturated vapours by the effusion method. H. E. Eyring (J. Amer. Chem. Soc., 1928, **50**, 2398—2401).—The liquid, of vapour pressure p_1, is allowed to evaporate in an evacuated glass apparatus and the time necessary for the pressure in a receiving chamber beyond the glass orifice (0·1 sq. mm.) to reach some predetermined value, p_2, is measured. The time taken by air at p_1 to produce a pressure p_2 beyond the orifice is also measured. The apparatus is simple and the method is rapid and accurate to 1%. The measurement with air may be dispensed with if the times taken by liquids to set up a pressure equal to some definite fraction (*e.g.*, one half) of p_1 are always measured. Theoretical considerations show that these times are independent of p_1 and so the apparatus may be calibrated permanently. No appreciable association of saturated water vapour, of the vapour from constant-boiling hydrochloric acid, or of organic vapours was detected with the apparatus. S. K. Tweedy.

Electrical resistance of alloys under pressure. C. W. Ufford (Physical Rev., 1928, [ii], **32**, 505—507).—Average pressure coefficients to 12,000 kg./cm.^{2} of electrical resistance for lithium–tin, bismuth–tin, and calcium–lead alloy series, and for a 10% magnesium in calcium alloy are given. The variation of the pressure coefficient with concentration, the temperature coefficient, and the relative change of the latter with pressure is comparable with structural variation as given by equilibrium diagrams. The conductivity and the pressure coefficient of a dilute solid solution of bismuth in tin are the same as those of pure tin under pressure. As hydrostatic pressure and impurities have the same effect on the pressure coefficient, electric conduction probably depends on the geometrical properties of the conductor. R. A. Morton.

Change of resistance of lead by the action of radium. K. Prasad and S. Basu (Nature, 1928, **112**, 610).—A temporary change in the resistance of lead takes place when a thin plate of the metal is exposed to the action of β-particles and γ-rays from radium. A. A. Eldridge.

Electrical conductivity of vaporised potassium chloride. T. Peczalski and J. Chichocki (Compt.

rend., 1928, **187**, 534—536).—The measurements were made by means of copper electrodes in a glass tube heated in a furnace. The resistance of the vapour increased with the length of time of heating from $0·7\times10^{-5}$ to $2·8\times10^{-5}$ ohm. The electrodes became polarised. The conductivity is due to the dissociation of the potassium chloride.

W. E. DOWNEY.

Isotherms of monatomic substances and their binary mixtures. XXVI. Isotherms of helium at −183·0° and −201·5° and 3—8 atm. G. P. NIJHOFF and W. H. KEESOM. **XXVII. Isotherms of helium between −103·6° and −259·0° and 1·5—14 atm.** G. P. NIJHOFF, W. H. KEESOM, and B. ILIIN (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 404—409).—The construction of two closed manometers for use between pressures of 2 and 6 atm. is described. The required isotherms of helium have been determined by the method previously given (A., 1926, 463). Values of B_A have been calculated and plotted against temperature along with those of other investigators.

M. S. BURR.

Isotherms of diatomic substances and their binary mixtures. XXXIV. Isotherms of hydrogen at 0° and 100°. XXXV. Isotherms of hydrogen at −225·5° to −248·3° and 1·6—4·2 atm. G. P. NIJHOFF and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 410—414). —Values of B_A and C_A have been calculated from the experimental data obtained at the higher temperatures and of B_A from those at the lower temperatures.

M. S. BURR.

Effect of magnetic fields on thermal conductivity of iron, copper, gold, silver, and zinc. H. M. BROWN (Physical Rev., 1928, [ii], **32**, 508—514).—In a longitudinal field of 10,000 gauss iron showed a 1·14% decrease in heat conductivity, whilst a transverse field of 4000 gauss caused a 0·4% decrease. For copper, the 10,000 gauss field caused a 0·23% decrease. The remaining metals showed no change greater than 0·04%. The values of electrical and thermal conductivity were higher in crystal bars than in the ordinary cast form, but magnetic fields produced no change in either case.

R. A. MORTON.

Generalised Gibbs–Boltzmann equation. F. R. BICHOWSKY (Physical Rev., 1928, [ii], **32**, 494—496).—Mathematical. A generalised form of the Gibbs–Boltzmann canonical equation is derived without the assumption of the Maxwell distribution law. The equation allows a treatment of statistics of the most generalised type of systems.

R. A. MORTON.

Chemical equilibrium in the vapour of a mixture of paraffins and unsaturated hydrocarbons. H. A. WILSON.—See this vol., 1190.

Steam tables and equations, extended by direct experiment to 4000 lb./sq. in. and 400°. H. L. CALLENDAR (Proc. Roy. Soc. 1928, **A**, **120**, 460—472).—The densities of water and steam have been investigated near the critical point. It is found that they are not equal at this point, 374°, but at about 380°, there being an unstable region of equilibrium between these temperatures. This is illustrated by curves, which do not agree with those calculated from a formula of the Thiesen type. The total heat has also been measured for water and for steam, and it is shown that air-free water gives values for H and h which are different from those given by ordinary distilled water, and the curves so obtained agree with those found by the previous method. The equations for the total heat, the entropy, and the saturation pressure have been extended, and are discussed. Extended steam tables for the equilibrium states of steam up to 4000 lb. pressure have been calculated.

J. L. BUCHAN.

Entropy and vibration frequency of solid inorganic compounds. W. HERZ (Z. anorg. Chem., 1928, **175**, 245—248).—It is shown for 44 compounds of the type AB and for 41 compounds of the type AB_2 that the product $S\nu^{1/2}$ is approximately a constant, where S is the entropy of the compound calculated by Latimer's formula (A., 1921, ii, 380) and ν is the vibration frequency. The recorded values of $S\nu^{1/2}$ for the first-named type of compounds vary from 3·49 to 5·94 with a mean value of about 4·5, and for the second type from 5·59 to 8·55 with a mean value of nearly 7.

A. R. POWELL.

Volume studies. III. Calculation of limiting values. F. WRATSCHKO (Pharm. Presse, 1927, **32**, 435—438; Chem. Zentr., 1928, i, 1492).—Limiting values of d_4^0 are computed for various classes of hydrocarbons.

A. A. ELDRIDGE.

Volume chemistry. III. Oxygen compounds. Carbonyl group. F. WRATSCHKO (Pharm. Presse, 1928, **33**, 36—39, 61—63; Chem. Zentr., 1928, i, 1833).—"E-values" for various classes of compounds are calculated.

A. A. ELDRIDGE.

Vapour pressure of barium oxide. M. DE K. THOMPSON and W. G. ARMSTRONG (Amer. Electrochem. Soc., Sept., 1928. Advance copy. 4 pp.). —The vapour pressure of barium oxide between 1280° and 1470° has been determined by Wartenberg's method (A., 1912, ii, 1137).

H. J. T. ELLINGHAM.

Characteristic density and the properties of liquids. W. HERZ (Z. anorg. Chem., 1928, **175**, 277—280).—Values of the quantity $\gamma^{1/3}/(d-d_\kappa)$, where γ is the surface tension, d the density, and d_κ the critical density, have been calculated for a number of organic liquids, and are shown to be approximately constant for any one liquid over a wide temperature range. If the viscosity be employed in place of the surface tension, a constant is again obtained, which, however, below the b. p. decreases slowly with rise of temperature.

H. F. GILLBE.

Measurements on the equation of state for solid argon. F. SIMON and (FRL.) F. KIPPERT (Z. physikal. Chem., 1928, **135**, 113—128).—A method for the direct measurement of the thermal pressure of condensed gases has been devised and the following values of $\partial P/\partial T$ in atmospheres and degrees over temperature intervals from about 68° to 90° Abs. have been obtained: argon (solid), 38, argon (liquid), 25; methane (solid), 28; oxygen (liquid), 24; nitrogen (liquid), 24. The density of solid argon is 1·505 at

76° Abs. The compressibilities in the liquid state for argon at 86° Abs., oxygen at 82° Abs., and nitrogen at 75° Abs. are 180, 169, and 247×10^{-12} abs. units, respectively. The magnitude $\gamma=-d\log\nu/d\log V(=3\alpha V/KC_{v})$ is 4·5 for solid argon, as against 2·3 for metals and 1·8 for ionic lattices. R. A. Morton.

Periodic classification of the hardness and m. p. of the elements. S. A. Korff (Science, 1928, 67, 370—371).—The classification of elements according to hardness and m. p. accords with an 18-period table based on spectroscopic similarities; hence these properties are related to the electronic configuration. A. A. Eldridge.

Internal friction in metals. R. H. Canfield (Physical Rev., 1928, [ii], 32, 520—530).

Thermal conductivity of gas mixtures. H. Grüss and H. Schmick (Wiss. Veröff. Siemens-Konz., 1928, 7, (i), 202—224).—The thermal conductivity (air=1) of mixtures of air with steam, ammonia, acetylene, methane, and carbon monoxide, and of mixtures of carbon monoxide with ammonia, has been determined at atmospheric pressure between 20° and 80°. The conductivity–composition curves for air–ammonia, carbon monoxide–ammonia, air–steam, and air–acetylene mixtures are concave to the composition axis, whereas those for air–methane and air–carbon monoxide are straight lines. The deviation of the first-named series from the mixture rule is ascribed to the presence of dipolar and quadripolar molecules, whereby the attractive force is appreciably reduced with a corresponding decrease in the number of impacts, *i.e.*, an increase in the thermal conductivity. The subject is discussed theoretically and mathematically and the curves derived from this treatment are shown to be in fair agreement with experiment. A. R. Powell.

Determination of the concentration of solutions. G. Jaeger (Ber., 1928, 61, [*B*], 1654—1659).—The concentration of a comparison solution is adjusted until waves do not appear, when it is mixed with the solution under investigation. The maximum error is about 0·2%. The light from a small electric lamp, rendered parallel by passage through a convex lens, passes through a tube containing the comparison solution and is then brought nearly to a focus on a screen. The solution under investigation is added to the comparison solution from a burette fitted with a very narrow jet bent to a right angle beneath the liquid. The relative concentrations are indicated qualitatively by the production and movement of the waves and the comparison solution is adjusted in concentration until these no longer appear. In a second process, the comparison solution in the tube is stronger than that under investigation and is diluted with solvent from a burette until equality of concentration is attained.

H. Wren.

Coefficient of expansion of binary liquid mixtures. K. M. Stachorski (Ukraine Chem. J., 1928, 3, 219—222).—The expression $\alpha=M_1v_1\alpha_1x+M_2v_2\alpha_2(1-x)/M_1v_1x+M_2v_2(1-x)$ is derived, where α, α_1, and α_2 are the coefficients of expansion of the mixture and of its respective components, M_1v_1 and M_2v_2 the gram-molecular volumes of the components, and x is the proportion of one component in the mixture. Values of α calculated from this expression are in good agreement with those found experimentally for mixtures of various organic liquids.

R. Truszkowski.

Dielectric constants of binary mixtures. VII. Electric moments of certain diphenyl derivatives. Their relation to the several structures. J. W. Williams and A. Weissberger (J. Amer. Chem. Soc., 1928, 50, 2332—2336; cf. this vol., 355).—Dielectric constants and densities for benzene solutions of *p*-phenylenediamine, *p*-dichloro-, *p*-dinitro-, *p*-diethoxy-, and *p*-diamino-diphenyl at 25° are recorded. The calculated electric moments of the molecules indicate that in the dichloro-, dinitro-, and diethoxy-derivatives the benzene nuclei are coaxial, whilst in the diamino-derivative the nuclei cannot be extended (cf. Kuhn and Albrecht, A., 1927, 876). A modified apparatus for the accurate determination of dielectric constants is described.

S. K. Tweedy.

Dielectric constants of binary mixtures. VIII. Electric moment as a vector quantity. J. W. Williams (J. Amer. Chem. Soc., 1928, 50, 2350—2357; cf. preceding abstract).—Electric moments, calculated from the dielectric constants and densities of benzene solutions, are recorded for 11 benzene derivatives. A substituent in a molecule is characterised by a definite electric moment which can be considered to be a vector quantity, the electric character being assigned with reference to a standard group (*e.g.*, methyl group). Two substituents do not interact if they are of very simple type; in general, however, the vectors characterising such groups cannot be considered to act in the plane of the benzene ring. Thus, *s*-trinitrobenzene has a finite but small electric moment (cf. this vol., 355), so that interaction between the groups causes them to be extended slightly above the plane of the benzene nucleus. The data offer strong support for the planar structure of the benzene molecule.

S. K. Tweedy.

Application of Debye's dipole theory to binary liquid mixtures. II. J. W. Williams (Physikal. Z., 1928, 29, 683—688).—The electric moment has been calculated from the dielectric constant and density in benzene solutions at 25° for 33 different substances. It is shown that each atom or group substituted in the benzene ring is characterised by a more or less well-defined vectorial moment, *e.g.*, NO_2 −3·8; CHO −2·8; OH −1·7; Cl −1·5; Br −1·5; OMe −1·2; CO_2H −0·9; Me +0·4; NH_2 +1·5. When two or more atoms or groups are substituted in the benzene ring, the reciprocal effects of the substituents cannot in general be neglected. It is probable that the only possible structure for the benzene ring is the arrangement of all the carbon atoms in one plane. The structure of diphenyl and its derivatives cannot be depicted simply. The electric moment of an inorganic molecule can be determined by the method used for organic molecules. Judging from compounds of the type CA_4, there is no simple relation between the structure of a crystal and that of the molecules in solution.

R. A. Morton.

Association in liquid dielectrics. J. Rolinski (Physikal. Z., 1928, 29, 658—667).—Benzene, carbon disulphide, and carbon tetrachloride are dipole-free liquids, whereas ethyl ether, chlorobenzene, and quinoline are typically dipolar. From the relation $P=M/c\ .\ [(\varepsilon-1)/(\varepsilon+2)d-(1-c)(\varepsilon_2-1)/(\varepsilon_2+2)d_2]$, P being the molecular polarisation of a solute of mol. wt. M, c the percentage concentration in grams, ε the dielectric constant of the mixture, d its density, and ε_2, d_2 the values for the solvent, the following values of P were obtained: carbon disulphide (in benzene) 21·1—22·0; carbon tetrachloride 27·3—28·2. In these cases P is independent of the concentration. The volume polarisation of carbon tetrachloride–carbon disulphide mixtures obeys the simple mixture rule. Mixtures containing a dipole-free and a dipolar liquid show that the molecular polarisation of the latter decreases with increasing concentration owing to molecular association. By assuming that the dipolar moments of associating molecules disappear, the degree of association in dipolar liquids is calculated, and it is found that the higher the concentration and the stronger the dipolar moment the greater is the tendency towards association. Binary mixtures of dipolar liquids do not obey the additivity law, the discrepancies being again due to association. R. A. Morton.

Vapour pressures of binary systems; aqueous solutions of orthophosphoric acid, sodium hydroxide, and potassium hydroxide. U. Nakaya (Trans. Faraday Soc., 1928, 24, 543—544).—A continuation of the work of Porter (this vol., 710). For the above solutions calculations are tabulated, equations proposed, and curves are given showing the relation between the molar fractions and the vapour pressures at 100°. Deductions therefrom are discussed. N. M. Bligh.

Physical properties of phenol in benzene. L. E. Swearingen (J. Physical Chem., 1928, 32, 1346—1353; cf. this vol., 703).—The densities, viscosities, and surface tensions of mixtures of benzene and phenol have been determined at 25°. The density–concentration curve is linear. The calculated partial molal volumes of the phenol in the various mixtures are practically constant, indicating that the two components form an ideal solution. It is stated that the viscosity–concentration and the surface tension–concentration curves show minima; that of the former is attributed to association of the phenol molecules in the more concentrated solutions followed by dissociation on dilution, whilst that of the latter is explained on the basis of negative adsorption of the phenol at the phenol–benzene interface. L. S. Theobald.

Electrical conductivity of tellurium and of liquid mixtures of tellurium and sulphur. C. A. Kraus and E. W. Johnson (J. Physical Chem., 1928, 32, 1281—1293).—The specific resistance of pure tellurium has been measured over the range 363—500°, and that of mixtures of tellurium containing up to 85 at.-% of sulphur over the range 382—477°. In all cases, the specific resistance decreases exponentially with rise of temperature, whilst at constant temperature the specific resistance of a liquid mixture increases rapidly with an increase in sulphur content. The specific resistance of liquid tellurium at its m. p. is approximately one fifteenth of that of the solid. Liquid tellurium is, comparatively, a good conductor, its specific conductance, at 500°, being one sixth of that of mercury at the ordinary temperature. Methods and apparatus, including a thermo-regulator giving trustworthy results over the range 200—600°, are described. L. S. Theobald.

X-Ray analysis of thallium–antimony alloys. E. Persson and A. Westgren (Z. physikal. Chem., 1928, 136, 208—214).—Four phases can be recognised in the X-ray analysis of the thallium–antimony system. The lattice of α-thallium is of the close-packed hexagonal type with unit cells of base 3·449 Å. and height 5·513 Å. A second phase, apparently a solid solution of antimony in β-thallium, which occurs in alloys moderately rich in antimony, contains about 7% Sb, and possesses a face-centred cubic lattice of edge 4·842 Å. A second intermediate phase, corresponding in composition with Tl_7Sb_2, has a complex cubic lattice in which the unit cell contains 54 atoms and has an edge of 11·59 Å. Antimony has a face-centred rhombohedral lattice, with an axial angle of 87° 24′ and an edge 6·226 Å.
F. G. Tryhorn.

Recrystallisation of steel, cast but not further treated, after heat treatment. H. Heike and F. Westerholt (Z. anorg. Chem., 1928, 174, 244—256).—The microcrystalline structure and the fracture exhibited by various specimens of cast steel after heating at 700—900° for periods up to 12 hrs. have been studied. Apart from the more or less regular subdivision exhibited by ferrite, that which is not dissolved as mixed crystals up to 800° undergoes no regular orientation on working. The general law of recrystallisation, viz., that particle size is dependent on temperature and working, is valid to only a limited extent. H. F. Gillbe.

Solubility of aluminium bromide in carbon disulphide. H. H. Kaveler and C. J. Monroe (J. Amer. Chem. Soc., 1928, 50, 2421—2426).—Aluminium bromide, m. p. 97·1°, was prepared by passing a mixture of hydrogen and bromine vapour over aluminium at 400°. The salt is very soluble in carbon disulphide, *e.g.*, 32·3 mol.-% at 25° and 87·8 mol.-% at 85°. This is in accordance with the principles laid down by Hildebrand. The saturated solutions are dark red in colour, possibly because of solvation. The experimental data show negative deviation from Raoult's law at low temperatures and practically no deviation at higher temperatures. The solutions have an appreciable conductivity. An electrically heated siphon is described for sampling saturated solutions at high, constant temperatures. A method of analysing aluminium bromide is given in which the salt is first converted into the compound $AlBr_3,2PhNO_2$, which is allowed to react with water, the resulting solution being titrated by the Volhard method. S. K. Tweedy.

Solubility of diphenylamine in water, alcohol, and other organic solvents. L. Desvergnes (Ann. Chim. analyt., 1928, [ii], 10, 253—255).—Tables are given showing the solubility of diphenylamine in water, alcohol, and other organic solvents at various temperatures. The solutions in organic liquids containing combined chlorine are deeply coloured, the coloration being due to the presence of a small quantity of free chlorine. Alcoholic solutions become coloured when exposed to light. A. J. Mee.

Solubility relations of isomeric organic compounds. VIII. Solubility of the aminobenzoic acids in various liquids. C. L. Lazzell and J. Johnston (J. Physical Chem., 1928, **32**, 1331—1341; cf. this vol., 579).—The solubilities in benzene, chloroform, ethyl alcohol, and ethyl acetate have been determined at 25° by the analytical method and at temperatures up to the respective m. p. by the synthetic method. Methyl and butyl alcohols were also used as solvents. The results are compared with similar data for the nitroanilines (Collett and Johnston, A., 1926, 237) and for the monosubstituted hydroxy-, chloro-, and nitro-benzoic acids (Sidgwick and Ewbank, J.C.S., 1921, **119**, 979). Corresponding curves, in many cases, are similar in shape, as is the case with the amino-acids in any one solvent, but the irregularities which occur indicate that the solubility even of closely-related compounds is influenced by the specific chemical nature of both solute and solvent. In the present case, no particular solvent offers any special advantage in the separation of the isomerides by crystallisation. Solubility data are given. L. S. Theobald.

Influence of salts on the solubility of other salts in non-aqueous solvents. C. A. Kraus and R. P. Seward (J. Physical Chem., 1928, **32**, 1294—1307; cf. King and Partington, A., 1927, 1020).—Results previously summarised (A., 1927, 1020) are presented and discussed. The solubility of salts in non-aqueous solvents is influenced by the presence of traces of water. The solubility of sodium chloride in *iso*propyl alcohol containing varying amounts of water in the presence of sodium nitrate is recorded. The addition of 2% of water to the alcohol increases the solubility of sodium chloride approximately 2½ times. The diminution of the solubility in the pure solvents on the addition of a salt with a common ion is approximately one fourth that in water, whilst the increase on addition of a salt without a common ion is four times that in water as solvent. The divergence of the experimental results from the Debye–Hückel theory bears no apparent relationship to the dielectric constant and cannot be explained on the basis of a change in dielectric constant due to the added salts. It is suggested that the inter-ionic attraction theory must include factors which take account of the specific attractive forces between the ions and the solvent. L. S. Theobald.

Effect of one salt on the solubility of another in ethyl alcohol solution. III. F. S. Hawkins and J. R. Partington (Trans. Faraday Soc., 1928, **24**, 518—530; cf. A., 1927, 1020).—The influence of sodium iodide and magnesium iodide on the solubility of potassium iodide in alcohol at 25° has been investigated. At concentrations below 0·5N the solubility in sodium iodide and alcohol solutions is given by Brönsted's equation $-\frac{1}{3}\log R=3\alpha(\sqrt{2\mu}-\sqrt{2\mu_0})+\beta c$; where R=activity product ratio$=C_{A_0}C_{B_0}/C_AC_B=$ concentrations of ions A and B in pure solvent÷ their concentrations in a solution of another salt, α and β are constants, c=concentration of added salt, μ_0=ionic strength of salt AB in pure solvent, μ= ionic strength of a solution of the two salts. In the case of magnesium iodide+alcohol solutions evidence is given for the formation in solution of the complex MgI_2,KI. The viscosities and conductivities of the solutions have been measured, and values of the ionic radius were calculated. The conductivity of potassium iodide was also measured. N. M. Bligh.

Wood charcoal as adsorbent for gases. A. Magnus, E. Sauter, and H. Kratz (Z. anorg. Chem., 1928, **174**, 142—144).—The anomalous curvature of the isotherms for the adsorption of carbon dioxide by charcoal at low pressures vanishes if the adsorbent be previously boiled with hydrochloric acid and washed thoroughly. It is probable that the impurity thus removed is alkali or alkaline-earth carbonate, which is converted into oxide when the charcoal is heated in a vacuum before use. H. F. Gillbe.

Adsorption of gases by graphitic carbon. II. *X*-Ray investigation of the adsorbents. H. H. Lowry and R. M. Bozorth (J. Physical Chem., 1928, **32**, 1524—1527; cf. A., 1925, ii, 1053).—An *X*-ray examination of three samples of graphite, graphitic acid, and natural graphite shows that carbon prepared by the explosion of graphitic acid is composed of small graphite flakes, averaging 50 atom diameters across and 10 atom layers thick. The apparent disagreement with the results of Ruff and co-workers (A., 1927, 1138) is explained, and it is reiterated that a graphitic carbon can be prepared which shows an adsorptive capacity of one fourth to one third that of the best adsorptive charcoal. L. S. Theobald.

Unimolecular character of the adsorption of gases by glass and wood-charcoal. H. Zeise (Z. physikal. Chem., 1928, **136**, 385—418).—The adsorption of methane, nitrogen, oxygen, and hydrogen has been studied at pressures from 2×10^{-4} to 7×10^{-2} mm. and 90° Abs., using as adsorbent thin glass microscope cover-glasses separated from one another by means of glass threads. The results can be expressed by the adsorption isotherm $q=\sqrt{k_1k_2p/(1+k_2p)}$, where q=mols. of gas adsorbed/sq. cm., p=pressure, and k_1, k_2 are constants. This expression is also derived theoretically by reasoning similar to that used by Langmuir, assuming that two elementary spaces can adsorb one molecule. The Freundlich isotherm is a first approximation to this expression, which leads to a maximum adsorption at high pressures and is in qualitative agreement with the Langmuir unimolecular layer theory. Measurements of the adsorption of methane, nitrogen, and oxygen at higher pressures (4—307 mm.) support this view. Berényi's confirmation of the Polányi multimolecular adsorption theory based on the results of other workers on the adsorption of gases by charcoal (A., 1920, ii, 591) is criticised. It is shown that the original Langmuir isotherm agrees better with the experimental results cited by Berényi. The theories of Williams and of Iliin are also discussed. O. J. Walker.

Reversal of Traube's rule of adsorption. H. N. Holmes and J. B. McKelvey (J. Physical Chem., 1928, **32**, 1522—1523).—The adsorption of acetic, propionic, butyric, and octoic acids from toluene solutions by silica gel has been measured. Adsorption decreases as the series is ascended, showing the reversal of Traube's rule (cf. Freundlich, "Colloid and Capillary Chemistry," 1926).

L. S. Theobald.

Adsorption in solutions. XVI. Reversal of Traube's adsorption law. B. Nekrassov (Z. physikal. Chem., 1928, **136**, 379—384).—The adsorption of the normal fatty acids (C_1—C_9) by sugar charcoal from aqueous solution has been examined. Traube's adsorption law is completely reversed, probably on account of the strongly polar nature of the charcoal. H. F. Gillbe.

Existence of Volmer's adsorption layer. F. Moll (Z. physikal. Chem., 1928, **136**, 183—185).—Positive evidence for the existence of adsorption layers on mercury has been obtained with phthalic anhydride, coumarin, and diphenylmethane. Paraffin and cetyl alcohol, which do not wet mercury, gave negative results. A new interference method for the detection of these layers gave satisfactory results with benzophenone and salol. F. G. Tryhorn.

Adsorption and dissolution phenomena encountered in precipitations. F. R. Balcar and G. Stegeman (J. Physical Chem., 1928, **32**, 1411—1421).—The adsorption of thorium by barium sulphate when the latter is precipitated from solutions of thorium chloride has been investigated. The redissolving of the adsorbed thorium increases with time and stirring, and the particle size of the precipitated barium sulphate passes through a maximum and a minimum when the concentration of the thorium chloride solution increases. The solubility, S, of barium sulphate in thorium chloride of concentration C (mol./litre) can be represented by $\log S=0{\cdot}68 \log C+0{\cdot}0789$; the solubility of lead sulphate also can be similarly represented. The influence of barium chloride on the solubility of barium sulphate in the thorium chloride solution has also been investigated. The variations in the "constants" for the adsorption of thorium by barium sulphate are discussed. L. S. Theobald.

Structure of salts adsorbed on cellulose. R. H. Aborn and R. L. Davidson (Nature, 1928, **122**, 440).—X-Ray examination of salts (sodium chloride and tungstate) adsorbed on cellulose shows that up to a certain saturation concentration the salt is molecularly or ionically dispersed throughout the cellulose units, whilst above that concentration it is probably held mechanically. No new structural arrangement was observed. A. A. Eldridge.

Blue coloration given by iodine in presence of starch. E. Angelescu and J. Mircescu (J. Chim. phys., 1928, **25**, 327—342).—In the adsorption of iodine and potassium iodide by starch it would seem that the potassium iodide is adsorbed as potassium tri-iodide and that most of the iodine is taken up in this way. The blue colour formed is due to free iodine either directly adsorbed or liberated from the adsorbed potassium tri-iodide, and is not due to chemical combination between iodine and starch. This is also the case for starch in colloidal solution. With reference to the colour change blue $\rightleftharpoons$ violet $\rightleftharpoons$ red which may occur in iodine–starch solutions, observations on the influence of electrolytes on the colour changes in dextrin–iodine solutions and also on the viscosity of starch solutions lead to the conclusion that substances which increase the degree of dispersion of the colloidal particles tend to produce a red colour and conversely. These colour changes are interpreted in a similar manner to the colours of colloidal gold solutions.

L. F. Gilbert.

Reversible and irreversible chemical phenomena at interfaces. D. Deutsch (Z. physikal. Chem., 1928, **136**, 353—378).—Aqueous solutions of certain indicators when shaken with immiscible inert liquids such as hydrocarbons show a colour change at the interface. Acidic indicators show an apparent acidification and basic indicators the reverse. The change of colour vanishes as the two liquids separate. Air produces a similar effect, the foam on a yellow solution of thymolsulphonephthalein being violet in colour. Aqueous solutions of heavy metal salts of coloured acids, *e.g.*, the silver salt of eosin, undergo a colour change when shaken with inert liquids, and the salt is precipitated. It appears therefore that the ionisation at the interface between an aqueous solution and air or a liquid having a smaller dielectric constant than the solution is less than in the body of the solution. A colourless benzene solution of a dye exhibits at the interface between the solution and water a colour change which is ascribed to the disturbance of a lactoid–quinonoid equilibrium, whereas the corresponding phenomenon with rhodamine ester solutions is due to increased dissociation of the ester at the interface. The increased aggregation of colloidal particles in the surface of aqueous solutions is a result of the greater surface activity of the larger particles compared with that of the smaller, whilst the relatively small lowering of surface tension produced by hydrophobic colloids is due to the reduction of the number of particles present in the surface.

H. F. Gillbe.

Surface tension and solvation in salt solutions. P. P. Kosakewitsch (Z. physikal. Chem., 1928, **136**, 195—207).—Measurements of the surface tension of solutions of alkali halides in pyridine, acetone, methyl alcohol, formic acid, and in mixtures of ethyl alcohol and water show that the usual lyotrope series $Cl>Br>I$ and $K>Na>Li$ are reversed for solutions in these solvents. For mixtures of alcohol and water a minimum usually occurs in the surface tension as the amount of alcohol in the mixture is increased. It is suggested that the solutes in these solutions are bound partly to alcohol molecules (solvation) and partly to water molecules (hydration) and that inversion of the lyotrope series occurs as the extent of solvation diminishes. F. G. Tryhorn.

Permeability of colloidal substances to gases. K. Kanata (Bull. Chem. Soc. Japan, 1928, **3**, 183—188).—The relative permeabilities of membranes of rubber, celluloid, and gelatin with respect to hydrogen, oxygen, carbon dioxide, and ammonia were determined. The sorption is not an adsorption phenomenon. The mechanism of the permeability is discussed, and it is shown that viscosity flow is not the main cause, but that the permeability is probably due to the dissolution of the gas in the membrane.

A. J. Mee.

Osmosis of ternary liquids. III. F. A. H. Schreinemakers and B. C. van B. Walter (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 560—568; cf. this vol., 702).—In extension of previous work, the directions in which substances will pass through membranes are investigated mathematically.

A. J. Mee.

Osmosis of ternary liquids. General considerations. V. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 459—468).—Preceding communications (cf. this vol., 583) have dealt with a "theoretical" membrane which does not contain any of the diffusing substances. The "real" membrane, containing some of the diffusing substances, is now considered. M. S. Burr.

Apparatus for the determination of electro-endosmosis. N. Schönfeldt (Wiss. Veröff. Siemens-Konz., 1928, 7, (1), 301—303).—The apparatus comprises a central horizontal tube which carries the diaphragm and is bent upwards at right angles at both ends, the openings being ground to admit the shorter arms of two inverted U-tubes carrying the measuring capillaries. The longer arms of these U-tubes are joined by means of conical ground glass joints to the longer arms of the electrode U-tubes, the shorter arms of which are closed with rubber stoppers carrying zinc plate electrodes. The electrode tubes are filled with zinc sulphate solution (d 1·5), which, in the longer arms of the tubes, is covered with a layer of glycerin added in two portions, the lower portion mixed with a little zinc sulphate solution and the upper with a little of the solution to be tested. The remainders of the tubes on both sides of the diaphragm are filled with the solution to be tested; observations are made successively from both directions and the mean value is taken, so as to avoid variations in the concentration. A. R. Powell.

Diaphragms. II. Porosity and endosmosis. K. Illig and N. Schönfeldt (Wiss. Veröff. Siemens-Konz., 1928, 7, (1), 294—300).—Some results obtained with potassium chloride and copper sulphate solutions in a new apparatus for determining endosmotic processes (cf. preceding abstract) are recorded using diaphragms of varying porosity. Assuming the validity of the Helmholtz formula, the results show that the charge on the diaphragm decreases with increasing porosity, whereas this charge has always been considered to be a material constant dependent only on the nature of the substance of which the diaphragm is made and on the solution in which it is immersed.

A. R. Powell.

Lyotropic properties of the nitrite ion. D. Deutsch and S. Loebmann (Kolloid-Z., 1928, 46, 22—23).—Some physical properties of nitrite solutions have been examined with the view of assigning a place to the nitrite ion in the lyotropic series. Measurements of the surface tension of solutions of sodium nitrite show that the increase in surface tension bears a linear relation to the concentration over a wide range. Comparison of the curve with those obtained with other sodium salts gives the series F, Cl, NO_3, NO_2. Determination of the coagulation value of a positively-charged ferric oxide sol for potassium nitrite and for other potassium salts gave the series NO_3, Cl, CNS, NO_2, the value for the nitrite ion being very close to that for the thiocyanate ion. Experiments were also conducted on the influence of potassium salts on the partition of basic colouring matters between a benzene phase and a water phase. The following series was obtained: Cl, NO_3, I, SCN, NO_2. It is concluded that the position of the nitrite ion is in the neighbourhood of iodide and thiocyanate. E. S. Hedges.

Influence of pressure on the temperature of maximum density of water and of solutions of varying concentration. G. Tammann and E. Schwarzkopf (Z. anorg. Chem., 1928, 174, 216—224).—Isobars for aqueous solutions of lithium chloride, hydrogen chloride, and ethyl alcohol have been determined by the dilatometric method over the temperature ranges −1° to −72°, −1° to −38°, and +0·4° to −15·6°, respectively. The temperature of maximum density of lithium chloride solutions decreases in a linear manner as the concentration increases from 0 to 27%, but thereafter the fall is much more rapid; for 22·5, 28·05, and 31·1% solutions the observed temperatures are −26·5°, −42°, and −57·5°, respectively. The corresponding values for 11·1 and 13·6% ethyl alcohol solutions are −0·2° and −2·8°, and for 8·1% hydrogen chloride, −12°.

H. F. Gillbe.

Relation between the internal pressure of solutions and the nature of the dissolved substance. G. Tammann (Z. anorg. Chem., 1928, 174, 231—243).—The change $\delta\kappa$ of the internal pressure of a liquid when a non-volatile substance is dissolved therein yields a measure of the molecular attraction between solvent and solute. The relation between this attraction and the nature of the solute is subject to three rules: (1) the attraction for strong electrolytes is additive, and suggests complete ionisation at concentrations up to N; that of the ions is specific and decreases with the ionic volume; (2) for weak electrolytes and non-electrolytes, which have an internal pressure greater than that of water, the attraction is not differentiated from that shown by strong electrolytes; (3) for volatile non-electrolytes the relation between molecular attraction and concentration is complex in character; in dilute solutions negative $\delta\kappa$ values are obtained which usually pass through a minimum as the concentration increases.

H. F. Gillbe.

Apparent hydration of ions. II. Densities and viscosities of mixed aqueous solutions of lithium chloride and hydrochloric acid. J. W. Ingham (J.C.S., 1928, 2381—2388; cf. this vol., 948).—The densities of concentrated mixed aqueous solutions of lithium chloride and hydrochloric acid may be calculated with fair accuracy by means of the equation $d=K+k_1a+k_2b$. Scarpa's method (A., 1911, ii, 17) for the measurement of viscosities gives results which agree well with those obtained by the Ostwald U-tube method. It is suggested that the decrease in viscosity which accompanies the replacement of lithium chloride by hydrochloric acid in these solutions is due to the greater hydration of the lithium ions as compared with the hydrogen ions. It is further shown that lithium ions are hydrated to a greater degree than sodium ions under the same conditions and that the degree of hydration decreases as the proportion of acid in the solution increases. From a consideration of the viscosities of mixed solutions of lithium, sodium, or potassium chlorides and hydrochloric acid it is apparent that variations of free space alone (cf. McLeod, Trans. Faraday Soc., 1926, 22, 401) cannot account for the viscosity effects.

F. J. Wilkins.

Spectroscopic method of studying the formation of complex salts in dilute solution. II. Y. Shibata and T. Inoue (Japan. J. Chem., 1926, **2**, 109—115).—By a spectroscopic method previously described (*ibid.*, 1922, **1**, 1), the formation of complex mercuric salts has been studied. On plotting the wave-length corresponding with the end of the absorption spectrum for various mixtures of two salts a maximum is found when a complex salt is formed, the position of the maximum indicating the composition of the complex salt. The greater the dilution at which this maximum can be observed the more stable is the complex salt. Mixtures of mercuric chloride with a number of chlorides, bromides, iodides, and thiocyanates have been examined. The general similarity in the behaviour of these mixed solutions suggests a similarity of constitution. They probably all contain a mercury atom as the central metallic atom in a complex radical. In the case of mixtures of chlorides, the greater the number of chlorine atoms which are contained in the complex ion the more stable is the complex salt; *e.g.*, the salts obtained with chlorides of univalent metals, forming the ion $[HgCl_3]M^{\cdot}$ or $[HgCl_3(H_2O)_3]M^{\cdot}$, are less stable than those with chlorides of bivalent metals forming the ion $[HgCl_4]M^{\cdot\cdot}$ or $[HgCl_4(H_2O)_2]M^{\cdot\cdot}$, and so on. Those in which the second component is not a chloride are generally far more stable than those containing only chlorine atoms in the complex ion. In general the complex salts examined are far more stable in alcoholic than in aqueous solution.

M. S. Burr.

Spectrochemical studies on complex formations between mercuric salts and other metallic salts in dilute aqueous solutions. I. Formation of complex salts due to double decomposition of mercuric salts. II. Formation of complex salts in solution between mercuric cyanide and other metallic salts. T. Inoue (Japan. J. Chem., 1928, **3**, 131—146, 147—163).—I. The absorption spectrum method (cf. *ibid.*, 1922, **1**, 1; also preceding abstract) has been applied to the study of solutions containing mercuric salts and other metallic salts. The absorption curves for the systems mercuric nitrate–metallic chloride and mercuric sulphate–metallic chloride all show a minimum for the mixture containing two atoms of chlorine to one atom of mercury, indicating that the minimum is caused by the formation of mercuric chloride in solution by double decomposition. Maxima obtained with increasing quantities of metallic chloride indicate the formation of complex ions such as $[HgCl_3]'$, $[HgCl_4]''$, and $[HgCl_5]'''$ with chlorides of univalent, bivalent, and tervalent metals, respectively. Similarly, $[HgBr_4]''$, $[HgI_4]''$, $[Hg(SCN)_3]'$, and $[Hg(SCN)_4]''$ are obtained. It has also been shown that, although it is possible to have a complex thiocyanate ion containing cobalt, the complex thiocyanates produced between mercury and cobalt thiocyanates contain a mercury and not a cobalt atom as co-ordination centre in the complex ion. In mixtures of mercuric thiocyanate with metallic halides maxima are obtained only in the case of the iodides, and this is probably due to the initial formation of mercuric iodide by double decomposition and subsequent combination of this with more iodide to form a complex salt. No complex ion containing both halogen and thiocyanate appears to be formed. The tendency to the formation of complex ions appears to be in the order $Cl' < Br' < SCN' < I'$.

II. With chlorides, bromides, and thiocyanates mercuric cyanide produces the complex ions $[Hg(CN)_2Cl]'$, $[Hg(CN)_2Br_2]''$, and $[Hg(CN)_2(SCN)_2]''$. With alkali or alkaline-earth iodides the ion $[Hg(CN)_2I_2]''$ is first obtained, but double decomposition with the formation of the ion $[HgI_4]''$ then takes place. With zinc or cadmium iodide the $[HgI_4]''$ ion is obtained without any intermediate complex formation. The following order of stability was established: $[Hg(CN)_2Cl]' < [Hg(CN)_2Br_2]'' < [Hg(CN)_2(SCN)_2]'' < [Hg(CN)_2I_2]'' < [HgI_4]'' < [Hg(CN)_4]''$. The existence in solution of the compounds $[Hg(CN)_2S_2O_3]K_2$ and $[Hg(CN)_2(MeCO_2)]Na$ has been confirmed.

M. S. Burr.

Ebullioscopic determination of double salts and complexes in aqueous solution. F. Bourion and F. Rouyer (Ann. Chim., 1928, [x], **10**, 182—262).—A detailed account of the theoretical basis, experimental technique, and results of work previously published (A., 1927, 515, 729, 841; this vol., 233, 477).

J. W. Baker.

Modern colloid chemistry. H. R. Kruyt (Rec. trav. chim., 1928, **47**, 883—895).—A lecture.

Non-existence of the amorphous state. P. P. von Weimarn and T. Hagiwara (Japan. J. Chem., 1926, **3**, 15—70).—See A., 1927, 410.

Human saliva as a reagent for preparing red dispersoid solutions and dispersible precipitates of gold. P. P. von Weimarn (Japan. J. Chem., 1926, **2**, 123—128).—See A., 1926, 792.

Degree of dispersion of solutions of metals in molten salts (pyrosols). E. Heymann (Z. anorg. Chem., 1928, **175**, 241—244).—From considerations based on the thermodynamic theory of March (this vol., 235) it is shown that the particles of lead in the lead "fog" observed by other workers in molten lead chloride have a diameter of the order of 3×10^{-8}—8×10^{-8} cm., and those of cadmium in a "fog" of that metal in molten cadmium chloride a diameter of the order of 2×10^{-7} cm. Hence the lead particles have approximately atomic or molecular dimensions, but those of cadmium must be considered as amicronic colloid particles. These results agree with the experimental facts observed by Eitel and Lange (this vol., 700). A. R. Powell.

Colloidal and elastic properties of polyvinyl acetate. G. S. Whitby, J. G. McNally, and W. Gallay (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 27—32; cf. Staudinger, Frey, and Starck, A., 1927, 1051).—Polyvinyl acetate is an organophilic colloid which exhibits elastic properties when swollen or heated. It dissolves and swells in polar organic liquids and in some liquids of very high dielectric constant. The elastic properties are shown in a comparatively low state of polymerisation. *X*-Rays give no fibre diagram. The viscosity relative to that of the solvent is almost unaffected by temperature changes. C. W. Gibby.

Alcosol of silicic acid. K. Inaba (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 92—93).—The alcosol of silicic acid is best prepared by hydrolysis of an alcoholic solution of ethyl orthosilicate with the calculated amount of water in the presence of sulphuric or hydrochloric acid ($<0\cdot04N$) which is subsequently removed by silver or lead oxide or by electrodialysis. The sol is a transparent, colourless, and viscous liquid $\kappa=2\cdot5-3\cdot0\times10^{-5}$ and $\eta=3\cdot35$ (at 25°) for a silica content of 17%. The concentration of silica (C) is related to the time required for spontaneous coagulation (t) by the expression $C=C_0/(1+at^n)$ where a and n are constants depending on the nature of the sol, and C_0 is the concentration when $t=0$. Electrolytes, particularly inorganic acids, decrease the stability slightly, whilst certain organic substances increase it. J. Grant.

Structure of the filaments obtained by the desiccation of colloidal ferric oxide solutions. P. Bary (Compt. rend., 1928, 187, 538—540).—The filaments were obtained by the evaporation of a solution of ferric oxychloride of the composition $10Fe_2O_3,Fe_2Cl_6$. On evaporation fine filaments with a parallel disposition are obtained at first; at a later stage thicker filaments are formed which are radially arranged. The former have the composition $20Fe_2O_3,Fe_2Cl_6$. An explanation of the formation of the two types of filaments is given.
W. E. Downey.

Sol–gel systems with anisotropic particles. I. Dibenzoylcystine. II. Barium malonate. H. Zocher and H. W. Albu (Kolloid-Z., 1928, 46, 27—33, 33—36).—I. A microscopical examination has been made of gels of dibenzoylcystine at various concentrations. The particles are composed of positive doubly-refracting, needle-like particles, which exhibit a strong double refraction when under deformation. The diameter of the particles is below the limit of microscopic resolution. The weak double refraction shown in absence of deformation indicates that the gel is composed of spherical aggregates of radially disposed needles. When the gel is dried, there remains a varnish-like layer composed of needles oriented radially; these give negative double refraction, as does pure dibenzoylcystine crystallised from alcohol. The double refraction changes to positive when the substance is moistened with water or with salt solutions. From these observations, the existence of a hydrate in the gel is deduced. Unlike the higher alcohols, gels in a medium of ethyl alcohol do not show the presence of needles at first, but do so on ageing. At certain concentrations, sols are obtained which show visible streaming in reflected light and strong streaming-double refraction under the polarisation microscope. Marked dichroism is observed by colouring with methylene-blue or neutral-red.

II. The influence of various conditions on the formation of the malonate gels described by Flade (A., 1913, i, 824) has been investigated, and it is shown that by using anhydrous glycerol perfectly clear gels are produced, whereas the gels made with commercial glycerol described by Flade are turbid. The turbidity rises with increasing water content. These gels, especially those free from water, are thixotropic. Gels prepared with methyl alcohol in absence of glycerol are very stable so long as care is taken to exclude air. Sols exhibiting marked streaming-double refraction are produced by addition of water to gels free from glycerol. Attempts to produce dichroism by addition of various colouring matters met with failure. E. S. Hedges.

Regular micellar structure of caoutchouc. H. Mark and G. von Susich (Kolloid-Z., 1928, 46, 11—21).—*X*-Ray examination has shown that when natural caoutchouc is stretched, an orientation of particles takes place, not only in the direction of stretching, but also in a perpendicular direction. The stretched caoutchouc belongs to the rhombic crystal system and the identity periods of the elementary cell are $a=12\cdot3$ Å., $b=8\cdot3$ Å., and $c=8\cdot1$ Å. There are eight isoprene residues in the elementary cell. The crystal class is probably V or V_h. Caoutchouc was treated in the stretched state with various chemical reagents, and the derivatives were examined by the *X*-ray method. All the derivatives gave only an amorphous *X*-ray diagram.
E. S. Hedges.

Micellar state of starch. G. Malfitano and M. Catoire (Kolloid-Z., 1928, 46, 3—11).—A comprehensive theory of colloids is outlined, which characterises and explains the micellar state of starch. The micelle is considered to consist of units of many grades of complexity, each unit being composed of polymerised molecules. The complexes may be of the Werner type, or polymerised polymerides, or crystals formed by the aggregation of micro-crystals. The colloid state is further characterised by a duality of composition involving an electrolytic part and a non-electrolytic part. A colloid is formed when both of the above conditions operate simultaneously. It is considered that the electrolytic part is present along with the non-electrolytic complexes in the central kernel of the micelle. The alternative hypothesis, that the electrolytic part is adsorbed at the surface of the particle, is not excluded, but is insufficient to explain all the facts. The dependence of the stability, flocculation, sedimentation, and formation of colloids on the nature and valency of added electrolytes is explained by the change in the degree of ionisation and consequently dispersion of the micellar ion.
E. S. Hedges.

Effect of non-electrolytes on the stability of colloids. I. Arsenious sulphide sol. S. G. Chaudhury (J. Physical Chem., 1928, 32, 1481—1487; cf. A., 1927, 413).—Adsorption experiments using arsenious sulphide sol in methyl and ethyl alcohols with barium chloride as coagulant indicate that adsorbability as measured analytically does not run parallel with the tendency towards coagulation. Measurements of the rate of migration of the sol with hydrochloric acid in substitution for barium chloride indicate that a diminution in ϵ sensitises the sol. Explanations are advanced, and it is suggested that the addition of a non-electrolyte may alter ϵ, which generally sensitises the sol, and also the interfacial tension which, in turn, influences the electrical potential below which coagulation takes place.
L. S. Theobald.

Stabilisation of colloids. V. Koulikov (Compt. rend. Soc. Biol., 1927, 97, 1337—1339; Chem. Zentr., 1928, i, 1779).—A series of substances has been prepared which permit the formation of a colloidal solution from two mutually insoluble substances.
A. A. Eldridge.

Ionic equilibrium, phagocytosis, and age of colloids. V. Koulikov (Compt. rend. Soc. Biol., 1927, 97, 1335—1336; Chem. Zentr., 1928, i, 1779).

Viscosity theory of Sen, Dhar, and collaborators. P. C. van der Willigen (Kolloid-Z., 1928, 46, 55-57).—Objections are raised against the viscosity theory proposed by Sen (A., 1926, 470) and Chakravarti and Dhar (*ibid.*, 677), for in presence of large amounts of electrolytes other phenomena besides viscosity play a part, and in presence of small quantities of electrolytes the supposed relation between charge and viscosity has not been proved either experimentally or theoretically. E. S. Hedges.

Viscosity of glycogen and some dyes and the relation between gelatinisation and double refraction. S. N. Banerji and N. R. Dhar (Kolloid-Z., 1928, 46, 24—26).—Measurements of the viscosity of ponceau-red, Victoria-blue BA, dianil-blue B, Victoria-blue B, Bordeaux B extra, aniline-brown, and dianil-orange G showed that in each case the viscosity falls on addition of small quantities of electrolytes. The viscosity of a 5% solution of glycogen is higher than that of most hydrophobic colloids of equal concentration. The viscosity of glycogen and of Bordeaux B extra rises slightly on keeping. Methyl-orange, patent-scarlet, imperial-green, tropæolin D, theonine, mercury sulphosalicylate, orange III, orange N.R. II, and aniline-orange exhibit streaming-double refraction. Many of these substances can be obtained in the gel form. It is considered that high viscosity, strong hydration, tendency to form stable gels, and double refraction are factors connected with a non-spherical form of the particles. E. S. Hedges.

Reactions in gelatin gels. S. M. Kuzmenko (Ukraine Chem. J., 1928, 3, 231—235).—Liesegang rings are produced when the sulphides of manganese, iron, nickel, zinc, and cobalt are precipitated in gelatin gels. Where mixtures containing pairs of the above cations are used, the less soluble sulphide is precipitated from the pairs Co–Mn, Ni–Fe, Zn–Fe, and Co–Fe. From the pair Fe–Mn the more soluble sulphide separates, whilst the sulphides are precipitated in approximately equal amount from the pairs Zn–Mn, Zn–Ni, Co–Ni, Co–Zn, and Ni–Mn. The above results are in accordance with Ostwald's theory of the formation of Liesegang rings.
R. Truszkowski.

Rhythmic formation of precipitates in gels. D. Avdalian (Ukraine Chem. J., 1928, 3, 222—235).—The presence of neutral salts such as sodium chloride and potassium nitrate diminishes the distance between the Liesegang rings formed in gelatin gels by the reaction between silver nitrate and potassium dichromate to an extent which depends on the concentration of the substrates. This effect is explained by the lowering of the metastable boundary of supersaturated solutions, and supports Ostwald's interpretation of this phenomenon ("Lehrb. allgem. Chem," 1902, II, 2, 782). R. Truszkowski.

Denitration in artificial silk manufacture. A. Nádai (Z. physikal. Chem., 1928, 136, 289—313).—Denitration of cellulose nitrates by hydrosulphides is analogous to the alkaline hydrolysis of esters. The kinetics of the reaction in a heterogeneous system, however, are those of a reaction of the first order. Increase of the temperature or of the hydrosulphide concentration, or the presence of substances such as alcohol, acetone, or certain inorganic salts at high concentration, which produce swelling of the cellulose nitrate, results in an increase of the velocity coefficient. During the reaction the hydrosulphide is oxidised to polysulphide, whilst the nitro-group eliminated is reduced to nitrite and ammonia; no nitrate appears to be produced. H. F. Gillbe.

Limiting condition "concentration=0" in diffusion problems. W. de Groot (Physica, 1928, 8, 23—34; Chem. Zentr., 1928, i, 1943).—Mathematical. A. A. Eldridge.

Heat of vaporisation at absolute zero. J. E. Verschaffelt (J. Chim. phys., 1928, 25, 408—409).—Polemical against Kolosovski (cf. this vol., 241).
L. F. Gilbert.

Limiting value of the latent heat of vaporisation and the specific heat of the saturated vapour at absolute zero. N. de Kolosovski (Z. physikal. Chem., 1928, 136, 314—316).—Polemical. All attempts to evaluate the true limiting value of latent heat of evaporation, the entropy of a gas, or the specific heat of a saturated vapour at 0° Abs. from thermodynamical considerations are illusory.
H. F. Gillbe.

Formulæ for the internal energy and entropy of a substance or mixture. R. D. Kleeman (J. Physical Chem., 1928, 32, 1396—1410).—Theoretical. From relations previously given (A., 1927, 520, 936), the more important formulæ for the controllable internal energy and the controllable entropy of a substance or mixture are derived. Both these quantities are additive for substances in the gaseous state. On mixing substances of the same type at infinite dilution, no change in internal energy or entropy takes place. Formulæ for the maximum work and free energy of a substance or mixture are also given. From the additive laws developed, it is possible to calculate the entropy, free energy of formation, and the mass-action constant of compounds at present undiscovered. L. S. Theobald.

New mass-action law. VI. Interchange of the components in the equation of the mass-action law. R. Lorenz (Z. anorg. Chem., 1928, **175**, 257—269).—A discussion of alternative methods of expressing states of equilibrium in terms of the law of mass action. H. F. Gillbe.

Thermal dissociation of steam into hydrogen and free hydroxyl. K. F. Bonhoeffer and H. Reichardt (Z. Elektrochem., 1928, **34**, 652—654).—The absorption spectrum of steam containing suitable amounts of oxygen shows at 1200° the presence of free hydroxyl. The heat of the reaction $2H_2O=H_2+2OH$ is determined as −125,000 g.-cal., or possibly higher, at about 1400°. The equilibrium constants for this reaction, calculated by Nernst's heat theorem, are very close to those determined experimentally for the reaction $2H_2O=2H_2+O_2$. S. K. Tweedy.

Activity coefficients and mass-action law in electrolytes. L. Onsager (J. Physical Chem., 1928, **32**, 1461—1466).—The deductions of Soper (this vol., 24, 26), which lead to limiting formulæ for the activity coefficients of electrolytes other than those given by Debye and Hückel, have been analysed and shown to be in error. The Debye–Hückel theory is satisfactory in all points attacked by Soper, so far as the deductions are concerned. The agreement of Soper's formulæ with experiments on reaction velocity is attributed to the application of the limiting square root formulæ at concentrations which are too high. L. S. Theobald.

Theory of the acidic–basic function. J. N. Brönsted (Ber., 1928, **61**, [*B*], 2049—2063).—The conception of an acid as a substance which can lose a proton and a base as a material which can add a proton is further developed (cf. A., 1926, 797). Since it is admitted that a proton cannot exist as such in aqueous or other solution, the acidic function can manifest itself only when a second molecule is present which can combine with the proton. The general scheme for the stoicheiometric acidic–basic function is therefore $A^1(\text{acid}_1)+B^2(\text{base}_2) \rightleftharpoons A^2(\text{acid}_2)+B^1(\text{base}_1)$. The production of hydrogen ions is not a necessity for the manifestation of acidic properties, but occurs in aqueous solution thus: $A(\text{acid}_1)+H_2O(\text{base}_2) \rightleftharpoons B(\text{base}_1)+H_3O^-(\text{acid}_2)$. The intimate connexion assumed previously between salt formation and the acidic–basic function is accidental, since salt formation from two electrically neutral molecules can occur by transference not only of a proton, but also of an electrically-charged particle of any kind from one to the other electrically neutral molecule. The behaviour of acids in indifferent solvents such as benzene illustrates the development of acidic and basic properties without participation of hydrogen or hydroxyl ions. The non-acidity of a solution of picric acid in benzene is due, not to low dielectric constant of the medium, but to absence of an acceptor for the proton. If, however, a base is added the colour of the picric ion is developed thus: $(NO_2)_3C_6H_3{\cdot}OH(\text{acid}_1) + PhNH_2(\text{base}_2) \longrightarrow (NO_2)_3C_6H_2{\cdot}O^-(\text{base}_1) + PhNH_3^+(\text{acid}_2)$. Similarly, the presence of the hydrogen ion is unnecessary for the development of the indicator equilibrium in benzene, but indicator reactions are possible, as the equilibrium is only a special case of the reaction $A(\text{acid})+I_B(\text{indicator-base}) \longrightarrow B(\text{base})+I_A(\text{indicator acid})$. The acidity of a solution is defined in general as its proton activity, so that the basicity is the reciprocal of the acidity. Measurement of acidity is based on the expression $a_H^+\times C_B/C_A=K_{\text{acid}}$, in which C_A is the concentration of the acid A, C_B that of the corresponding base B, and a_H^+ the acidity of the solution as defined above. The basicity constant of the base is given by the formula $C_A/(a_H\times C_B)=K_{\text{base}}$. The values of K are constant only for a constant medium. In benzene, a direct determination of a_H is impossible and the relative magnitudes of the constants must be elucidated from measurements of equilibrium. By use of the equation $K_1/K=C_{1B}\times C_A/(C_{1A}\times C_B)$, the constants K and K_1 are compared by the indicator method. The following sequence is determined in benzene: hydrogen chloride, methyl-red, dimethyl-yellow, trichloroacetic acid, dichloroacetic acid, picric, *o*-nitrobenzoic, monochloroacetic, and salicylic acids, bromophenol-blue, β-dinitrophenol, *o*-chlorobenzoic acid, neutral-red, *m*-chlorobenzoic acid, bromocresol-green, benzylammonium ion, formic, phenylacetic, benzoic, and acetic acids, *iso*amylammonium ion, bromocresol-purple, piperidinium ion, bromothymol-blue. H. Wren.

Effects of the spatial position of substituent groups on acidic strength. D. H. Hey (J.C.S., 1928, 2321—2323).—A criticism of the analogy drawn by Rule, Hay, and Paul (this vol., 765) between the influence of substituents on the acidity of geometrically isomeric acids and the effect of terminal alkoxyl and carboxyl groups on rotatory power. It is suggested that in the light of recent work on the configuration of the crotonic acids, this analogy is invalid. Further, the increase in the dissociation constants of these acids produced by the spatial proximity of the substituent group is in close conformity with the influence of *ortho*-substituents on the acidity of benzoic acid. F. J. Wilkins.

Superacid solutions. III. Titration and dilution curves of bases dissolved in acetic acid. N. F. Hall and T. H. Werner (J. Amer. Chem. Soc., 1928, **50**, 2367—2386; cf. this vol., 129).—The influence exerted by the nature and concentration of the titrating acid (sulphuric, hydrochloric, perchloric) and the strength of the base being titrated on the shape of the titration curves is investigated for solutions with acetic acid as solvent. The first two factors have a much greater effect on the p_H of a mixture of a weak base and its salt in acetic acid than in water. The weaker bases give anomalous titration curves, whilst the curves for bases which act like strong bases in water conform to theory. The influence of dilution on acetic acid solutions of bases is studied by an *E.M.F.* method, using a chloranil electrode, in preference to the conductivity method. Anomalies which are often present when the latter method is used are not apparent with the former method. Bases which behave during titration in acetic acid solution like strong bases are nevertheless weak electrolytes. The liquid junction potential between the solutions used and aqueous potassium chloride solution is practically constant. Factors are suggested which may explain certain minor anomalies. S. K. TWEEDY.

Hydrolysis measurements in solutions of stannous salts. M. PRYTZ (Z. anorg. Chem., 1928, **174**, 355—375).—The hydrolytic constants of stannous chloride, bromide, and perchlorate have been determined by potentiometric titrations, the results of which are recorded graphically. The values obtained indicate that hydrolysis takes place with the formation first of the ion $Sn(OH)^{\cdot}$, which then passes into the dimeric form $Sn_2(OH)_2^{\cdot\cdot}$ or its anhydride $Sn_2O^{\cdot\cdot}$. The value of $K=\alpha^2m/(1-\alpha)$ for $Sn^{\cdot\cdot}+H_2O=SnOH^{\cdot}+H^{\cdot}$ decreases with the dilution, whereas the value of $K'=\alpha^3m(1-\alpha)^2$ for $2Sn^{\cdot\cdot}+2H_2O=Sn_2(OH)_2^{\cdot\cdot}+2H^{\cdot}$ is independent of the dilution. In the presence of potassium salts the value of K' is considerably reduced owing to the formation of complexes. When the neutralisation point is passed in the titrations, a white precipitate is obtained; assuming this to be $Sn(OH)_2$, the results indicate that stannous hydroxide has a solubility product of 5×10^{-26} and that in feebly alkaline solutions it has no tendency to form stannites. A. R. POWELL.

Hydrolysis of solutions of zinc sulphate and the presence of univalent zinc ions. H. G. DENHAM and N. A. MARRIS (Trans. Faraday Soc., 1928, **24**, 510—515).—When the hydrolysis of zinc sulphate solutions is measured by the hydrogen electrode method anomalous values are obtained. Subsequent work with the allied element cadmium showed that the hydrogen electrode causes a reduction of the bivalent cadmium ion to a univalent state, suggesting a similar reduction in the case of zinc. A quinhydrone electrode was found to give a steady and normal value for the hydrolysis of zinc sulphate solutions. The authors' views are confirmed by the successful results of an attempt to reduce zinc sulphate by means of platinum-black kept vigorously stirred in the solution by a stream of hydrogen. It is suggested that the low hydrogen pressure peculiar to the quinhydrone electrode is incapable of setting up such reduction. N. M. BLIGH.

Hydrolysis of certain easily reducible metallic salts. H. G. DENHAM and N. A. MARRIS (Trans. Faraday Soc., 1928, **24**, 515—518; cf. preceding abstract).—The quinhydrone electrode has been successfully used in the determination of the hydrolysis of solutions of cadmium sulphate, lead chloride and nitrate, and thallous sulphate, all of which had previously been shown to be capable of reduction to a univalent or a subvalent condition. N. M. BLIGH.

Amphoteric nature of cadmium hydroxide. J. PIATER (Z. anorg. Chem., 1928, **174**, 321—341).—The solubility of cadmium oxide in water at 25° is $1{\cdot}7\times10^{-5}$ mol./litre and that of cadmium hydroxide $1{\cdot}11-1{\cdot}18\times10^{-5}$ mol./litre, according to its age and method of preparation. The solubility decreases on the addition of sodium hydroxide to a minimum of about $0{\cdot}13\times10^{-5}$ mol./litre in $0{\cdot}01$—$0{\cdot}1N$-sodium hydroxide. In more strongly alkaline solutions the solubility increases rapidly, reaching 9×10^{-5} mol./litre in $5N$-alkali, thus showing that cadmium hydroxide is an extremely weak acid. By the use of Bjerrum's theory of strong electrolytes the magnitude of the activity product of cadmic acid has been found to be of the order of 1×10^{-19}. A. R. POWELL.

Influence of intensive drying on inner equilibria. III. A. SMITS (J.C.S., 1928, 2399—2409).—A review is given of the present position of the problem of intensive drying and the apparent contradiction between the results of the author and Baker (*ibid.*, 1051) is discussed. It is pointed out that with the exception of his measurements of surface tension all Baker's experiments were carried out under conditions of rapid evaporation or distillation. The author suggests that neither Baker nor he has stopped the inner transformations in the liquid phase of a single substance and that, therefore, the differences between their results are to be expected, as his static methods are favourable to the establishment of equilibria in the gas phase, whilst Baker's methods are not. The results obtained from surface tension experiments are rejected on the ground that this property is not a trustworthy criterion for internal equilibria. Electric fields have no influence on either the vapour pressure or the b. p. of benzene.

F. J. WILKINS.

Intensive drying of liquids. S. LENHER and F. DANIELS (Proc. Nat. Acad. Sci., 1928, **14**, 606—609).—After about 4 years' intensive drying with phosphoric oxide in sealed glass tubes at the ordinary temperature, no abnormal rise was observed in the b. p. of benzene and of carbon tetrachloride (cf. Baker, J.C.S., 1922, **121**, 568). M. S. BURR.

Glass. II. Transition between the glassy and liquid states in the case of dextrose. G. S. PARKS, H. M. HUFFMAN, and F. R. CATTOIR (J. Physical Chem., 1928, **32**, 1366—1379; cf. this vol., 115).—Crystalline dextrose when heated at 160° for 10—15 min. and cooled to the ordinary temperature under a pressure of 4 atm. in nitrogen yields a clear, colourless glass, which softens at 40° and becomes, at 60°, a thick, viscous liquid. The glass is stable in dry air or under xylene, but eventually crystallises, especially if traces of a solvent for dextrose are present. Water (10%) or sodium acetate (1%) with dextrose can form two-component glasses with modified properties. The specific heat, coefficient of thermal expansion, and refractive index of dextrose glass have been determined over the ranges 90—340°, 262—348°, and 7—77° Abs., respectively. Up to 275° Abs., the curve relating C_p and temperature for dextrose glass is slightly higher than the corresponding curve obtained by Simon (A., 1922, ii, 684) for crystalline dextrose, but over the range 275—287° Abs. there is a sharp, 62% increase in the values of C_p. The corresponding values of C_v have been calculated. The coefficient of thermal expansion, measured by a dilatometric method, shows a sharp, 200% increase over the range 293—303° Abs. Below this transition region the coefficient for the glass is somewhat greater than that for the crystalline form, which is uniform at the value $0{\cdot}84\times10^{-4}$ over the range 273—323° Abs.; above this region it is identical with that of the liquid. The refractive index–temperature curve shows a change in slope over the interval 20—30°. L. S. THEOBALD.

Thermal decomposition of Bayer's alumina. N. PARRAVANO and G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 970—975).—Arrest points were found at 190°, 270°, and 450° in a thermal analysis of an alumina of composition very close to $Al_2O_3,3H_2O$. From *X*-ray spectrograms of this alumina taken after heating to various temperatures it is inferred that decomposition occurs in stages, giving perhaps $Al_2O_3,2H_2O$, and certainly Al_2O_3,H_2O, the final product being anhydrous alumina of a high density, which therefore differs from Blanc's alumina.

F. G. TRYHORN.

Effect of gelatin on the polymorphic transformation of mercuric iodide. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1928, 3, 189—191).—The transition temperature of mercuric iodide (red $\rightleftharpoons$ yellow) is made less sharp by the presence of gelatin. It is necessary to heat considerably above 127° to transform the red form into the yellow, whilst the yellow form will remain unchanged indefinitely at the ordinary temperature. The gelatin acts as a protective colloid in the solid phase. Light energy accelerates the change of mercuric iodide from the metastable to the stable form. A. J. MEE.

General theory of distillation of liquid mixtures of many components and its experimental verification. Y. TSUKAMOTO (Japan. J. Chem., 1926, 2, 129—147).—On the basis of the kinetic theory equations have been derived for the determination of the composition of the liquid and gaseous phases in the distillation of liquid mixtures. If $N_1, N_2 \ldots$ are the molecular quantities of each component in the original mixture, and $n_1, n_2 \ldots$ those in the residual liquid mixture, $n_2=N_2(1/N_1)^{K_1}n_1^{K_1}$, $n_3=N_3(1/N_1)^{K_2}n_1^{K_2}$, and so on, $K_1, K_2 \ldots$ being obtained from the expressions $K_1=\sqrt{m_1/m_2}\times e^{L_1/RT}/e^{L_2/RT}$, $K_2=\ldots$, $m_1, m_2 \ldots$ being the mol. wts. and $L_1, L_2 \ldots$ the molecular latent heats of evaporation. If the solution is non-ideal the partial molecular latent heat of evaporation must be substituted for the molecular latent heat of the pure substance. The equations have been verified experimentally in the system benzene–chlorobenzene–bromobenzene and can also be applied to the calculation of the composition of the vapour phase in equilibrium with a given mixture. Such calculations have been carried out for the systems oxygen–nitrogen, nitrogen–argon, carbon tetrachloride–alcohol, chloroform–benzene, and chloroform–methyl alcohol. M. S. BURR.

Vapour pressure of water over sulphuric acid–water mixtures at 25°, and its measurement by an improved dew-point apparatus. J. R. I. HEPBURN (Proc. Physical Soc., 1928, 40, 249—260).—A critical study is made of the data used by Wilson (cf. B., 1921, 421) in the construction of a mean curve for the vapour pressure of water over sulphuric acid–water mixtures at 25°. Sorel's observations are shown to be inconsistent with calculated values and with determinations using an improved dew-point apparatus. The mean curve has been reconstructed and a table of the most probable values compiled.

C. J. SMITHELLS.

Vapour pressures of the heptahydrate and the saturated solution of sodium sulphite. K. ARII (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 83—84).—The vapour pressures of the systems $Na_2SO_3,7H_2O$–Na_2SO_3, $Na_2SO_3,7H_2O$–sat. solution, and Na_2SO_3–sat. solution were determined between 15° and 50° by the statical method, and good agreement with the calculated values was found. The transition point heptahydrate–anhydride, determined from the point of intersection of the three vapour pressure–temperature curves, is 33·6° (33·49° calc.). J. GRANT.

Chemical equilibrium in the vapour of a mixture of paraffins and unsaturated hydrocarbons. H. A. WILSON (Proc. Roy. Soc., 1928, A, 120, 247—251; cf. A., 1927, 1139).—Unsaturated hydrocarbons containing more than one double linking are considered and their partial pressures in the mixture calculated by making use of their heats of formation and chemical constants in Planck's approximate equation for the equilibrium constant. A table is given showing the percentage of unsaturated hydrocarbons at various temperatures and pressures. The equilibrium in the formation of coke from oil is discussed. J. L. BUCHAN.

Equilibrium in binary systems cresols–amines. N. A. PUSHIN and L. SLADOVIC (J.C.S., 1928, 2474—2483).—Equilibrium diagrams for *o*-, *m*-, or *p*-cresol paired with dimethylaniline, *p*-toluidine, quinoline, piperidine, 1 : 5-naphthylenediamine, or carbamide are described. These indicate the formation of the compounds $CO(NH_2)_2,o\text{-}C_6H_4Me\cdot OH$ (cf. Kremann, A., 1907, i, 912); $NPhMe_2,o\text{-}C_6H_4Me\cdot OH$, m. p. −6°; $p\text{-}C_6H_4Me\cdot NH_2,o\text{-}C_6H_4Me\cdot OH$, m. p. 38°; $p\text{-}C_6H_4Me\cdot NH_2,m\text{-}C_6H_4Me\cdot OH$, m. p. 12·9°; $p\text{-}C_6H_4Me\cdot NH_2,p\text{-}C_6H_4Me\cdot OH$, m. p. 20·5°; $C_9H_7N,o\text{-}C_6H_4Me\cdot OH$, m. p. 34·2°; $C_9H_7N,2o\text{-}C_6H_4Me\cdot OH$, m. p. 34·5°; $C_9H_7N,p\text{-}C_6H_4Me\cdot OH$, m. p. 31·8°; $C_9H_7N,2p\text{-}C_6H_4Me\cdot OH$, m. p. 24·5°; $C_5H_{11}N,2p\text{-}C_6H_4Me\cdot OH$, m. p. 42·1°; 1 : 5-$C_{10}H_6(NH_2)_2,2p\text{-}C_6H_4Me\cdot OH$, m. p. 118°. Dimethylaniline and *p*-cresol do not combine.

F. J. WILKINS.

Binary systems cadmium–antimony and cadmium–lead. E. ABEL, O. REDLICH, and J. ADLER (Z. anorg. Chem., 1928, 174, 257—268).—Thermal and micrographical study of the system cadmium–antimony shows that the compound Cd_3Sb_2 does not exist in a stable region. The activities of the components in the cadmium–lead system have been calculated from the thermal diagram and are in agreement with *E.M.F.* measurements. Cadmium and lead are not soluble in one another to any appreciable extent in the solid phase. H. F. GILLBE.

Constitution of the iron–tungsten and iron–molybdenum alloys. H. ARNFELT (Iron and Steel Inst. Carnegie Schol. Mem., 1928, 17, 1—21).—Portions of the equilibrium diagrams for these systems have been investigated microscopically and by *X*-ray analysis. The crystalline compound Fe_2W has a hexagonal structure and when it is in equilibrium with the iron phase the dimensions of the lattice are $a_1=4·727$ Å., $a_3=7·704$ Å., four Fe_2W groups being present in the unit cell. This compound is unstable at higher temperatures and decomposes somewhere between 1000° and 1450°; it forms solid solutions to some extent, but their range is probably narrow. Direct determination gave the density as 13·0. A second compound, Fe_3W_2, is formed by a peritectic reaction at a high temperature, and has a trigonal lattice with parameters a_1=4·731 Å., a_3=25·7 Å., with 40 atoms in the unit cell, the density being 12·9. This also is associated with a short range of solid solutions. The iron–molybdenum system contains a trigonal compound, Fe_3Mo_2, analogous to Fe_3W_2; the lattice parameters are a_1=4·743 Å., a_3=25·63 Å., with 40 atoms to the unit cell. This compound also forms solid solutions to a small extent. There is no iron–molybdenum compound corresponding with the hexagonal iron–tungsten compound, but there is one compound and possibly two in addition to the trigonal Fe_3Mo_2, but these have not been isolated. W. HUME-ROTHERY.

Fluorine tension of metallic fluorides and the chemical constants of fluorine and hydrogen fluoride. K. JELLINEK and A. RUDAT (Z. anorg. Chem., 1928, **175**, 281—320).—The equilibrium conditions for the reduction of silver, cupric, lead, nickelous, cobaltous, ferrous and ferric, cadmium, zinc, chromic and chromous, and manganous fluorides by hydrogen at temperatures from 100° to 800° have been determined. The equilibrium $FeF_2+H_2 \rightleftharpoons Fe+2HF$ may be reached from either side, and the same is probably true of the reduction of manganous and chromous fluorides. In all other cases, however, equilibriun can be reached only from the hydrogen side; this is probably due to the small rate of diffusion of hydrogen fluoride through the film of fluoride which is first formed on the surface of the metal, that of hydrogen through the film of metal formed by reduction being relatively high. The calculated heats of formation of the metallic fluorides are in good agreement with calorimetric determinations. The ease of reduction of certain fluorides is discussed and compared with that of other halides. The chemical constants of hydrogen fluoride and of fluorine are $-1·0 \pm 0·3$ and $+0·7 \pm 0·3$, respectively. H. F. GILLBE.

Ternary system lead–antimony–cadmium. E. ABEL, O. REDLICH, and J. ADLER (Z. anorg. Chem., 1928, **174**, 269—280).—The system has been thoroughly investigated, but no evidence has been obtained for the existence of mixed crystals. H. F. GILLBE.

Equilibrium in the systems $ZnSO_4$–Na_2SO_4–H_2O at 0° and 25°; $MnSO_4$–Na_2SO_4–H_2O at 0°, 25°, and 35°; and $CoSO_4$–K_2SO_4–H_2O at 25°. R. M. CAVEN and W. JOHNSTON (J.C.S., 1928, 2506—2514; cf. A., 1924, ii, 683; 1927, 1142).—The recorded solubility data show the range of existence of the double salts $ZnSO_4,Na_2SO_4,4H_2O$, $MnSO_4,Na_2SO_4,2H_2O$, and $CoSO_4,K_2SO_4,6H_2O$ at the various temperatures. The equilibrium relations in the third system are compared with those shown by the corresponding systems in which cobalt is replaced by copper and by nickel. F. J. WILKINS.

Equilibrium of the system barium carbide, barium oxide, carbon, and carbon monoxide. M. DE K. THOMPSON (Amer. Electrochem. Soc., Sept. 1928. Advance copy, 16 pp.).—Equilibrium pressures for the system $BaO+3C \rightleftharpoons BaC_2+CO$ have been measured at three temperatures in an Arsem vacuum furnace. To ensure true equilibrium with carbon monoxide the charge was made in the form of a tube using a double-walled paper container. The pressures measured were corrected for the vapour pressure of barium oxide (see this vol., 1179). The equilibrium pressure was found to depend, not only on the temperature, but also on the percentage of carbide and on the ratio of barium oxide to carbon. This indicates that the three solid substances must form a solid solution. Consistent results were obtained at 1141° and 1295°, but at 1375° dissociation of the carbide or some other disturbing factor entered. H. J. T. ELLINGHAM.

Thermodynamics of mixtures. V. FISCHER (Z. Physik, 1928, **50**, 419—424; cf. this vol., 955).—The influence of temperature and volume as independent variables in the thermodynamic equations of mixtures is examined. Further, the bearing of free energy, internal energy, and heat content on the equilibrium conditions for a mixture of two components is discussed. W. E. DOWNEY.

Derivation of the phase rule. O. REDLICH (Z. anorg. Chem., 1928, **174**, 281—284).—The derivation postulates that for two closed systems in equilibrium to be identical, the quantities of the independent phases, the total energy, and the total volumes must be equal; the procedure is applicable to all systems which are not acted on by any external force. H. F. GILLBE.

Heat of combustion of benzoic acid. W. A. ROTH (Z. physikal. Chem., 1928, **136**, 317—320).—Various results are compared; the most probable value is 6323 g.-cal./g., weighed in air against platinum weights. H. F. GILLBE.

Heat of dissociation of oxygen as estimated from photochemical ozonisation. O. R. WULF (Proc. Nat. Acad. Sci., 1928, **14**, 614—616).—The heat of dissociation of oxygen in the photochemical formation of ozone was estimated by Warburg (Z. Elektrochem., 1920, 26, 58) from the energy of the absorbed wave-length 2070 Å., and by Born and Gerlach (Z. Physik. 1921, 5, 433) from the wave-length 2530 Å. It is supposed, however, that molecules are dissociated by light absorption only when such absorption lies in the continuous spectrum that stretches to shorter wave-lengths from the point of confluence of a band progression. There is no continuous spectrum in the Schumann–Runge band system, but in the absorption by gaseous oxygen under pressure, or by liquid oxygen, wave-length 2070 Å. lies in such a continuous spectrum. Apparently, however, it refers to the dissociation of the O_4 molecule and not of the O_2 molecule (cf. this vol., 1168) as supposed by Warburg (*loc. cit.*). The wave-length 2530 Å. does not lie in a continuous spectrum, and therefore cannot be used as a basis for the determination of the heat of dissociation. M. S. BURR.

Electronic thermochemistry of inorganic compounds. A. BERKENHEIM (Z. physikal. Chem., 1928, **136**, 231—258).—The arithmetical relations existing among the heats of formation of analogous inorganic compounds are considered in the light of the accepted structure of atoms and molecules. It is shown that heats of formation may be calculated with considerable accuracy by the summation of terms due respectively to heats of sublimation, heats of ionisation or dissociation, and the work, mechanical and electrostatic, of bringing together the component atoms or ions of the compound. F. G. Tryhorn.

Method of conductivity determination. O. Redlich (Z. physikal. Chem., 1928, **136**, 331—352).—An alternating-current compensation method has been developed for the measurement of the conductivity of solutions of electrolytes with uncoated electrodes. It is said that the error is about 0·02%. H. F. Gillbe.

Light-sensitivity of commercial selenium cells. G. P. Barnard (Proc. Physical Soc., 1928, **40**, 240—248).—For commercial selenium cells the change in conductance C due to an intensity of illumination I is given by $C \propto I^x$, where x varies from cell to cell, depending on the construction. A sensitivity curve for a Fournier d'Albe type of cell is given. The change in conductance of selenium cells is shown to depend on the amount of radiant energy received, and not on the number of foot candles incident on the cell. For equal radiant energy the action of the infra-red is relatively much weaker than that of some shorter waves. The light-sensitivity of selenium is attributed to changes in crystalline structure. C. J. Smithells.

Transport numbers of ions in solid sodium chloride at high temperatures. T. E. Phipps and R. T. Leslie (J. Amer. Chem. Soc., 1928, **50**, 2412—2421).—Between 410° and 510° the transport number of the sodium ion in solid sodium chloride is unity; at 558° it is about 0·57 and it gradually increases, probably because of polarisation effects, to 0·72 at 655°. The change from uni-ionic to bi-ionic conductivity occurs in the temperature region in which the slope of the conductivity curve ($\log \kappa$ against $1/T$) is doubled. A reversible sodium electrode is described. S. K. Tweedy.

Theory of electrical migration of ions. J. N. Mukherjee (Nature, 1928, **122**, 608).—The theory of moving boundaries as developed by Kohlrausch and Weber overlooks the unequal transfer of the common ion at the boundary, and rests on a misconception of the conditions on the "indicator" side of the boundary. A. A. Eldridge.

Electrochemistry of the proteins. D. M. Greenberg (Amer. Electrochem. Soc., Sept. 1928. Advance copy, 12 pp.).—Transport numbers have been measured for solutions of casein and of A, B, and C fibrin in 0·1N-solutions of various acids and alkalis. These proteins are deposited on the cathode or the anode according as the solution is acid or alkaline, and the amounts deposited are found to be proportional to the quantity of electricity passed and inversely proportional to the amount of acid or alkali per g. of protein in the solution. For casein the weight of the deposit is very close to that calculated on the assumption that all the acid or alkali present is taken up by the protein, giving positive or negative "protein ions" which are discharged at 100% current efficiency; for the fibrins considerably lower weights are obtained. The transport number measurements indicate that the only carriers of the current are the negative protein ion and the alkali metal cation in alkaline solutions, and the positive protein ion and the acid anion in acid solutions. Thus, for casein in various alkali hydroxide solutions the equivalent ionic conductivity of the casein ion calculated on this assumption is practically independent of the nature of the cation, and has the high value of 44·5±2 at 30°. With casein in solutions of alkaline-earth hydroxides abnormally high transport numbers (sometimes >1) were obtained, indicating the formation of complex negative ions containing the alkaline-earth metal. This result agrees with the observation that milk and blood normally contain more dissolved calcium than would be expected from the solubility of the phosphate and carbonate, and only part of this calcium will diffuse through a parchment membrane. H. J. T. Ellingham.

***E.M.F.* between copper and its amalgam and the reproducibility of the copper electrode.** M. Oku (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 84—86).—A reproducible copper electrode may be prepared by electrolysis of a 0·1M-solution of copper sulphate acidified with sulphuric acid, with a platinum cathode and a copper anode at a current density of 0·5—1·0 amp./cm.^{2} The *E.M.F.* of the combination $Cu|CuSO_4$ solution|Cu amalgam (heterogeneous) at 25° were then found to be 0·00513±0·00005 volt and 0·00511±0·00003 volt for M- and 0·05M-copper sulphate solutions, respectively, and $dE/dT = -0·0000737$ volt/1° between 0° and 40°. Both the electrode and amalgam should be protected from oxidation by the air. J. Grant.

Oxidation potential of the quinquevalent–tervalent niobium system. II. S. J. Kiehl and D. Hart (J. Amer. Chem. Soc., 1928, **50**, 2337—2345; cf. this vol., 846).—The above oxidation potentials were measured at 25° with a mercury electrode in an atmosphere of hydrogen, the niobium concentration, expressed as pentoxide, being 0·024M and 0·012M. Sulphuric acid was present at the concentrations 3·14, 5·91, and 9·87M and the corresponding normal electrode potentials were −0·3730, −0·3849, and −0·4261 volt. The results confirm the tervalent nature of reduced niobium. S. K. Tweedy.

Lead–mercurous iodide cell. W. C. Vosburgh (J. Amer. Chem. Soc., 1928, **50**, 2386—2394).—The *E.M.F.* at 15—40° of the following cells: Pb amalgam (10 or 12·7%)|xM-KI satd. with PbI_2|xM-KI+PbI_2+Hg_2I_2|Hg; Pb amalgam|soln. satd. with PbI_2+CdI_2|Hg_2I_2+soln. satd. with PbI_2+CdI_2|Hg; Cd amalgam|CdI_2 satd. soln.|CdI_2 satd. soln.+Hg_2I_2|Hg, where $x=0·01—0·02$, are given by $E=0·31748+0·000129(t-25)$ for the first two cells and $E=0·41702+0·000360(t-25)$ for the third. The following thermal data are calculated (at 25°): $Pb(s)+Hg_2I_2(s) \longrightarrow PbI_2(s)+2Hg(l)$, $\Delta F=-14,915$ g.-cal., $\Delta S=6·69$ g.-cal./1°, $\Delta H=-12,920$ g.-cal.; $2Hg(l)+I_2(s) \longrightarrow Hg_2I_2(s)$, $\Delta H=-28,939$ g.-cal.; $Cd(s)+Hg_2I_2(s) \longrightarrow CdI_2(s)+2Hg(l)$, $\Delta F=-21,575$ g.-cal., $\Delta S=5·35$

g.-cal./1°, $\Delta H=-19{,}979$ g.-cal.; $Cd(s)+I_2(s) \longrightarrow CdI_2(l)$, $\Delta H=-48{,}918$ g.-cal. S. K. TWEEDY.

Capillary phenomena and film formation in liquid gallium. A. FRUMKIN and A. GORODETZKAJA (Z. physikal. Chem., 1928, **136**, 215—227).—Measurements have been made at 30° of the electrocapillary curves of liquid gallium in various solutions, chiefly of potassium chloride to which different amounts of acid or alkali had been added. The maximum surface tension of 592 absolute units occurs in *N*-potassium chloride+0·1*N*-hydrochloric acid solution, and corresponds with an interfacial potential of 0·9 volt between the gallium and a normal calomel electrode. The surface tension is markedly lowered in the presence of hydroxyl ions, the maximum value attained in *N*-potassium hydroxide solution being 519 absolute units. At a certain polarisation potential, which approaches the cathodic end of the curve as the alkalinity of the solution increases, a solid but elastic film forms on the surface of the gallium, which causes the surface tension to fall gradually to a very low value. Similar films may be produced on the surface of gallium drops by atmospheric oxygen or by nitric acid. F. G. TRYHORN.

Measurement of the electrokinetic potential on proteins by the streaming potential method. D. R. BRIGGS (J. Amer. Chem. Soc., 1928, **50**, 2358—2363).—Dilute egg-albumin solutions containing lithium chloride and hydrochloric acid and having a p_H range of 3·6—7·5 were forced through a diaphragm of quartz powder, the surface of which had previously been saturated with albumin so that the diaphragm behaved as though it were wholly composed of protein, and the electrokinetic potentials were measured in the manner previously described (this vol., 713). The results are in agreement with the cataphoretic experiments of Abramson (*ibid.*, 364) between p_H 3·8 and 5·2. The divergence beyond this range is primarily a concentration effect, although the nature of the ions present may have some effect. The method may be used to measure the isoelectric point of a water-soluble protein. S. K. TWEEDY.

Electrocapillary phenomena in amalgams. I. Thallium amalgams. A. FRUMKIN and A. GORODETZKAJA (Z. physikal. Chem., 1928, **136**, 451—472).—The electrocapillary curves of thallium amalgams of various concentrations in solutions of sodium sulphate and other salts and of thiocarbamide, *iso*amyl alcohol, and pyrogallol have been measured by the capillary electrometer method of Gouy. The curves do not coincide with those of pure mercury, the maximum being displaced in the direction of higher cathodic polarisation. In *N*-sodium sulphate solution the displacement of the maximum is 0·45 volt for a 41·5% thallium amalgam. The value of the maximum surface tension falls at first, then passes through a minimum, and finally increases with increasing thallium content. The curves are affected in the same way as the mercury curves by the electrolyte concentration and by the presence of capillary-active substances. The results are discussed from the point of view of the Gibbs theory of surface phenomena. The amount of thallium adsorbed is a function of ϕ, the *P.D.* at the boundary amalgam/solution. For small values of ϕ the adsorption is positive, but gradually becomes negative with increasing values of ϕ. O. J. WALKER.

Mechanism of homogeneous gas reactions. I. Effect of black-body radiation on a molecular beam of nitrogen pentoxide. F. O. RICE, H. C. UREY, and R. N. WASHBURNE (J. Amer. Chem. Soc., 1928, **50**, 2402—2412).—Reaction kinetics involve three simultaneous processes, viz., absorption and emission of radiation, intermolecular collision, and molecular collision with the walls of the vessel. Methods of separating these effects are outlined. Experiments are described in which a molecular beam of nitrogen pentoxide is passed through a furnace at 793° Abs. under such conditions that intermolecular collisions and collisions with the walls are eliminated. No decomposition occurs. The probability of absorption of radiation by a nitrogen pentoxide molecule is calculated; the experimental result is in agreement with the theory (cf. Mayer, this vol., 140). S. K. TWEEDY.

Homogeneous gas reactions at high concentrations. I. Decomposition of hydrogen iodide. G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1928, **50**, 2315—2332).—The kinetics of the thermal decomposition of hydrogen iodide at 300° and 321° has been investigated at concentrations between 0·02 and 7 mol./litre. The results agree with those of Bodenstein (A., 1899, ii, 637) to within 4%, indicating that in each case a true homogeneous reaction rate has been measured. The reaction is strictly bimolecular, even when the gases are intensively dried; the increase in the "constant" at concentrations greater than 1 mol./litre is probably to be attributed to the number of bimolecular collisions not being proportional to the square of the concentration. Allowance for this is made with the aid of van der Waals' theory, whence the value $3{\cdot}33\times10^{-8}$ cm. is derived for the diameter of the hydrogen iodide molecule. Calculations based on activation data indicate that the cross-sections of effective reacting (activated) molecules are smaller than those of the normal molecules. A method of deciding the origin of the activation energy is outlined. S. K. TWEEDY.

Velocity of flame in complex gaseous mixtures of low inflammability in closed vessels. K. YUMOTO (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 93).—The velocity of flame, determined kinematographically in mixtures of carbon monoxide or hydrogen with a large excess of air is constant in the former but not in the latter case. The mean velocities are almost equal, but are less than those obtained for complex mixtures of both gases with air. J. GRANT.

Gaseous combustion at high pressures. XI. Influences of hydrogen and steam on the explosion of carbonic oxide-air etc. mixtures. W. A. BONE, D. T. A. TOWNEND, and G. A. SCOTT (Proc. Roy. Soc., 1928, **A**, **120**, 546—563).—A repetition and extension of the work of Bone and Haward (cf. B., 1921, 802) with isothermic $2(mH_2+nCO)+O_2+3{\cdot}76N_2$ mixtures (where $m+n=1$). The peculiar effect of successive replacements of carbon monoxide by hydrogen previously observed is confirmed, but it is found to require a hydrogen content exceeding 0·65% in the mixture fired. It is of the nature of a "knock" effect, which may be eliminated by raising the bomb temperature to 100° without altering the charge density. Under these conditions, it is found that after the first 1% of hydrogen has definitely catalysed the carbon monoxide combustion up to a certain velocity (about twice that of the well-dried $2CO+O_2+3{\cdot}76N_2$ mixture), further amounts of hydrogen produce merely an "additive" accelerating effect. An investigation of the influence of steam on the rate of pressure development in theoretical carbon monoxide–air explosions at initial pressures of 32·2 and 64·4 atm., respectively, and with the bomb chamber at 100°, showed that, whereas the first small successive additions of steam markedly accelerated the rate of increase of pressure, optimum conditions were nearly reached in each case when about 1% of steam had been added. Evidence is cited which indicates that the rôle of the steam in such circumstances is not chemical, in the sense of its being continually decomposed and regenerated. The addition of a small quantity of hydrogen has a greater effect than its equivalent of steam in accelerating the explosion of a carbon monoxide–air mixture at high pressures, the purely catalytic effect of hydrogen probably exceeding that of steam under the same conditions. The progressively increasing lag in the pressure rise always observed in theoretical carbon monoxide–air explosions at high initial pressures, irrespective of the hygroscopic condition of the medium, is principally a nitrogen effect, since it is not observed at all when the nitrogen is replaced by its volume equivalent of either carbon monoxide or argon. L. L. Bircumshaw.

Gaseous combustion at high pressures. XII. Influence of steam and temperature, respectively, on the "explosion limits" of carbonic oxide–air mixtures. W. A. Bone, D. M. Newitt, and C. M. Smith (Proc. Roy. Soc., 1928, A, **120**, 563—572; cf. this vol., 248).—Carbon monoxide–air mixtures were fired at a temperature of 100° at either 32·2 or 64·4 atm. initial pressure, either (1) in a "well-dried" condition (moisture content <0·02%), or (ii) in an 80% saturated condition (moisture content 2·24 or 1·12%, according to the initial pressure). The results show that the effect of drying is to lower the explosion range at the high initial pressures employed. In the case of "moist" mixtures, the effect of doubling the pressure is to shift each limit slightly downwards without narrowing the explosion range, but with the "dry" mixture, the explosion range is definitely narrowed by increasing the initial pressure. On comparison of the results with those of the previous "dry" experiments (*loc. cit.*), it appears that the influence of temperature is to widen the explosion range. L. L. Bircumshaw.

Kinetics of the reaction between hydriodic and iodic acids. E. Abel and K. Hilferding (Z. physikal. Chem., 1928, **136**, 186—194; cf. Abel and Stadler, A., 1926, 1009).—The previous treatment of this reaction has been amended, since it is found that with very small iodine-ion concentrations the reaction velocity is proportional to the first and not to the second power of the concentration. F. G. Tryhorn.

Mechanism of reactions between hydrogen peroxide, iodine, and iodine ions. E. Abel (Z. physikal. Chem., 1928, **136**, 161—182; A., 1921, ii, 180).—The complete reactions occurring among these reactants can be expressed by the two independent and simultaneous reactions, $H_2O_2+2HI=2H_2O+I_2$ and $H_2O_2+I_2=2HI+O_2$. An analysis of earlier experimental results shows that an important part is played by the intermediate production of hypoiodous acid which functions, according to the concentrations of the main reactants, either as a reactant or resultant in a number of subsidiary and simultaneous reactions. The hypoiodous acid is formed primarily by the interaction of hydrogen peroxide and hydriodic acid; $H_2O_2+HI=HIO+H_2O$ and may then react either with additional hydrogen peroxide: $H_2O_2+HIO=HI+H_2O+O_2$, or with hydriodic acid: $HIO+HI=H_2O+I_2$. On the other hand, hypoiodous acid may be formed by a hydrolytic reaction from the free iodine: $I_2+OH'=I'+HIO$. The last two reactions are catalysed by hydrogen peroxide. The kinetics of this complicated series of reactions are considered and differential equations have been obtained which represent satisfactorily the experimental results. F. G. Tryhorn.

Kinetics of nitrous acid. V. Nitrous acid–nitric acid–nitric oxide reaction. E. Abel, H. Schmid, and S. Babad (Z. physikal. Chem., 1928, **136**, 419—429; cf. this vol., 374, 847).—The kinetic data for the two opposed reactions represented by $3HNO_2 \rightleftharpoons H^{\cdot}+NO_3'+2NO+H_2O$ have been applied in the interpretation of the kinetics of the reaction in which both are involved. The velocity equation $\mp d(HNO_2)/dt=\pm k_1[HNO_2]^4/P_{NO}{}^2\mp k_2[HNO_2][H^{\cdot}][NO_3']$ for the decomposition or formation of nitrous acid has been verified. O. J. Walker.

Kinetics of nitrous acid. VI. Relation between equilibrium and kinetics of the nitrous acid–nitric acid–nitric oxide reaction. E. Abel and H. Schmid (Z. physikal. Chem., 1928, **136**, 430—436; cf. preceding abstract).—From the velocity coefficients of the two opposed reactions the "equilibrium constant" $K_c=[H^{\cdot}][NO_3']P_{NO}{}^2/[HNO_2]^3$ is determined. K_c increases with increasing ionic concentration. Brönsted's theory of reaction velocity is applied to the reaction. O. J. Walker.

Rôle of phosphates in oxidation of dextrose. A. N. Kappanna (J. Indian Chem. Soc., 1928, **5**, 387—396).—The reaction between dextrose (1 mol.) and iodine (1 mol.) takes place only at $p_H>7$, either in absence or in presence of phosphates. At constant alkalinity the rate of oxidation is independent of the concentration of phosphate, and increases with increase in p_H. The rate of decomposition of aqueous hydrogen peroxide solution at 60° has been studied in presence of phosphate buffers at p_H 7·6 and 7·8. This decomposition is also independent of the phosphate concentration and increases with increased alkalinity. It is concluded that no hexose–phosphate or hydrogen peroxide–phosphate complexes are formed in solution. H. Burton.

Rate of hydrolysis of some αβ-oxy-compounds in acid solution. G. Wode (Svensk Kem. Tidskr., 1928, 40, 221—226).—The hydrolysis of a solution of glycide at 25° by means of perchloric acid has been examined, the progress of the reaction being followed by employing a dilatometer, since a considerable contraction in volume occurs. The reaction is strictly unimolecular, the velocity coefficient being between that obtained for ethylene oxide and epichlorohydrin. The above method could not be used in the case of *cis*- and *trans*-ethyleneoxide-αβ-dicarboxylic acids, the rate of hydrolysis being too slow at the ordinary temperature, so that here the course of the reaction was followed by means of conductivity measurements, the solutions being contained in a special closed cell immersed in a thermostat at 97·7°. The results in the case of the *cis*-acid do not exhibit the customary parallelism between the hydrogen-ion concentration and the velocity coefficient, the latter increasing with the degree of dissociation. The *trans*-acid is hydrolysed more slowly than the *cis*-, yielding a mixture of tartaric and mesotartaric acids, whereas the *cis*-acid gives only the former. Measurements carried out at 25° showed that the above acids have larger primary dissociation constants than those obtained from the isomeric hydroxymaleic and hydroxyfumaric acids, and that these constants, unlike those of tartaric acid itself, diminish markedly with rise of temperature.

H. F. Harwood.

Velocity of reaction between amylene and trichloroacetic acid in different solvents. L. M. Andreasov (Ukraine Chem. J., 1928, 3, 209—218).—The velocity of reaction between amylene and trichloroacetic acid is greatest in benzene, less in nitrobenzene, chloroform, carbon disulphide, and is least in carbon tetrachloride. The velocity coefficients of the reaction diminish steadily in all solvents, owing to the formation of a double compound between amyl chloroacetate and chloroacetic acid. R. Truszkowski.

Velocity of esterification of amides in alcohol. H. A. Taylor and T. W. Davis (J. Physical Chem., 1928, 32, 1467—1480; cf. Reid, A., 1909, ii, 650).—The velocity of esterification of formamide, acetamide, propionamide, and benzamide in dry and in aqueous solutions of ethyl alcohol, with hydrogen chloride as catalyst, has been measured. The reactions appear to be bimolecular, and formamide seems to contain a tautomeride which catalyses its esterification. Small concentrations of neutral salt are without marked effect on the velocity of reaction, but the addition of small quantities of water has an accelerating effect which reaches a maximum at 8—12%. Stieglitz's suggestion (J. Amer. Chem. Soc., 1910, 32, 221) that the catalytic effect of an acid is due to the transformation of a weaker into a stronger base is extended to explain the inhibiting or accelerating effect of water in various reactions. L. S. Theobald.

Spontaneous and linear crystallisation velocity in binary mixtures. W. Rawitzer (Z. anorg. Chem., 1928, 175, 321—334).—Parallel relationships exist for supercooled fused masses between the velocity of crystallisation and the velocity of nucleus formation on the one hand and the concentration on the other, in contradistinction to the differing relationships of the latter quantities. Application of this result to simple binary mixtures shows good agreement with the experimental determinations of Tammann and Botschwar (A., 1927, 196). Measurements with the binary system palmitic acid–stearic acid indicate that the relationship is accurately valid only for simple systems, and must be modified for complex systems. H. F. Gillbe.

Corrosion of chemical lead. D. W. Jones.—See B., 1928, 786.

Corrosion at discontinuities in metallic protective coatings. U. R. Evans.—See B., 1928, 751.

Phenomena of corrosion of iron and steel. A. Herrero and M. de Zubiria.—See B., 1928, 751.

Resistance of pure chromium–nickel–iron alloys to corrosion by acids. W. Guertler and W. Ackermann.—See B., 1928, 753.

Acid and basic catalysis. J. N. Brönsted (Svensk Kem. Tidskr., 1928, 40, 230—233).—The phenomena of acid and basic catalysis are discussed in the light of the author's conception of the nature of acids and bases, the view being taken that the catalytic effect is to be ascribed, not particularly to the hydrogen and hydroxyl ion, but to the action of acid and basic molecules in general (cf. J. Amer. Chem. Soc., 1927, 49, 2554). H. F. Harwood.

Conversion of thiosulphates into polythionates with the aid of catalysts. A. Kurtenacker and A. Czernotzky (Z. anorg. Chem., 1928, 175, 367—382).—The quantity of polythionate produced during the decomposition of *N*-sodium thiosulphate solution by hydrogen chloride diminishes as the acid concentration is increased. Mercuric chloride, lead acetate, bismuth trichloride, sodium tungstate, or sodium sulphide solutions have no marked influence on the reaction. On acidifying a thiosulphate solution which contains a small quantity of arsenite or arsenate, a strong odour of hydrogen sulphide is produced, which is rapidly replaced by that of sulphur dioxide; after some minutes a precipitate of sulphur and arsenious sulphide commences to form. For constant arsenic content, approximately equal quantities of tetra- and penta-thionate are formed at low acid concentrations; at moderate concentrations pentathionate alone is produced, whilst with higher concentrations penta- and hexa-thionates are obtained. At constant acid concentration an increase of the quantity of arsenate in the solution results in the formation of more tetrathionate, probably on account of partial neutralisation of the acid present by the arsenite solution. Although an excess of arsenic acid should convert all the thiosulphate into tetrathionate, some pentathionate appears to be formed. Arsenious sulphide has no influence on the thiosulphate decomposition, and arsenic trichloride but little. Tervalent antimony has much less effect than has arsenious acid, whilst with molybdic acid the yield of polythionate is very small; in presence of stannic chloride considerable quantities of polythionate are produced.

H. F. Gillbe.

Oxidative catalytic action of iron. O. Warburg (Biochem. Z., 1928, 195, 241—242).—The theory of Handovsky (this vol., 718) that it is not iron but the hydrogen dissolved in it which combines with

atmospheric oxygen forming hydrogen peroxide, and thus effects the oxidation of amino-acids, is discredited.
P. W. Clutterbuck.

Autoxidation and antioxygenic action. XXX. Autoxidation and polymerisation of chloral: action of light. XXXI. Autoxidation and polymerisation of chloral: action of various catalysts. C. Moureu, C. Dufraisse, and G. Berchet (Bull. Soc. chim., 1928, [iv], 43, 942—957, 957—962).—XXX. The autoxidation of chloral in presence of oxygen has been studied by following the increase in pressure resulting from the formation of the gaseous products hydrochloric acid, carbon dioxide, and carbonyl chloride. The process is autocatalytic and depends on the initial formation by the action of light of a catalyst, which is probably an oxidation product. The reaction can then proceed in the dark. Reaction with oxygen appears to take place in two ways, viz., $CCl_3{\cdot}CHO+O=CCl_3{\cdot}CO_2H$ and $CCl_3{\cdot}CHO+O_2=COCl_2+HCl+CO_2$, although the latter unusual type of reaction is not confirmed quantitatively. The mechanism of the formation of these gaseous products is discussed. Chloral hydrate does not undergo autoxidation unless it is first dehydrated.

XXXI. The autoxidation of chloral is inhibited by a large variety of substances, *e.g.*, phenols, aromatic amines, sulphur, iodine, etc. (antioxygenic catalysts). These substances also inhibit the spontaneous polymerisation of chloral to metachloral.
O. J. Walker.

Thermal decomposition of ammonia on mixed surfaces of tungsten and platinum. R. E. Burk (Proc. Nat. Acad. Sci., 1928, 14, 601—602).—The catalytic effect on the decomposition of ammonia of a surface alloy of platinum and tungsten, prepared by evaporating one metal from a spiral on to a filament of the other metal mounted axially within it, is greater than that of an equal surface of either constituent. The temperature coefficient for the mixed surfaces is also smaller than for either of the metals alone, in agreement with the generally accepted view that the accelerating effect of a contact catalyst is due to a lowering of the heat of activation. The "promoter action" is considered to be due to the fact that tungsten adsorbs nitrogen more strongly than hydrogen, whilst the opposite is true for platinum. The strain exerted by the mixed surface on the ammonia linking is thus much greater than that produced by one metal alone. The results suggest that, in the catalysis of the decomposition of ammonia, no other action, *e.g.*, atomic distortion (cf. this vol., 27; A., 1926, 915), is concerned. M. S. Burr.

Decomposition of hydrogen peroxide at surfaces. W. M. Wright and E. K. Rideal (Trans. Faraday Soc., 1928, 24, 530—538).—Experiments were made to find an explanation for the varying effects of adding traces of acids or alkalis on the reaction rate for a number of different surfaces. Fair agreement was found between the amount of acid or alkali which must be added to give a maximum rate of decomposition and that required to neutralise the electrokinetic potential at the solid–liquid interface. This potential was determined by the electro-endosmotic method, and the reaction rate by measuring the rate of evolution of oxygen. Tungstic acid showed certain abnormalities, probably associated with the formation of soluble pertungstic acid. The alteration in reaction rate can likewise be effected by the addition of multivalent ions such as aluminium chloride. At high concentrations the effects of poisoning by the adsorbed salt can be observed. The fraction of the surface of charcoal capable of effecting the decomposition is much larger than that capable of effecting oxidation of organic acids. N. M. Bligh.

Thermal decomposition of hydrogen peroxide. W. M. Wright (Trans. Faraday Soc., 1928, 24, 539—542).—The surface of glass treated with acids was known to be partly converted into silica gel. Since the rate of decomposition of hydrogen peroxide on glass in presence of silver nitrate is approximately proportional to the amount of silver adsorbed, investigation was made as to whether the silver which is catalytically active is in the form of silver silicate. The rate of decomposition of hydrogen peroxide on silica gel and on silver silicate was studied. The former has only slight catalytic activity, but this is greatly increased in presence of silver nitrate, and by further addition of a trace of alkali is increased several hundred times. Silver silicate caused a very rapid decomposition of the peroxide, probably through an intermediately formed silver oxide. The catalytic properties of glass in contact with silver nitrate are ascribed to the formation of traces of silver silicate.
N. M. Bligh.

Catalysis of solid-phase reactions by solids. S. Roginski and E. Schulz (Ukraine Chem. J., 1928, 3, 177—207).—Moles and Crespi's view that the thermal decomposition of solid potassium permanganate is of an autocatalytic nature (A., 1925, ii, 877) is confirmed, and shown also to apply to that of ammonium dichromate. Ostwald's equation is inapplicable to the kinetics of the former reaction, the velocity of which over the first section of the autocatalytic curve is better expressed by $K=(x_t^{1/3}-x_{t_0}^{1/3})/(t-t_0)$ where x is the mass of substrate decomposed at time t. This equation gives fair agreement with experiment where the permanganate is finely powdered, but not where whole crystals are taken, as in the latter case the number of active centres present is small, making the incubatory period comparatively long. An analogous equation is derived for the third section of the curve expressing diminishing velocity, which gives satisfactory agreement with experiment for powdered substrate, and fair agreement with crystalline substrate. The catalytic action of a number of metallic oxides on the decomposition of potassium permanganate is in the order of intensity $NiO>CuO>Al_2O_3>CdO$, and their action is most marked below 400°. At temperatures much above this, the catalytic action of the above substances undergoes inversion, the reaction being retarded in their presence, both for potassium permanganate and for ammonium dichromate. This effect is explained as being due to the high thermal capacity of these catalysts at high temperatures. R. Truszkowski.

Stationary nickel catalyst for a continuous hydrogenation process. A. Svizuin (Masloboino-Zhir. Delo, 1928, No. 3, 25—27).—Iron wire is coated electrolytically with a smooth layer of nickel, on which, by increasing the current density, a layer of greater surface is produced. The nickel is oxidised in a hydroxide bath and washed; spirals of the wire are employed in the autoclaves.

CHEMICAL ABSTRACTS.

Catalytic oxidation of furfuraldehyde in the vapour phase. W. V. SESSIONS (J. Amer. Chem. Soc., 1928, 50, 1696—1698).—Furfuraldehyde was volatilised in a current of air at 40—50° and the mixture passed over a vanadic oxide–asbestos catalyst at 200—300°. The product contains up to 14·5% of the theoretical yield of maleic acid, m. p. 138·5—140°, together with maleic anhydride, formaldehyde, water, and carbon dioxide, but no fumaric acid (cf. Milas, A., 1927, 973). H. E. F. NOTTON.

Catalysts used in the synthesis of higher hydrocarbons from water-gas. A. ERDELY and A. W. NASH.—See B., 1928, 775.

[Catalytic preparation of] methyl alcohol from hydrogen and carbon monoxide. R. L. BROWN and E. A. GALLOWAY.—See B., 1928, 780.

Cathodic halogen. R. H. CLARK and R. H. BALL (Amer. Electrochem. Soc., Sept. 1928. Advance copy, 6 pp.).—Solutions in various solvents of compounds containing so-called positive halogen, *i.e.*, halogen which on hydrolysis is replaced by hydrogen and appears as hypohalous acid, have been electrolysed between silver electrodes. *N*-Bromosuccinimide in acetonitrile yielded a deposit of silver bromide on the cathode, whilst at the anode silver succinimide free from bromide was deposited. *N*-Iodosuccinimide and *N*-bromoacetamide in acetonitrile yielded silver halide deposits on both electrodes. In other solvents no cathodic liberation of halogen was observed with these substances, but cyanogen iodide yielded iodine at the cathode when dissolved in pyridine.

H. J. T. ELLINGHAM.

Electrochemical reduction of solid electrodes. III. Chromites. IV. Sulphides. K. FISCHBECK and E. EINECKE (Z. anorg. Chem., 1928, 175, 335—340, 341—342).—III. When chromite is employed as third electrode, chromic acid is formed by anodic oxidation and then diffuses through the mineral under the influence of the potential fall, to appear finally at the cathode. Chromite, which has a remarkably high resistance, exhibits a high degree of porosity to the sulphate ion, as shown both by analysis and by the increase of its conductivity after being placed between electrodes in dilute sulphuric acid solution. The variation of conductivity has been studied in its relationship to the direction and strength of current; in general it is lower during anodic polarisation than during cathodic, on account principally of changes in the electrolyte and in the quantity of gas in the pores of the mineral. Hysteresis effects are also to be observed. The porosity of chromite is estimated at 0·15—0·4 c.c./100 g., the lower figure being the more probable.

IV. Both cobaltous and nickelous sulphides undergo reduction when spread on a lead plate and subjected to cathodic polarisation in a dilute sulphuric acid solution; hydrogen sulphide is formed and the metal partly enters into solution. Zinc blende, despite its low conductivity, reacts under the same conditions in an analogous manner. H. F. GILLBE.

Experimental technique of photochemistry. VI. Energy distribution of the Uviol lamp. E. BEESLEY and H. N. RIDYARD (J. Physical Chem., 1928, 32, 1342—1345; cf. this vol., 851).—The results of an investigation of the energy distribution of a Uviol lamp burning at 29·5 volts and 2·42 amp. are recorded, and are compared with those previously obtained by Allmand (J.C.S., 1915, 107, 682), and with the energy distribution of the quartz–mercury lamp.

L. S. THEOBALD.

Phototropic compounds of mercury. S. V. R. RAO and H. E. WATSON (J. Physical Chem., 1928, 32, 1354—1365; cf. A., 1923, i, 764).—Twenty mercury compounds of the types $Hg(X)CNY$ and $HgX_2,2HgY$, where X is chlorine, bromine, iodine, hydrosulphide, hydroselenide, thiocyanate, or selenocyanate, and Y is oxygen, sulphur, or selenium, have been prepared and found to be phototropic. The times required for darkening in diffused daylight vary from <1 to 200 min., but the times for recovery in darkness are all of the same order, viz., from 1·5 to 3 days. The compounds with the probable formulæ $Hg(HSe)CNS$ and $Hg(HSe)CNSe$ are not phototropic. Spectroscopic examination of the more sensitive compounds showed them to be darkened by exposure to light of wave-length of the order of 5500 Å. and less, with slight sensitiveness extending into the ultra-violet to the limit of transmission of quartz. A broad, well-defined maximum of sensitivity occurs usually in the green; this maximum tends to move towards the red with an increase in mol. wt. for related compounds. In the case of compounds darkened by exposure, reversal is effected by exposure to red light. No maxima were observed, but there is a limiting wave-length beyond which no reversal occurs. Heat causes reversal in all cases. Darkening is accelerated by the presence of agar agar, gelatin, and collodion, but is retarded by that of gum arabic; all four substances retard the reverse reaction. In the case of the compound $Hg(HS)CNS$, the light-sensitive region is extended towards the red by dyeing the compounds with eosin, erythrosin, methyl-green, malachite-green, and methylene-blue. The temperature coefficients of the direct and reverse reactions approximate to 1·0 and 1·9, respectively, for the compounds $Hg(HS)CNS$ and $HgI{\cdot}CNS$, and the time of exposure necessary to produce a given change is inversely proportional to the intensity of the light. No induction period has been observed.

L. S. THEOBALD.

Decomposition of ammonia by high-speed electrons. J. C. MCLENNAN and G. GREENWOOD (Proc. Roy. Soc., 1928, A, 120, 283—295).—The electrons are produced by a Coolidge cathode-ray tube and pass into the reaction vessel through a window of "resistal" metal. Decomposition of the ammonia sets in suddenly when the voltage is high enough to drive the electrons through this window. Increase in the pressure of the ammonia decreases the percentage decomposition, but in the first stages of the decomposition the ratio of the number of ammonia molecules decomposed to the number of electrons causing decomposition is independent of the pressure of the ammonia, and increases with the speed of the electrons. Excess of nitrogen increases the quantity of ammonia decomposed, whilst excess of hydrogen decreases the amount. Excess of nitrogen has no effect on the speed of the primary stage of the decomposition, which, however, is decreased by the addition of hydrogen. J. L. Buchan.

Chemical reactions of carbon monoxide and hydrogen after collision with electrons. A. Caress and E. K. Rideal (Proc. Roy. Soc., 1928, A, **120**, 370—385; cf. A., 1927, 943).—The rate of reaction of carbon monoxide with hydrogen has been determined for various electron speeds. The reactions are followed by measuring the rate of decrease of pressure, dp/dt, in the reaction chamber. It is calculated that $n=-0\cdot0944\, v/c\times dp/dt$, where n is the number of molecules removed by one electron, v the volume of the system, and c the effective current. With carbon monoxide alone the reaction has been shown to be $2CO=C+CO_2$ and dp/dt varies with the electron speeds, the curves showing this exhibiting definite breaks. The combination of carbon monoxide with hydrogen atoms and with hydrogen molecules has also been studied, and the reactions show similar curves. The product in these cases is first formaldehyde which then polymerises at the ordinary temperature. The electron efficiencies for these reactions have been tabulated, and the mechanism of the reactions is discussed. J. L. Buchan.

Formation of a polymeride of carbon monosulphide by ultra-violet irradiation of carbon disulphide. Absorption spectrum of carbon disulphide in carbon tetrachloride. W. Doran and A. E. Gillam (J.S.C.I., 1928, **47**, 259—260t).—A polymeride of carbon monosulphide has been obtained as a reddish-brown solid by irradiation of mixtures of carbon disulphide and carbon tetrachloride by means of a vitaglass-screened mercury-vapour lamp. Its properties and analysis agree with those recorded by previous investigators for the same product obtained by different means. The absorption spectrum of carbon disulphide in carbon tetrachloride is discussed, and the possibility of the detection and determination of the former in the latter by this means is pointed out.

Mechanism of photosensitisation and photo-inhibition from the point of view of absorption spectra. B. K. Mukerji and N. R. Dhar (J. Indian Chem. Soc., 1928, **5**, 411—415).—The absorption spectra of the various constituents of a reacting system (*e.g.*, reduction of Fehling's solution in presence of uranyl nitrate and ferric chloride) and of sensitising or inhibiting substances have been determined for six reactions. The results show that in photosensitised systems there is a marked increase in the light absorption, whilst in inhibited systems no increase takes place. H. Burton.

Photochemical studies. VII. Photochemical decomposition of formic acid liquid and vapour. W. N. Herr and W. A. Noyes, jun. (J. Amer. Chem. Soc., 1928, **50**, 2345—2350).—Data for the quantum efficiency of the decomposition of formic acid liquid and vapour by radiation are recorded, the number of molecules of gas uncondensed by liquid air formed per quantum being determined and also the number of additional molecules uncondensed by carbon dioxide and ether. For the liquid the quantum efficiency rises with increasing frequency; the vapour absorbs at short wave-lengths only. The primary reaction in both the liquid and vapour state may lead to the formation of carbon dioxide (cf. Allmand and Reeve, A., 1927, 29). S. K. Tweedy.

Influence of a change of intensity of the incident light on the velocity of certain photochemical reactions. A. K. Bhattacharya and N. R. Dhar (Z. anorg. Chem., 1928, **175**, 357—366).—The velocities have been studied of nine inorganic photochemical reactions in sunlight and under illumination from a 1000-watt lamp at various intensities. The velocities of the reactions between chromic and oxalic acids and between potassium persulphate and potassium iodide are directly proportional to the intensity of the illumination, but for all the other reactions investigated the velocity is proportional to the square root of the intensity; it appears that this latter condition obtains for reactions in which atomic oxygen is formed. If the reactants exhibit marked absorption the velocity increases more rapidly with increase of intensity, or is directly proportional thereto; whilst for the systems having but slight absorption the square root law is valid. H. F. Gillbe.

Influence of the intensity of incident light on the velocity of some photochemical reactions. B. K. Mukerji and N. R. Dhar (J. Physical Chem., 1928, **32**, 1308—1330).—Data on the influence of the intensity of light on the rate of reaction of 15 pairs of substances are submitted and discussed. The rate of reaction is proportional to (i) the square of the intensity of the incident light in the reactions between sodium formate and iodine (both in the presence of sodium acetate), Rochelle salt and bromine, and quinine sulphate and chromic acid in the presence of sulphuric acid, (ii) to the square root of the intensity in the reactions between potassium oxalate and iodine, ammonium oxalate and iodine, ammonium oxalate and mercuric chloride in the presence of eosin, and sodium nitrite and iodine in the presence of sodium acetate, and (iii) to the intensity of the light in the reactions between chromic and oxalic acids in the presence of manganese sulphate and sulphuric acid, sodium citrate and iodine, ferrous sulphate and iodine, sodium formate and mercuric chloride in the presence of sodium acetate, and in the bleaching of dicyanin, and in the oxidation of iodoform in benzene as solvent. In the reaction between potassium permanganate and oxalic acid, no relation between reaction velocity and intensity of the incident light is apparent. L. S. Theobald.

Quantum yield of the photochemical decomposition of light-sensitive diazo-compounds. Eggert [with W. Schröter] (Z. Elektrochem., 1928, **34**, 602—605).—The photochemical decomposition of the diazo-compounds derived from 2-amino-α-naphthol-4-sulphonic acid and *p*-aminodiphenylamine was investigated by measuring the rate of liberation of nitrogen. The latter is evolved at a constant rate which diminishes gradually when the illumination is withdrawn. The shape of the velocity curve depends on secondary phenomena and is altered, *e.g.*, by change in the force or rhythm with which the decomposition vessel is tapped (cf. Gleu, this vol., 601). The quantum yield (about 0·35) is independent of the intensity and wave-length of the light and of the temperature and concentration of the diazo-solution. The same quantum yield is obtained with the solid compounds. Under the influence of *X*-rays no nitrogen could be detected, although a perceptible colour change occurs.

S. K. Tweedy.

Hydrolysis of sodium chloride. H. Brückner (Z. physikal. chem. Unterr., 1928, **41**, 92—93; Chem. Zentr., 1928, i, 1833).—A small quantity of water, added to molten sodium chloride in a platinum crucible, is poured while in the spheroidal state into blue litmus solution after half has evaporated. The litmus solution becomes red, whilst a solution of the cooled mass reacts alkaline. A. A. Eldridge.

Sodium alum. H. Leffmann and L. W. Strock (Bull. Wagner Free Inst. Sci., 1928, **3**, 19—22).—Crystals (octahedra modified by cubes, cubes, or monoclinic) of sodium alum are best obtained by evaporation of a solution at the ordinary or a moderate temperature; slow cooling of the boiling saturated solution is unsuitable. Chemical Abstracts.

Decomposition of sodium thiosulphate in hydrochloric acid solution. E. H. Riesenfeld and G. Sydow (Z. anorg. Chem., 1928, **175**, 49—73).—The decomposition products of thiosulphate in hydrochloric acid of varying concentrations in the presence and absence of arsenious acid have been studied by a new method of quantitative analysis which is given in detail. In hydrochloric acid solution alone thiosulphate may decompose according to either of the following schemes, depending on the acidity: (1) $S_2O_3''+H^{\cdot}=HSO_3'+S$, and (2) $5S_2O_3''+6H^{\cdot}=2S_5O_6''+3H_2O$. The sulphurous acid formed in (1) then reacts with the pentathionic acid formed in the second reaction, giving first tetrathionic, then trithionic acid, thus (3) $S_5O_6''+SO_3''=S_4O_6''+S_2O_3''$, and (4) $S_4O_6''+SO_3''=S_3O_6''+S_2O_3''$. Trithionic acid may also be formed by the direct action of sulphurous acid on thiosulphuric acid, thus: (5) $S_2O_3''+4HSO_3'+2H^{\cdot}=2S_3O_6''+3H_2O$. In strongly acid solutions, however, trithionic acid decomposes rapidly as follows: (6) $S_3O_6''=S+SO_2+SO_4''$. Addition of arsenious acid to the reaction mixture of hydrochloric acid and thiosulphate retards the reaction (1) and in the absence of sulphurous acid reactions (3), (4), and (5) cannot take place. Hence pentathionic acid formed according to (2) is practically the sole product of the reaction in the presence of arsenious acid (cf. Kurtenacker and Czernotzky (this vol., 1201). A. R. Powell.

Silver alkali thiosulphates. A. Rosenheim and G. Trewendt (Ber., 1928, **61**, [*B*], 1731—1735).—Alkali silver thiosulphates are prepared by the gradual addition of aqueous silver nitrate to an ice-cold, well-agitated solution of the alkali thiosulphate. The sparingly soluble salts separate directly from the mixture, whereas the more freely soluble compounds are precipitated by addition of alcohol. The following *compounds* are described: sparingly and freely soluble *ammonium* salts, $NH_4AgS_2O_3$ and $(NH_4)_5[Ag_3(S_2O_3)_4]$; the *potassium* salt, $K[Ag(S_2O_3)]$, and also $K_5[Ag_3(S_2O_3)_4]$ and $K_3[Ag(S_2O_3)_2,H_2O$; sparingly soluble sodium salt, $Na[Ag(S_2O_3)]$, and the more freely soluble salt to which the structure $Na_5[Ag_3(S_2O_3)_4],3H_2O$, instead of $Na_4[Ag_2(S_2O_3)_3],2H_2O$, is ascribed; the last salt and technical rubidium sulphate (containing potassium sulphate) give an isomorphous mixture of the salts $K_5[Ag_3(S_2O_3)_4]$ and $Rb_5[Ag_3(S_2O_3)_4]$. H. Wren.

Basic carbonates of beryllium. T. Nishimura and T. Yamamoto (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 89—90).—Beryllium carbonate is unstable in air, but in the dry state decomposition is slow and the salt attains a composition depending on the proportion of carbon dioxide originally present in the wet salt and on the degree of drying. The salt $3Be(OH)_2,CO_2,nH_2O$ is produced by double decomposition of a solution of beryllium chloride ($<1{\cdot}0N$) saturated with carbon dioxide at 0°, by a saturated solution of a hydrogen carbonate of ammonium, or of an alkali metal. A suspension of this salt in excess of water is converted into a substance containing 0·047 mol. of carbon dioxide to 1 mol. of beryllium oxide by prolonged passage of air at the ordinary temperature. This and similar experiments with beryllium hydroxide indicate that the substance containing 5% of carbon dioxide is stable in contact with air or water.

J. Grant.

Synthesis of sapphirin. E. Dittler (Z. anorg. Chem., 1928, **174**, 342—354).—Natural sapphirin does not melt unchanged; at 1500° decomposition takes place with the formation of spinel, sillimanite, and a highly silicious glass containing a little alumina, thus: $Mg_5Al_{12}Si_2O_{27}=5MgAl_2O_4+Al_2SiO_5+SiO_2$. Attempts to synthesise the mineral by heating magnesia, alumina, silica, and small quantities of ferrous oxide (added as oxalate) yielded at 1400—1500° mixtures of spinel, sillimanite, and silica glass. No better results were obtained in the presence of boron trioxide as mineraliser. As natural sapphirin usually contains small quantities of water as well as, occasionally, boron trioxide, it is suggested that synthesis can be effected only in the presence of water vapour at about 900—1000° under high pressure. This would account for the paragenesis of sapphirin with biotite at Fiskernäs and other places, where the (001) face of mica has grown with the (010) face of sapphirin.

A. R. Powell.

Crystalline aluminium hydroxide of von Bonsdorff. R. Fricke (Z. anorg. Chem., 1928, **175**, 249—256).—The crystalline aluminium hydroxide precipitated from alkali aluminate solutions by hydrolysis or by the slow action of carbon dioxide is hydrargillite only when the precipitation takes place over a period of months. With more rapid precipitation a metastable hydroxide of the same composition, $Al_2O_3,3H_2O$, is obtained, which has a lattice structure identical with that of the aluminium hydroxide obtained by Böhm (A., 1926, 113) from acid solutions. This new form is named "bayerite," as it occurs in large quantities in the alumina precipitated by the Bayer process. A. R. Powell.

Efflorescence of carbon. P. H. Prausnitz (Naturwiss., 1928, 16, 57—58; Chem. Zentr., 1928, i, 1841).—Efflorescence on carbon tubes heated at 1200° in illuminating gas contained 99% C and 1% of water, and was formed by the decomposition of hydrocarbons at the carbon surface. A. A. Eldridge.

Carbonyl bromide. II. Preparation and properties. H. J. Schumacher and S. Lenher (Ber., 1928, **61**, [*B*], 1671—1675; cf. this vol., 847).—Carbonyl bromide is prepared by heating a mixture of carbon tetrabromide and concentrated sulphuric acid (*d* 1·83) at 150—170°, whereby a distillate containing carbonyl bromide, bromine, hydrogen bromide, and sulphurous acid is obtained. The bulk of the free bromine is removed by cautious treatment with mercury followed by distillation. The product is cautiously mixed with powdered antimony and distilled from an all-glass apparatus, the process being repeated if necessary. Carbonyl bromide is thus obtained as a colourless liquid, d^{15} 2·52. Its physiological action is similar to that of the corresponding chloride. It is less readily hydrolysed than the latter compound by water. The vapour-pressure curve between −50° and +25° is given. The thermal equilibrium even at the ordinary temperature lies strongly towards the components and is attained very slowly from carbon monoxide and bromine. Homogeneous carbonyl bromide is moderately stable to heat and, at 200°, suffers scarcely appreciable decomposition. At higher temperatures, the reaction is one of the first order at the glass walls. Decomposition is unusually strongly accelerated by catalysts, particularly organic substances. H. Wren.

Formation of ammonia from active nitrogen and active hydrogen. B. Lewis (J. Amer. Chem. Soc., 1928, **50**, 2427; cf. this vol., 258).—The comparatively high pressures used and the long gas exit tube of the apparatus suffice to explain why the formation of ammonia was not detected in the experiments of Koenig and Elöd (A., 1914, ii, 264, 266). S. K. Tweedy.

Ammonium polysulphides, hydrogen pentasulphide, and the thiocarbonic acids. H. Mills and P. L. Robinson (J.C.S., 1928, 2326—2332; cf. Bloxam. *ibid.*, 1895, 67, 277; Thomas and Riding, *ibid.*, 1923, **123**, 1726; Walton and Whitford, A., 1923, ii, 315).—Suspensions of sulphur in aqueous ammonia on saturation with hydrogen sulphide yield only ammonium pentasulphide, which by refluxing with carbon disulphide gives ammonium thiocarbonate and ammonium perthiocarbonate. *Hydrogen pentasulphide*, d^{16} 1·67, is obtained by treating ammonium pentasulphide with anhydrous formic acid. Tetrathiocarbonic acid and trithiocarbonic acid, f. p. −30·5°, $d_4^{17\cdot0}$ 1·47, $\gamma^{12\cdot5}$ 48·3 dynes/cm., have been isolated. F. J. Wilkins.

[**Radical-like alkali salts of a new acid containing nitrogen and oxygen.**] E. Zintl and O. Kohn (Ber., 1928, **61**, [*B*], 2063).—The authors' compound, Na_2NO_2 (cf. this vol., 258), has been isolated previously by Maxted (J.C.S., 1917, **111**, 1016). H. Wren.

Hydrazine selenate. J. Meyer and W. Aulich (Ber., 1928, **61**, [*B*], 1839—1840).—Hydrazine hydrate and dilute selenic acid afford colourless *hydrazine hydrogen selenate*, which is not decomposed by boiling water. When dry, it is caused to explode with unusual readiness by heat, shock, or gentle trituration. It explodes violently on contact with hydrochloric acid vapour. In analytical practice, therefore, selenic acid and selenates should be reduced to selenites by hydrochloric acid before hydrazine hydrate is added. H. Wren.

Tetraphosphorus triselenide and phosphorus thioselenides. J. Mai (Ber., 1928, **61**, [*B*], 1807—1811; cf. A., 1926, 1113).—The preparation of tetraphosphorus triselenide, d^{22} 3·161, from its components in the presence of tetrahydronaphthalene and its subsequent purification are described in detail. The colour varies from yellow to orange-red, according to the thickness of layer. The substance is slowly decomposed by atmospheric moisture, but does not appear sensitive to light. It is slowly decomposed by water. Sodium or potassium hydroxide or sodium sulphide converts it into sodium selenide; sodium carbonate and calcium or barium hydroxides behave similarly but less energetically. It has m. p. 242—243° after becoming lighter at 200°. It exhibits distinct phosphorescence at about 160° which becomes very marked at 280°.

Attempts to prepare phosphorus thioselenides from the components in tetrahydronaphthalene or from varying proportions of tetraphosphorus triselenide and trisulphide do not lead to the isolation of chemical individuals and indicate that the so-called phosphorus thioselenides are, at most, isomorphous mixtures. H. Wren.

Phosphates and arsenates of quadrivalent manganese. V. Auger and A. Yakimach (Compt. rend., 1928, **187**, 603—605).—*Ammonium manganiphosphate*, $(NH_4)_2H_2MnP_2O_9$, has been prepared by heating a solution of a mixture of diammonium phosphate and permanganate; black, rhombic crystals separate on cooling. *Manganiarsenic acid*, $Mn(H_2AsO_4)$, can be prepared by dissolving hydrated manganese dioxide in concentrated arsenic acid solution, by the action of arsenic acid on a permanganate, or by the interaction of arsenic acid with a mixture of manganous nitrate and a permanganate. *Ammonium manganiarsenate* resembles the corresponding phosphate. C. W. Gibby.

Constitution of hydrogen disulphide. Action of hydrogen disulphide on compounds of tervalent phosphorus. J. Dodonov and H. Medox (Ber., 1928, **61**, [*B*], 1767—1770).—In the hope of establishing a constitutional similarity between hydrogen disulphide and hydrogen peroxide, the behaviour of the former towards tertiary amines and phosphines has been investigated. Dimethylaniline causes vigorous decomposition of the compound into hydrogen sulphide and sulphur. Triethylphosphine and triethylarsine afford the corresponding sulphides. With phosphorus trichloride in benzene the disulphide yields phosphoryl thiochloride, phosphorus pentasulphide, hydrogen chloride, and a little hydrogen sulphide. It appears probable that the compound $PCl_3(SH)_2$ is formed initially and that a similarity in constitution exists between hydrogen disulphide and hydrogen peroxide. H. Wren.

Compound of sulphur with sulphurous acid. A. Kurtenacker and A. Czernotzky (Z. anorg. Chem., 1928, **175**, 231—240).—The yellow solution obtained by treating a thiosulphate solution with sulphur dioxide becomes colourless on keeping and then yields a precipitate of sulphur when treated with formaldehyde and sodium hydroxide or acetate, although no polythionate can be detected in the solution. Neutralisation of the colourless liquid with sodium hydroxide yields thiosulphate and sulphite, but no precipitate of sulphur. With ice-cold concentrated hydrochloric acid and thiosulphate a similar colourless solution is obtained without precipitation of sulphur; after 15 hrs. no thiosulphate can be detected. These reactions are ascribed to the formation of a loose compound of sulphur and sulphurous acid; thus, $[S_2O_3,SO_2]''+H_2O \rightleftharpoons [S_2O_3,SO_3H_2]''$; $[S_2O_3,SO_3H_2]'' \rightleftharpoons [S(SO_3H)_2]''$. A. R. Powell.

Higher polythionates. A. Kurtenacker and A. Czernotzky (Z. anorg. Chem., 1928, **174**, 179—188).—The action of concentrated hydrogen chloride solution on sodium thiosulphate solutions in presence of small quantities of sodium arsenite at −10° to −15° has been studied. Although pure hexathionates have not been prepared, mixed crystals of penta- and hexa-thionates have been obtained, which in aqueous and dilute acetic acid solution decompose rapidly with separation of sulphur. The reaction between sodium carbonate and pentathionates does not yield quantitatively sulphur and tetrathionate, as assumed by Raschig, but goes far beyond this stage even in dilute solution, and cannot therefore be made the basis of a method of determination of pentathionate. H. F. Gillbe.

Action of ammonia on alkali chromichlorides and on chromiammines which contain more than six molecules of ammonia. F. Ephraim and W. Ritter (Helv. Chim. Acta, 1928, **11**, 848—864).—The action of ammonia on dipotassium aquochromic pentachloride gives a greyish-violet mass containing hydroxypentamminechromic chloride. This dissolves in water to give a cherry-red solution from which nitric acid precipitates first the purpureonitrate and finally the roseo-nitrate in 27% yield. Hydrochloric acid precipitates from the aqueous solution the purpureo-chloride in 40% yield. The action of ammonia on the ammonium salt gives the same products. The formation of the compound $(NH_4)_3[CrCl_5(OH)]$ as an intermediate is suggested. No evidence of the existence of ammines of double salts was obtainable.

The action of ammonia on a number of chromiammines has been studied at the ordinary temperature and at the temperature of a salt freezing mixture. Amounts of ammonia varying from 1 mol. to 12 mols. per g.-mol. of salt are taken up. Decomposition curves of the additive products are given. The following salts have been investigated: luteobromide and -nitrate; roseo- and purpureo-nitrates, chlorides and bromides; thiocyanato-pentammine nitrate, bromide, iodide, and thiocyanate; oxalotetrammine nitrate; hydroxypentammine chloride; hexacarbamido-chloride, -bromide, and -iodide.

A method of preparation of the roseo- and purpureochromiammines by acting on potassium or ammonium chromichloride with a solution of ammonia in ammonium nitrate is described; yields of 45% have been obtained. R. N. Kerr.

Reduction of selenious acid. L. M. Clark (J.C.S., 1928, 2388—2393; cf. Keller, A., 1898, ii, 638).—The composition of the precipitate obtained by the reduction of selenious acid by sulphurous acid in the presence of copper sulphate and hydrochloric acid varies from that of cuprous selenide in slightly acid solutions to that of pure selenium in solutions containing much hydrochloric acid. It is suggested that the selenious acid is under all conditions first reduced to selenium, which subsequently affords cuprous selenide. The extent of the formation of cuprous selenide depends on the hydrogen-ion concentration of the solution. F. J. Wilkins.

Preparation of a tungsten carbonyl by means of a [Grignard] magnesium compound. A. Job and J. Rouvillois (Compt. rend., 1928, **187**, 564—565).—Job and Cassall's method (A., 1926, 1017) has been used for the production of *tungsten carbonyl*, $W(CO)_6$, by the action of pure carbon monoxide for 6 hrs. at 0° on pure tungsten hexachloride in the presence of magnesium phenyl bromide (to fix the former), ether, and benzene. Colourless, laminated crystals, subl. 50°, were obtained, decomposed at 100° or by fuming nitric acid, but not by water or ordinary acids. J. Grant.

Explosive properties of solid hypochlorites. J. Weichherz.—See B., 1928, 783.

Iron [and tin]. L. G. Knowlton (J. Physical Chem., 1928, **32**, 1572—1595).—The subjects investigated include new methods for the determination of carbon in iron, tin–iron alloys, the effect of aniline on the rate of dissolution of iron in acid, the reduction of nitrobenzene by iron, and the passivity of tin in nitric acid.

The total carbon in iron can be determined electrolytically by making iron turnings in a platinum dish the anode, a copper strip the cathode, and a 10% solution of sodium sulphate, renewed several times to remove ferric hydroxide, the electrolyte. The carbon can then be determined by combustion in the usual way. Graphitic carbon cannot be determined by making iron the cathode in an ammoniacal solution of ammonium nitrate. The current does not cause the corrosion, and the total carbon is left. The amount of carbon left by the action of acids on iron is increased when depolarisers are added during dissolution. With potassium permanganate of the correct concentration and a white iron, the total carbon present is left, but with grey iron some of the graphitic carbon is oxidised. Chlorine and aqua regia also increase the amount of residual carbon.

The addition of 25% of tin to molten grey cast iron throws carbon out of the iron, but not the total graphitic carbon as claimed by Eyferth (Percy's "Metallurgy of Iron and Steel," 1864). The addition of tin beyond a certain amount has little effect owing to the formation of two layers. The condition of the carbon present in molten iron is discussed. The increased combined carbon content of the alloy is attributed to the dissolution of silicon by the tin.

The action of 10% sulphuric acid, saturated with aniline, on iron at 50—60° removes the mill scale, but the amount of hydrogen evolved is greatly reduced. Further, the hydrogen overvoltage on iron is raised by the presence of aniline.

Grey iron reduces nitrobenzene approximately to the same extent when boiled with either sodium chloride or sulphate solutions, but, owing to the kind of iron used, the results disagreed with those of Snowdon (A., 1912, i, 100). Iron is not rendered passive by sodium chloride solution.

Tin becomes passive in nitric acid, *d* 1·426, when wrapped with a platinum wire; when connected with a platinum electrode, it becomes passive only with a more concentrated solution of the acid, and when made the anode with a cathode of platinum, it becomes passive in an acid more dilute than that required in the case with the platinum wire. The results are discussed. L. S. Theobald.

[Nitric oxide and carbon monoxide compounds of so-called univalent iron and nickel.] W. Manchot and H. Gall (Annalen, 1928, **465**, 304—305).—Polemical against Reihlen (cf. this vol., 35, 1114). E. W. Wignall.

Reactions and derivatives of iron carbonyl. II. Compounds of iron halides and carbon monoxide. W. Hieber and G. Bader (Ber., 1928, **61**, [*B*], 1717—1722; cf. this vol., 511).—Iodine reacts with a slight excess of iron pentacarbonyl in ether, giving the dark brownish-red *iodide*, $Fe(CO)_4I_2$. The analogous *bromide*, $Fe(CO)_4Br_2$, is prepared in light petroleum and is the sole compound even when the halogen is used in large excess. The less stable, yellow *chloride*, $Fe(CO)_4Cl_2$, is similarly obtained at −20°. Determinations of mol. wt. in indifferent solvents give normal values. The compounds do not appear preparable from ferrous halides and carbon monoxide. They are very sensitive to reagents containing oxygen and nitrogen. Water decomposes them rapidly into ferrous halide and carbon monoxide. Ammonia, amines, alcohols, and organic carbonyl compounds such as esters, ketones, and aldehydes behave similarly with varying readiness; the superior stability of the iodides is noteworthy. The bromide loses carbon monoxide completely in the presence of 2 mols. of pyridine. Under precisely similar conditions the iodide affords the *dicarbonyl* compound, $Fe(CO)_2I_2,2C_5H_5N$, which loses carbon monoxide completely when treated further with the base and decomposes spontaneously when preserved or exposed to light to the *monocarbonyl* derivative, $Fe(CO)I_2,2C_5H_5N$. With a large excess of pyridine, hexapyridine ferrous iodide is produced. Under the influence of light the chloride is rapidly and completely decomposed; the iodide is less readily affected than the chloride. The final products are the ferrous halides, which are thus readily prepared in the pure state. H. Wren.

Oxidation of ferrous hydroxide in air. A. Krause (Z. anorg. Chem., 1928, **174**, 145—160).—Precipitation of ferrous hydroxide from ferrous sulphate solutions by an equimolecular quantity of sodium hydroxide yields a product which on atmospheric oxidation is converted completely into hydrated ferric hydroxide, whereas that produced in presence of a greater concentration of sodium hydroxide oxidises in the air to products which always retain ferrous iron; the highest FeO/Fe_2O_3 ratio, resulting from high alkali concentrations, is 0·3 : 1, increase of the ferrous ratio causing a change of colour of the product from yellow to black, with a decrease of the water content, which corresponds with a change from hydrated meta-ferric hydroxide to ferrous ferrite. The isoelectric point of the hydroxide, the composition of which approximates to $Fe_2O_3,2H_2O$, lies at p_H 5·2. Confirmation of the theory of ferrite formation has been obtained by oxidising ferrous hydroxide in the presence of magnesium hydroxide, whereby magnesium ferrite is obtained. The meta-form of the hydroxide differs from the brown ortho-form, having its isoelectric point at p_H 7·7, in its ease of peptisation by ammonia, and its greater particle size. The ortho-form is the less stable and under water is gradually transformed into the meta-form. H. F. Gillbe.

Carbonatocobaltammines. J. Kranig (Bull. Soc. chim., 1928, [iv], **43**, 989—995).—The constitution of carbonatodecamminecobaltic sulphate, $[Co_2(NH_3)_{10}CO_3](SO_4),4H_2O$, has been confirmed. This is the only known salt of the series and is extremely unstable, giving by double decomposition salts of other series. Of the pentammine series the *chloride*, $[Co(NH_3)_5CO_3]Cl,H_2O$, and the *oxalate*, $[Co(NH_3)_5CO_3]_2C_2O_4,3H_2O$, have now been isolated. The bromide of this series described by Werner can be obtained more readily by double decomposition between the above chloride and potassium bromide. O. J. Walker.

Multinuclear cobaltammines, and method of preparation of the non-electrolyte $[Co(NH_3)_3Cl_3]$. E. Birk (Z. anorg. Chem., 1928, **175**, 405—412).—The complex $[\{Co(NH_3)_3\}_2(OH)_3]Cl_3,H_2O$ has been prepared from the compound $[Co(NH_3)_3(NO_3)_3]$ by conversion into triamminotriaquocobaltic nitrate, treating with concentrated hydrochloric acid at −20°, and then with potassium hydroxide and ammonium chloride. The compound $[Co\{Co(NH_3)_4(OH)_2\}]Cl_6,2H_2O$ may be obtained as a by-product. Better yields are obtained in the preparation of cobalt trichlorotriammine by Werner's method if hydrogen chloride saturated at the lowest possible temperature be employed. H. F. Gillbe.

Ruthenium [chlorides]. H. Gall (Z. angew. Chem., 1928, **41**, 1070—1071).—A reply to Krauss (this vol., 413). Evidence based on the work of other investigators and on Gall's earlier work is adduced in support of the bivalency of ruthenium in the blue chloride and its quadrivalency in the product obtained by the reduction of the tetroxide with concentrated hydrochloric acid. A. R. Powell.

Compounds of osmium tetroxide. F. Krauss (Z. anorg. Chem., 1928, **175**, 343—346).—Polemical. Fritzmann's experiments confirm the author's opinion that Tschugaev has not prepared compounds of octavalent osmium. H. F. Gillbe.

Applicability of the analytical quartz lamp to mixtures of solid substances. F. Hein and W. Retter.—See B., 1928, 733.

Physical methods in chemical laboratories. VIII. Electrical methods of titration. E. Thilo (Z. angew. Chem., 1928, **41**, 1057—1061).—An account of the principles and methods of electrometric titrations, both potentiometric and conductometric procedures being discussed.

A. R. Powell.

Importance and examination of standards for titration. N. Schoorl (Chem. Weekblad, 1928, **25**, 534—537).—A *résumé* of the methods of examining the commoner reagents for volumetric analysis.

S. I. Levy.

Potentiometric titration using monometallic electrode pairs. E. Müller and H. Kogert (Z. physikal. Chem., 1928, **136**, 437—445).—A modification of the bimetallic electrode method (cf. A., 1923, ii, 33) of potentiometric titration using two electrodes of the same metal is described. The end-point is marked, not by the maximum change of *P.D.* between the electrodes, but by the maximum *P.D.* itself. The titration can therefore be performed more quickly. Smooth and platinised platinum are used as the electrodes, but the method is not restricted to these metals. The method is illustrated by means of permanganate, dichromate, and thiosulphate titrations.

O. J. Walker.

Two new potentiometric titration methods. E. Müller and H. Kogert (Z. physikal. Chem., 1928, **136**, 446—450).—Two electrodes of the same kind are placed not too close together in the solution to be titrated, which is stirred in a circular direction. The standard solution is allowed to drop in close to one of the electrodes, which is thereby momentarily in contact with a solution containing excess of the added reagent and therefore acquires a different potential from the second electrode, which is always in contact with the thoroughly mixed solution. The course of the titration near the end-point is followed by connecting a galvanometer across the two electrodes and measuring the temporary deflexion produced by the addition of each drop. At the end-point this deflexion is practically zero.

In a modification of the above method the positions of the two electrodes and the direction of stirring are so arranged that the change in concentration produced in the reaction vessel by the addition of each drop takes place sooner at one electrode than at the other. The temporary *P.D.* between the electrodes on the addition of each drop passes through a sharp maximum at the end-point.

These methods, particularly the second method, give good results with precipitation reactions, but are unsuitable for oxidation–reduction processes.

O. J. Walker.

Accuracy and practice of quantitative kinetic analysis in the case of bimolecular reactions. L. Smith and J. Lindberg (Ber., 1928, **61**, [*B*], 1709—1717).—The mathematical method developed previously (Smith, A., 1920, ii, 607) for ascertaining the composition of a mixture of two allied and difficultly separable substances when the reaction constants for the mixture and one component are known is examined experimentally. Mixtures of α- and β-glyceryl chlorohydrin or of the α-compound with barium β-chloro-α-hydroxybutyrate are hydrolysed with barium hydroxide under somewhat unusually careful conditions. Experiments are recorded under the conditions, $k_1/k_2=14\cdot9$ and 2·7. The accuracy obtained in the latter circumstances indicates that kinetic analysis is doubtless applicable even at $k_1/k_2=2$ with an error of a few %, provided only that k_1 and k_2 are well-defined and accurately determinable constants of the second order.

H. Wren.

Use of simple metallic electrodes in the potentiometric titration of acids and bases. J. O. Closs and L. Kahlenberg (Amer. Electrochem. Soc., Sept. 1928. Advance copy, 24 pp.).—Preliminary experiments showed that the single potentials of the metals tungsten, molybdenum, arsenic, antimony, bismuth, aluminium, and tin in 0·1N-acids differed greatly from their potentials in 0·1N-alkalis. The possibility of using these metals as indicator electrodes in the titration of an acid with an alkali was therefore examined. From the numerous titration curves obtained with various strong and weak acids it is evident that all these metals yield sharp end-points in titrations with N-sodium hydroxide. In some cases, notably with aluminium, the change of potential at the end-point is much greater than with a hydrogen electrode. Except with tin electrodes in oxalic acid solutions and with cadmium electrodes the potential always changed towards baser values at the end-point. With tin electrodes a second discontinuity was generally observed in the alkaline region of the curve, but its position depends on the nature of the acid being titrated and is influenced by shaking the electrode. In most cases the potentials of the metals became constant within a minute after each addition of alkali, and, even in some instances where the potential tended to drift, the effect was not great enough to interfere with the determination of the end-point. Satisfactory results were also obtained with platinised platinum electrodes, but thallium, lead, and zinc electrodes give anomalous results. The theory of the method is discussed and it is concluded that the potentials observed arise from the adsorption of oxygen or hydrogen by the metal surface.

H. J. T. Ellingham.

$p_{\rm H}$ Value of distilled water. C. van der Hoeven (Collegium, 1928, 440—443).—The most accurate method is the colorimetric method using a dilute solution of methyl-red neutralised with sodium hydroxide. This gives $p_{\rm H}$ 6·7—6·6 for distilled water. There is always an error on the acid side with the quinhydrone electrode method for all $p_{\rm H}$ measurements, which diminishes in proportion to the amount of buffering.

D. Woodroffe.

Methods of expressing acidity of solutions. A. J. J. Vande Velde (Natuurwetensch. Tijdschr., 1928, **10**, 145—151).—The various methods of stating the concentration of hydrogen ion and hydroxyl ion in solutions are discussed, and a table is given in which the coefficients of Giribaldo, Derrien-Fontes, and Wherry are set out with the hydrogen-ion values, $p_{\rm H}$ values, normalities, and volumes containing 1 g. of hydrogen ion corresponding.

S. I. Levy.

Micro-determination of vapour pressure and water of hydration of solid compounds. F. E. E.

Germann and O. B. Muench (J. Physical Chem., 1928, 32, 1380—1386; cf. Wilson, A., 1921, ii, 376).—The micro-method described consists in introducing solutions of sulphuric acid of known concentration in dishes into the tightly-closed case of a sensitive assay balance which bears the thin film of the sample painted from a saturated solution of the salt on a tared microscope cover-glass. Changes in weight and the equilibrium weight are ascertained by means of a system of riders of different weights. With thermostatic temperature control and other slight modifications of the method, the vapour pressure for a hydrate-pair can be found by a bracketing method from the concentrations of sulphuric acid used. Data for disodium phosphate and barium chloride show the method to be accurate and quick, and to require only small amounts of material which are recoverable. Methods for the preparation and preservation of pure hydrates, and for the determination of heat of hydration, are described. L. S. Theobald.

Determination of moisture by rapid drying. S. H. Meihuizen.—See B., 1928, 696.

Gravimetric determination of fluorine as calcium fluoride, using a membrane filter. G. G. Kandilarov (Ber., 1928, 61, [*B*], 1667—1671).—For the determination of fluorine in sodium fluoride, the aqueous solution is heated nearly to its b. p. and a slight excess of calcium chloride solution is added very gradually and with continuous stirring. The precipitated calcium fluoride is filtered on a membrane filter and washed three times with cold and four times with warm water. The precipitate and filter are dried in a specially-designed vacuum desiccator. The precipitate is removed from the membrane and heated at about 500° for 30—40 min. An addition of 0·0016 g. per 100 c.c. of mother-liquor is made to the weight of the precipitate, but the effect of the wash water may be neglected. If alkali carbonate is present, the solution is treated with so much nitric acid that it is neutral to methyl-red after the dissolved carbon dioxide has been expelled; after addition of a further few drops of acid sufficient to produce a faint red colour, the determination is carried out as above. The presence of nitrate ions causes the precipitate to be filtered much more rapidly; if the added acid is insufficient for this purpose, alkali nitrate may be added. H. Wren.

Diffusion of oxygen through rubber and various other substances. S. E. Hill (Science, 1928, 67, 374—376).—For the approximate evaluation of the amounts of oxygen diffusing through various materials, use is made of a tube containing luminous bacteria which give a perceptible glow at an oxygen pressure of 0·005 mm.; the lengths of the luminescent columns are compared. A. A. Eldridge.

Gravimetric determination of sulphuric acid in presence of antimony. S. von Fináły (Z. anal. Chem., 1928, 75, 17—27).—The determination of the sulphur content of antimony sulphides involves oxidation of the sulphur to sulphuric acid and the precipitation of barium sulphate from media containing tartaric acid, etc. The results thus obtained are not always trustworthy. The conditions under which the precipitation of sulphuric acid as barium sulphate from media containing antimony, tartaric acid, hydrochloric acid, and chlorides is reproducible and the necessary corrections minimal and independent of the concentration of antimony have therefore been determined. J. S. Carter.

Determination of polythionates. E. H. Riesenfeld and G. Sydow (Z. anorg. Chem., 1928, 175, 74—79).—For the determination of trithionate the solution is heated for 1 hr. to boiling with a mixture of 30 c.c. of 10% copper sulphate solution, 100 c.c. of 10% barium chloride solution, and 20 c.c. of hydrochloric acid (*d* 1·12), whereby the trithionate is quantitatively precipitated as barium sulphate, thus: $S_3O_6''+8Cu^{\cdot\cdot}+6H_2O=3SO_4''+8Cu^{\cdot}+12H^{\cdot}$. Tetrathionate, thiosulphate, and sulphite interfere, but pentathionate is without action. All polythionates, except dithionate, are oxidised completely to sulphate by heating with iodine and sodium hydrogen carbonate in a closed tube for 1 hr. or by keeping the mixture for 48 hrs. at the ordinary temperature in a closed flask. Titration of the excess of iodine affords a means of determining the sum of the polythionates present. A. R. Powell.

Detection of pentathionate in presence of sulphurous acid. A. Czernotzky (Z. anorg. Chem., 1928, 175, 402—404).—The pentathionate ion may be detected, even at a concentration of 0·004*M*, in presence of 25 times the quantity of sulphite ion by adding 5 c.c. of formaldehyde solution to 10 c.c. of the solution, rendering slightly alkaline, and observing the appearance of opalescence within 2—3 min.; opalescence after a longer period is no longer characteristic of pentathionate. H. F. Gillbe.

Elimination and determination of nitrogen in argon. C. Leu (Helv. Chim. Acta, 1928, 11, 761—763).—The exact conditions for removing nitrogen from, and determining it in, argon by passing the gas over magnesium containing small quantities of lime and sodium are described. The most favourable temperature is 850—870°. The nitride formed is decomposed by passing air containing water vapour over the cooled mixture and the ammonia produced is collected. Experiments show that 98% of the nitrogen content of a mixture containing 5% of nitrogen can be removed and determined in this way. R. N. Kerr.

Micro-Kjeldahl determination [of nitrogen]. B. Saiko-Pittner (Pharm. Presse, 1928, 33, 60—61; Chem. Zentr., 1928, i, 1892).—In the determination of nitrogen in pyramidone, phenylhydrazine, or semicarbazide the evolution of nitrogen or oxides of nitrogen is largely prevented by the addition of selenium. A. A. Eldridge.

Analysis of nitrates. P. Rischbieth.—See B., 1928, 745.

Assay of phosphoric acid. F. A. Maurina.—See B., 1928, 709.

Use of liquid amalgams in volumetric analysis. XI. Determination of phosphoric acid by employment of zinc or cadmium amalgam. Note to part VII. Method of determining chromium in chromium steels. K. Someya (Z. anorg. Chem., 1928, **175**, 347—356).—Zinc and cadmium amalgams reduce sexavalent molybdenum quantitatively to the tervalent state. Phosphate ion may be determined by precipitating as ammonium phosphomolybdate, dissolving the precipitate in ammonia solution, evaporating to small volume, reducing with amalgam, and titrating the resulting solution with 0·14*N*-potassium permanganate.

Satisfactory results are obtained for the determination of chromium in chromium alloys only if clean amalgam is used and if the method of procedure be somewhat modified. H. F. Gillbe.

Picric acid as an artificial standard in the colorimetric determination of silica. E. J. King and C. C. Lucas (J. Amer. Chem. Soc., 1928, **50**, 2395—2397).—The addition of the reagents of Diénert and Wandenbulcke (A., 1923, ii, 507) to a silicate solution containing 50 mg. of silica per litre produces a yellow coloration which matches that of a solution containing 25·6 mg. of pure vacuum-dried picric acid per litre. The discrepancy between this and previous results may be due to previous workers not having dried the acid thoroughly before use.

S. K. Tweedy.

Micro-elementary analysis. R. Goubau (Natuurwetensch. Tijdschr., 1928, **10**, 129—136).—An apparatus for micro-analysis in which the water formed in the combustion is collected in a U-tube immersed in a mixture of solid carbon dioxide and alcohol, and the carbon dioxide in a tube immersed in liquid oxygen is described. The limbs of the absorption tubes contain spirals of silver wire to bring the gases into contact with the cooled surfaces. The precautions described allow an accuracy of 0·2—0·5% with quantities of 5—10 mg. of material.

S. I. Levy.

Accurate gas burette for the volumetric determination of carbon [in steel]. O. Meyer.—See B., 1928, 753.

Detection of carbon dioxide. G. Elteste.—See B., 1928, 709.

Improved Orsat apparatus for the analysis of flue gases. K. Münzer.—See B., 1928, 733.

Micro-determination of potassium as cobaltinitrite. A. Leulier, L. Velluz, and H. Griffon (Bull. Soc. Chim. biol., 1928, **10**, 891—904).—The precipitate obtained by treatment of a solution of the sample with excess of sodium cobaltinitrite is separated and washed by centrifuging under standardised conditions. The precipitate is then decomposed by heating at 100° with a solution of sodium phosphate and acidified with sulphuric acid; potassium iodide is added, and the liberated iodine titrated with sodium thiosulphate solution. The error is below 3%. G. A. C. Gough.

Determination of potassium as perchlorate. A. T. Dalsgaard (Dansk Tidsskr. Farm., 1928, **2**, 257—273).—The perchlorate process for the determination of potassium has been critically examined and the following procedure is recommended. The solution is evaporated almost to dryness in a Pyrex dish after the addition of 1·5 times the theoretical amount of perchloric acid. After cooling, water and perchloric acid (1 c.c.) are added and the resulting solution is evaporated to complete dryness. The cold residue is crushed with a glass rod, 10 c.c. of absolute alcohol are added, and the whole is left for 30 min. with occasional stirring. The liquid is decanted through a glass filter crucible and the precipitate washed by decantation with 3—5 c.c. of 96% alcohol containing 0·2% of 70% perchloric acid. The remaining alcohol is carefully evaporated, water added, and the whole again evaporated to dryness. After cooling, the residue is treated with a special wash liquid (96% alcohol containing 0·2% of perchloric acid and saturated with potassium perchlorate) and the potassium perchlorate filtered, washed, and dried at 150—200°. If the redissolution of the precipitate after the first washing with alcohol be omitted, the results are invariably 2—3 mg. too high when considerable amounts (0·1 g. or more) of sodium are present, and a similar, although smaller, error occurs if the crystals of potassium perchlorate are not crushed finely before filtration. The method as given yields accurate results in the presence of sodium, barium, calcium, magnesium, and iron, and is recommended for technical purposes. A comprehensive summary of previous work on the perchlorate process accompanies the paper. H. F. Harwood.

Micro-determination of sodium. E. di Benedetto and A. D. Marenzi (Rev. Centr. Estud. Farm. Bioquim., 1927, **16**, 592—595; Chem. Zentr., 1928, i, 1794).—In Nau's modification of Blanchetière's method, the uranyl magnesium sodium acetate is precipitated, separated, and washed in the centrifuge tube. A. A. Eldridge.

Electrometric determination of calcium by the use of secondary electrodes. M. H. Corten and L. Estermann (Z. physikal. Chem., 1928, **136**, 228—230).—The chains $Ag|Ag_2C_2O_4|CaC_2O_4|Ca^{\cdot\cdot}$, and $Zn|ZnC_2O_4|CaC_2O_4|Ca^{\cdot\cdot}$ may be used as reversible secondary electrodes for the determination of calcium ions. The latter must be used for determinations in blood and serum, and gives reproducible results, maintaining a constant potential over considerable periods. F. G. Tryhorn.

Wolff's calcimeter for the continuous gasometric determination of calcium carbonate. A. Hock (Chem. Fabr., 1928, 548).—An apparatus for the determination of the calcium carbonate content of fertilisers etc. by which series of determinations can be carried out in succession is described and illustrated. It comprises a number of reaction flasks coupled with an automatic shaking apparatus which permits of the continuous agitation of the sample with the acid for any desired period. The reaction flasks are each connected to a gas-measuring burette graduated in c.c., a manometer for adjusting the level of the liquid in the burette, and a reservoir containing the necessary acid. A. R. Powell.

Quantitative separation of barium and calcium. M. Lemarchands (Compt. rend., 1928, **187**, 601—603).—The solubilities of barium sulphate in water and in hydrochloric acid solutions have been determined at 100°, also its solubility in calcium chloride solution. C. W. Gibby.

Differentiation of dolomite and magnesite. F. Feigl and H. Leitmeier (Zentr. Min. Geol., 1928, A, 74—87; Chem. Zentr., 1928, i, 1795).—Magnesite, but not dolomite, is coloured reddish-violet by alkaline-alcoholic diphenylcarbazide solution. Dolomites containing magnesium carbonate, brucite, and breunnerite give the reaction. A. A. Eldridge.

Identification of cadmium by the drop method. P. G. Popov (Ukraine Chem. J., 1928, **3**, 158—160).—Two or three drops of the solution to be analysed, which may contain, besides cadmium, lead, bismuth, copper, mercury, and silver, are acidified by the addition of 2—3 drops of sulphuric acid, and the solution is evaporated until dense white fumes of acid are evolved, when it is diluted, and excess of iron powder added, and the whole immediately filtered. A solution of hydrogen sulphide is then added to the solution on a watch-glass, when, if cadmium is present, it will be precipitated as a yellow sulphide. R. Truszkowski.

Separation of cadmium from copper in qualitative analysis. P. G. Popov (Ukraine Chem. J., 1928, **3**, 153—155).—The filtrate obtained in group II after the precipitation of bismuth by ammonia is slightly acidified by sulphuric or hydrochloric acid and zinc or iron powder is added. The mixture is shaken for 10—20 sec., and immediately filtered; the cadmium is precipitated as sulphide from the filtrate, which is free of copper. R. Truszkowski.

Determination of copper in molybdenite. M. G. Roeder.—See B., 1928, 787.

Volumetric determination of mercuric oxide. P. Rây and J. Das-Gupta (J. Indian Chem. Soc., 1928, **5**, 483—485).—Mercuric oxide reacts with sodium thiosulphate according to the equation $HgO+2Na_2S_2O_3=Na_2[Hg(S_2O_3)_2]+2NaOH$. The liberated alkali is determined by titration. The method gives trustworthy results provided a large excess of sodium thiosulphate is avoided. H. Burton.

Confirmatory test for aluminium. E. H. Pañganiban and (Miss) F. A. Soliven (J. Amer. Chem. Soc., 1928, **50**, 2427—2428).—The solution obtained by Noyes' procedure ("Quantitative Chemical Analysis," 1923, 190) is passed through a filter-paper having a few asbestos fibres at the apex of the cone. The latter are withdrawn and burned on a platinum wire. This modification renders thorough washing unnecessary, and the ignition takes less time. S. K. Tweedy.

Electrometric iron–dichromate titrations. F. J. Watson (Chem. Eng. Min. Rev., 1928, **20**, 396—399).—In the absence of a satisfactory indicator the electrometric method of titrating ferrous iron and dichromate is more successfully used. The non-reversibility of the reaction renders investigations empirical and prevents a quantitative application of electrode theory. The use of a calomel electrode and potassium chloride bridge was eliminated in favour of bimetallic electrodes. Bright platinum is used as the "indicator electrode" on account of the high *E.M.F.* change at the end-point. A large number of metals maintained practically a constant *E.M.F.* with respect to the solution over the end-point region and were suitable as "reference electrodes," although gold was a marked exception. Tungsten appeared to be most suitable. Silver was found suitable for the titration of iron with dichromate but not *vice versa*, owing to the rapid oxidation of the metal by chromic acid. C. A. King.

Determination and separation of chromium, iron, aluminium, and phosphorus. K. K. Järvinen (Z. anal. Chem., 1928, **75**, 1—16).—The oxidation of chromium in alkaline media is accomplished most rapidly and satisfactorily by bromine. Considerable occlusion of chromate is observed when aluminium and iron are precipitated as hydroxides from solutions containing chromate. No chromate is occluded when these metals are precipitated as phosphates. The constituents in a mixture of chromium, iron, aluminium, and phosphate are determined in the following manner. A portion of the solution is treated with bromine (1—2 c.c.) and a distinct excess of 2*N*-sodium hydroxide added with constant shaking. After 15 min. the precipitate is dissolved in the minimum amount of hydrochloric acid and the solution again made alkaline. The solution is warmed for some time, acidified, and the excess of bromine removed by boiling. A sufficient amount of 2*N*-ammonium phosphate is added to the hot solution and iron and aluminium are precipitated by careful addition of ammonia. The cooled solution is diluted to a suitable volume and chromate determined iodometrically in a portion of the acidified filtrate. The precipitate, which need not be washed, is dissolved in hydrochloric acid and any chromate reduced by sodium hydrogen sulphite. Iron is oxidised by bromine water and the excess of bromine removed by boiling. The solution is boiled with 1—2 g. of potassium iodide in a retort and the liberated iodine absorbed in dilute sodium hydroxide solution. Rubber etc. connexions are inadmissible and the retort end must be sealed in the receiving liquid. The latter is acidified and the iodine titrated with thiosulphate. If the phosphate content of the original solution is known all constituents may be precipitated by ammonia and aluminium determined from the weight of the ignited precipitate by difference. J. S. Carter.

Diphenylcarbazide as a test for chromium. N. M. Stover (J. Amer. Chem. Soc., 1928, **50**, 2363—2366; cf. Brandt, A., 1906, ii, 309).—Diphenylcarbazide as a reagent for dichromate and chromium ions is much superior to a mixture of hydrogen peroxide and ether. It is more sensitive in presence of sulphuric acid than in the presence of either acetic or citric acids. Zinc and nitrate ions may be present. S. K. Tweedy.

Quantitative separation and determination by evaporation with gaseous hydrogen chloride. VII. Separation and determination of the components of tungstates. G. Jander and D. Mojert (Z. anorg. Chem., 1928, **175**, 270—276).—The hydrogen chloride method has been applied to the analysis of sodium and barium tungstates. H. F. Gillbe.

Precise determination of thorium by precipitation as subphosphate. F. Hecht (Z. anal. Chem., 1928, **75**, 28—39).—Thorium is precipitated quantitatively as subphosphate, $ThP_2O_6,11H_2O$, from boiling solutions containing about 10% of hydrochloric acid. Cerium is not precipitated alone under these conditions, particularly in presence of hydrogen peroxide. Conversion into pyrophosphate by ignition is, however, not quantitative. The precipitated subphosphate may be treated with sulphuric acid and sodium nitrate, and thorium precipitated as oxalate from the resulting solution. If sulphuric acid is not removed after the oxidation the solution obtained on dilution may be used for the precipitation. If sulphuric acid is removed, the suspension obtained on treating with water is made alkaline with ammonia and the precipitated phosphate (previously held to be a hydroxide) dissolved after filtration in hydrochloric acid. The oxalate is ignited and weighed as oxide. Alternatively, the subphosphate may be fused with sodium and potassium carbonates, the cooled mass treated with water, and the insoluble matter ignited. This ignited material is fused with potassium pyrosulphate, the cooled mass dissolved in hydrochloric acid, and thorium precipitated as oxalate.

J. S. Carter.

Determination of vanadium. B. S. Evans and S. G. Clarke.—See B., 1928, 786.

Determination of vanadium in steel. A. T. Etheridge.—See B., 1928, 714.

Ceric sulphate as a volumetric oxidising agent. VII. Determination of vanadium in presence of chromium, tungsten, and iron. H. H. Willard and P. Young (Ind. Eng. Chem., 1928, **20**, 972—974).—Vanadyl salts may be titrated electrometrically with ceric sulphate in hot (70—80°) solutions containing 5—10 c.c. of sulphuric acid (*d* 1·83), nitric acid (*d* 1·42), perchloric acid (70—72%), or hydrochloric acid (*d* 1·18) per c.c. Conversely, ceric salts may be accurately determined by electrometric titration with vanadyl sulphate in hot solutions containing sulphuric, nitric, or perchloric acids. For the determination of vanadium in steel 4—5 g. of turnings are dissolved in 10 c.c. of sulphuric acid and 35—40 c.c. of water. The solution is boiled vigorously until salts begin to separate, diluted with 20 c.c. of water, and cautiously oxidised with nitric acid, avoiding excess. After diluting to 100 c.c., 2 c.c. of silver nitrate solution (2·5 g./litre) and 2 g. of ammonium persulphate are added; the solution is boiled for 15 min., cooled, treated with 40 c.c. of sulphuric acid (*d* 1·5) and 0·05*N*-ferrous sulphate solution in slight excess as indicated by a drop in the voltage, and set aside for 10 min. After a slight excess of permanganate has been added, the solution is cooled to 5—10°, titrated with ferrous sulphate until the reduction of vanadic acid to vanadyl sulphate is complete, diluted to 300 c.c., heated to 70—75°, and titrated with 0·05*N*-ceric sulphate to reoxidise the vanadium. If the steel contains tungsten, the tungstic acid precipitated by the nitric acid treatment is collected, washed, and dissolved in sodium hydroxide, the solution being returned to the main solution prior to titration.

A. R. Powell.

Cerium salts in quantitative analysis. Determination of antimony in presence of arsenic. H. Rathsburg (Ber., 1928, **61**, [*B*], 1663—1665).—Antimony is determined by titration with 0·05*N*- or 0·01*N*-ceric sulphate solution in presence of methylene-blue, Congo-red, methyl-orange, or methyl-red; alternatively, the end-point is measured electrometrically. After determination of antimony, arsenic may be determined in the same solution either by titration with potassium bromate or with ceric salt until a sudden alteration of potential is observed.

H. Wren.

Analytical chemistry of tantalum, niobium, and their mineral associates. XII. Pyrosulphate–hydrolysis method. XIII. Separation of zirconium and hafnium from tantalum and niobium. W. R. Schoeller and E. F. Waterhouse (Analyst, 1928, **53**, 467—475, 515—520).—XII. An experimental investigation of the pyrosulphate–hydrolysis method shows that the earth acids cannot by any of the modifications of the method be quantitatively separated from zirconia or titania. The method is regarded as a balanced reaction in which a colloidal phase gradually flocculates with adsorption of almost any of the constituents of the solution, and should be disregarded. In mixtures of earth acids and titania no practical separation occurs at any stage preceding total precipitation; zirconia prevents hydrolytic precipitation of titania, and in the presence of titania the earth acids cannot be separated from ferric sulphate, but may be imperfectly separated from ferrous sulphate.

XIII. The term " zirconia " is used for the mixture $(Zr,Hf)O_2$. Small quantities of earth acids may be separated from much zirconia by fusing the mixed oxides with potassium hydrogen sulphate, dissolving the product in a saturated solution of ammonium oxalate containing as much salt as hydrogen sulphate taken, and treating the boiling liquid with 0·2 g. of tannin in hot water and dilute ammonia. The colour of the precipitate varies according to the ratio of oxides present. The precipitate is washed with 2% ammonium chloride solution and ignited. To precipitate zirconia-free pentoxide, the ignited precipitate is treated the same way as the mixed oxides, and the clear solution neutralised while boiling until cloudiness is perceptible; this is removed with the minimum amount of hydrochloric acid. The boiling solution is then treated with 1 g. of ammonium chloride and a freshly-prepared solution of tannin, which imparts a yellow, orange, or red colour, followed by flocculation of the coloured precipitate. After 1—2 hrs. at 50—70°, the liquid is filtered and the precipitate weighed as $(Ta,Nb)_2O_5$. Since the tannin and earth acid precipitate is very bulky, it is preferable to separate zirconia from quantities of earth acid exceeding 0·02—0·03 g. by first using the potassium carbonate fusion followed by the tannin process. The potassium fusion is carried out by fusing 6 parts of potassium carbonate with 1 part of the mixed oxides, digesting with 1 g. of potassium hydroxide and enough water to cover, stirring filter pulp into the diluted liquid, and filtering. The zirconia residue is washed with 2% potassium carbonate solution and ignited, and if heavy and derived from a mixture rich in tantalic oxide, fused again. The alkaline filtrate is acidified with hydrochloric acid, boiled with a small excess of ammonia, the precipitate mixed with filter pulp, washed with dilute ammonium nitrate solution, ignited, digested with hot water acidulated with hydrochloric acid, again ignited strongly, and weighed as $(TaNb)_2O_5$. The zirconia residue from the carbonate fusion is ignited, moistened with dilute sulphuric acid, dried, fused with hydrogen sulphate, and the product dissolved in ammonium oxalate solution. After filtering to remove impurities such as silica it is submitted to the tannin process.

D. G. Hewer.

Wilson's ray-track apparatus. T. Wulf (Z. physikal. chem. Unterr., 1928, 41, 70—73; Chem. Zentr., 1928, i, 1832).—An improved apparatus is described. A. A. Eldridge.

Light source devised by Auer von Welsbach. K. Warm (Z. wiss. Phot., 1928, 25, 365—379).—The light source consists of a spark between two electrodes which alternately touch and separate as a result of the effect of an interrupted electromagnet. The source gives both arc and spark lines, and a continuous passage from one type of spectrum to the other can be made by increasing the current.

W. E. Downey.

Physical methods in chemical laboratories. VII. Spectroscopy as an aid in chemical research. II. E. Rabinovitsch (Z. angew. Chem., 1928, 41, 1021—1028; cf. this vol., 728).—A review showing the value of spectroscopic methods in determining the state of molecular aggregation of elements, in distinguishing between polar and non-polar molecules in the gaseous state, in discovering new compounds, and in chemical analysis. A. R. Powell.

Design of equipment for measuring the specific volume of carbon dioxide vapour. C. H. Meyers (Refrig. Eng., 1928, 15, 157—158).

Chemical Abstracts.

Friction coefficient for gas flow through small glass tubes. M. Elliott (Ind. Eng. Chem., 1928, 20, 923—924).—Small rates of gas flow can be conveniently measured by the pressure drop through a capillary tube. In order to obtain absolute results by this means determinations of the constant f in the equation $\Delta h=2fLu^2/gd$ (where Δh is the pressure drop, u the velocity, and L and d are respectively the length and diameter in feet) were made. The factor f is a function of $Du\rho/\mu$, where ρ and μ are the density and viscosity of the gas. The values of f found were plotted against this modulus on log–log paper, giving a curve which was nearly a straight line. For a known gas, therefore, the curve affords a means of obtaining the relation between f and u and thus plotting pressure drop against velocity. C. Irwin.

Exact determination of the coefficient of internal friction of molten salts. R. S. Dantuma (Z. anorg. Chem., 1928, 175, 1—42).—An apparatus is described for the determination of the viscosity of molten salts by measuring the damping of a freely-swinging platinum sphere suspended in the liquid by means of a platinum strip carrying a mirror, the movements of which are registered photographically on a revolving drum which also acts as a time recorder. The whole apparatus is mounted above, and heat-insulated from, a well-lagged wire-wound resistance furnace, the temperature of which is automatically recorded by means of a thermocouple. The viscosities of sodium, potassium, and lithium nitrates and of sodium chloride have been determined for temperatures up to about 200° above their respective m. p., and the results are recorded graphically and in a series of tables. Except in the case of lithium nitrate, they agree well with the results of other workers. A. R. Powell.

Precision pipette viscosimeter. S. W. Ferris (Ind. Eng. Chem., 1928, 20, 974—977).—The bulb of the pipette has a capacity of 4·5 c.c.; the tip is drawn out to an inside diameter of 2 mm. and this is further drawn out to 0·5 mm., the decrease in diameter throughout being kept gradual. The tip is then broken off at the narrow point and polished on a fine emery stone to obtain a smooth, circular orifice. The pipette is enclosed in a water-jacket provided with paddles driven by an air-jet paddle-wheel. Calibration graphs, in which Saybolt seconds (s) are plotted against pipette seconds (p), are always straight lines conforming to the equation $s=kp+4$; hence the instrument may be calibrated with any oil of known viscosity or, to an accuracy of about 1%, with water. The results obtained are more accurate than those from the Saybolt viscosimeter.

A. R. Powell.

Measurement of [temperature with] a resistance thermometer. A. Michels and Geels (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 485—491).—The relationship between the various factors concerned, necessary for the accurate measurement of temperature by the resistance thermometer, is discussed theoretically. A circuit with overlapping shunts is described. M. S. Burr.

Zambelli's vacuum evaporator. R. Giordano (Rev. Centr. Estud. Farm. Bioquim., 1927, 16, 596—601; Chem. Zentr., 1928, i, 1793).

Continuous extraction apparatus. H. L. Maxwell.—See B., 1928, 695.

Large-capacity laboratory extractor. F. E. Holmes (Ind. Eng. Chem., 1928, 20, 888).—The vaporised solvent is delivered through a vertical tube centrally placed within a bulb. An expansion in the bottom of the latter is packed with cotton wool on which the material to be extracted is placed. Above the bulb is a reflux condenser. C. Irwin.

Mechanical agitator. G. N. Quam (Ind. Eng. Chem., 1928, 20, 922).—An agitator designed for determining rates of corrosion of metal samples by fluids was made of soft wood and mounted a number of test-tubes resting obliquely towards each side which contained the sample. These were fitted with bent breathing tubes to ensure aëration. The rocking (through 30°) is controlled by a hinge on the rocker arm and by the walls of the thermostat.

C. Irwin.

Adjustable thermostat. B. Noyes, jun. (J. Opt. Soc. Amer., 1928, 17, 127—131).—The *E.M.F.* of a thermocouple is used, by way of a potentiometer, galvanometer, photo-electric cell, and an amplifier, to actuate a series of relays which vary the current in the winding of the furnace which it is desired to keep at a constant temperature. W. E. Downey.

Constant-rate aspirator. C. F. Hottes and A. L. Hafenrichter (Science, 1928, 67, 320—322).—The aspirator is described and figured.

A. A. Eldridge.

Exclusion of atmospheric oxygen by superimposed surface layers. H. Schmalfuss and W. Peschke (Biochem. Z., 1928, 198, 487—493).—Of 13 liquids investigated, amyl alcohol when floated on the surface of oxygen-free water was most and anisole least efficient in preventing oxygen from reaching the aqueous layer. The curve showing the degree of protection at different temperatures shows a sharp minimum. The influence of the thickness of the protective layer is strikingly small. Atmospheric oxygen penetrates into a fluid between the glass wall and the medium and not through the medium, the passage of oxygen being rendered visible by a colour reaction. Oxygen is excluded completely either by superimposing a layer of a liquid paraffin which by cooling can be quickly solidified or, in experiments at high temperatures, by covering with a layer of a fluid which at the temperature concerned boils very vigorously.

P. W. Clutterbuck.

Modified Hartmann diaphragm. J. R. Green (J.C.S.I., 1928, 47, 224T).—A description of a diaphragm by the use of which, for every spectrum of the substance under examination, six comparison spectra can be obtained, instead of two when using the ordinary three-aperture Hartmann form.

Apparatus for delivering gas at constant pressure. T. Gray (J.S.C.I., 1928, 47, 187—188T).—An attachment to the ordinary laboratory aspirator bottle is described, which obviates the variation of pressure due to the changing level of the confining liquid and ensures delivery at a constant pressure during the whole period of discharge. With the addition of this device any gas-tight metal drum, such as is used for the transport of liquids, may be converted into a serviceable gas-holder.

Automatic time switch for prolonged heating etc. A. Guthrie (J.S.C.I., 1928, 47, 202T).—The winder of an alarm clock is bolted to a gas tap. The turning of the winder when the alarm is released automatically cuts off the gas.

Densi-tensimeter. A. Smits (J.C.S., 1928, 2409—2410; cf. A., 1927, 819).—A number of improvements are described in an apparatus designed to measure vapour pressures and vapour densities simultaneously.

F. J. Wilkins.

Extraction of krypton and xenon from air and from gases dissolved in water. G. Claude (Compt. rend., 1928, 187, 581—585; cf. Lepape, this vol., 970).—A description of modifications in plant for the fractionation of liquid air, in the form of an additional vaporiser, for obtaining krypton and xenon as by-products.

C. W. Gibby.

Nomographic conversion of percentages by weight into atomic percentages in ternary systems. O. Redlich (Z. anorg. Chem., 1928, 174, 285—289).—A graphical method is described and illustrated.

H. F. Gillbe.

Geochemistry.

Effect of ozone on the temperature of the upper atmosphere. E. H. Gowan (Proc. Roy. Soc., 1928, A, 120, 655—669).—From the abnormally high values obtained for the density of the atmosphere, calculated from observations of meteors, Lindemann and Dobson (*ibid.*, 1922, A, 102, 411) concluded that the temperature above 60 km. is of the order of 300° Abs. Whipple (Nature, 1923, 111, 187), from observations of the zones of audibility occurring at some distance round big explosions, found that near 60 km. a temperature of about 280° Abs. was to be expected. A theoretical consideration of the radiative equilibrium of the upper atmosphere, taking into account the effects, with selective absorption, of water vapour and ozone, leads to a region of high temperature in the neighbourhood of, and above, 60 km. The equation of equilibrium, considering only vertical radiation, for any layer of air in a non-convective region is $\int R_{\lambda T}d\lambda=\int(X_\lambda'+Y_\lambda'+E_\lambda'+S_\lambda')d\lambda$, where $R_{\lambda T}$ is the radiation from any layer at temperature T, X_λ' and Y_λ' are the absorbed portions of the atmospheric radiations from above and below the layer, and E_λ' and S_λ' are the portions of the terrestrial and solar radiations absorbed in the layer. An analytical solution of this equation can be found when the coefficient of absorption does not vary with the wave-length. When selective absorption is used a graphical solution is possible, and has been obtained by successive approximation. The results, as regards both temperature and height of the warm region, agree well with those of indirect observations.

L. L. Bircumshaw.

Height of the ozone in the upper atmosphere. F. W. P. Götz and G. M. B. Dobson (Proc. Roy. Soc., 1928, A, 120, 251—259).—Measurements have been made by the spectrographic method of the thickness of the ozone layer at different times of the day at Arosa (Switzerland), and from this the height of the layer is calculated. The results are not conclusive, but the average height appears to be between 30 and 40 km. above sea-level. A table is given showing the height at various times of the year. Measurements have also been made during cyclones and anticyclones and the results are discussed.

J. L. Buchan.

Helium. VI. Helium content of terrestrial gases. F. Paneth, H. Gehlen, and K. Peters (Z. anorg. Chem., 1928, 175, 383—401).—The percentages of helium in a number of gases occurring naturally in various parts of the world have been determined.

H. F. Gillbe.

Volcanic gases from Agnano. C. Olita (Z. Vulkanol., 1923–194, 7, 155—161; Chem. Zentr., 1928, i, 2075).

Pozzuoli solfatara gases. E. Salvatore (Z. Vulkanol., 1923, 7, 149—154; Chem. Zentr., 1928, i, 2075).—The gases contain CO_2 99·19, H_2S 0·47, CH_4 0·0086, H_2 0·0682, N_2 and rare gases, 2·620, A+He 0·0021%. A. A. Eldridge.

Determination of steam in the fumarole exhalations of Pozzuoli solfataras. E. Salvatore (Z. Vulkanol., 1923—194, 7, 215—217; Chem. Zentr., 1928, i, 2075).—The average steam content was 91·03% for 9·37% CO_2. A. A. Eldridge.

Physical and chemical conditions in San Francisco Bay, especially in relation to the tides. R. C. Miller, W. D. Ramage, and E. L. Lazier (Univ. Calif. Pub. Zool., 1928, **31**, 201—267).—Observations of salinity, temperature, turbidity, dissolved oxygen, dissolved hydrogen sulphide, and hydrogen-ion concentration are recorded. Chemical Abstracts.

Petroleum and the filtering earths. P. G. Nutting (J. Washington Acad. Sci., 1928, **18**, 409—414).—The filtering material is active only when there are free terminal hydroxyl radicals, which may combine with the alkyl radicals of certain hydrocarbons. Good results are obtained with silica, alumina, and ferric oxide gels from which most, but not all, of the water has been expelled. Materials such as greensand and serpentine with –OK and $-O_2Mg$ radicals are active after these basic radicals have been removed by acid treatment. Clays contain no hydroxyl that can be driven off leaving open linkings, and consequently they are not good filtering materials. The deposition of a sparingly soluble film of some silico-hydrocarbon on the mineral grains is discussed in connexion with the genesis of petroleum and asphalt. L. J. Spencer.

Theory of the formation of petroleum. G. Stadnikov and E. Ivanovski.—See B., 1928, 735.

Occurrence of hydrocarbons in volcanic rocks. J. Friedländer and E. Salvatore (Z. Vulkanol., 1924—1925, 8, 73—83; Chem. Zentr., 1928, i, 2074).—Extraction of 0—0·007% of hydrocarbons and 0·002—0·028% S is reported. A. A. Eldridge.

Columbian glass meteorites. T. Döring and O. Stutzer (Zentr. Min. Geol., 1928, **A**, 35—41; Chem. Zentr., 1928, i, 1642—1643).—The meteorites have d^4 2·310, soften at 905°, swell considerably when more strongly heated, and contain SiO_2 76·37, TiO_2 0·11, Al_2O_3 12·59, Fe_2O_3 0·26, FeO 0·48, MnO 0·14, MgO 0·17, CaO 0·79, Na_2O 3·36, H_2O 0·97, SO_3 0·13, Sb_2O_3 0·07, P_2O_5 0·02%. The gas evolved on heating contained (Heinrich) CO_2 27·1, CO 24·4, H_2 35·3, CH_4 2·2, O_2 1·1%. A. A. Eldridge.

Origin and organisation of coal. E. C. Jeffrey (Mem. Amer. Acad. Arts Sci., 1924, **15**, 1—52). Chemical Abstracts.

Changes in the oxidation of iron in magnetite. L. H. Twenhofel (Econ. Geol., 1927, **22**, 180—188).—The oxidation of magnetite and formation of hæmatite are functions of time and source of material, as well as of temperature. The additional oxygen atoms are irregularly spaced within the magnetite crystal structure. Chemical Abstracts.

Sagvandite, an eruptive rock containing magnesium. T. Barth (Norsk geol. Tidsskr., 1926, 9, 271—303; Chem. Zentr., 1928, i, 2074).

Members of the zoisite–epidote group poor in iron. A. Orlov (Sitzungsber. Königl. böhm. Ges. Wiss., 1926, II, No. 19, 42 pp.; Chem. Zentr., 1928, i, 2073).—The clinozoisites correspond with the formula $6SiO_2,3R_2O_3,4RO,H_2O$; *d* 3·349, the yellower portions being denser. The constants of Zillertal clinozoisite poor in iron are not regarded as limiting values in the clinozoisite–epidote group. A. A. Eldridge.

Hydrothermal alteration of certain silicate minerals. R. J. Leonard (Econ. Geol., 1927, **22**, 18—43).—Alunite was produced at 20°, 65°, and 100° at 1 atm. and at 200° at 15 atm., but not at 350° at 1 atm., by the action of water, aluminium sulphate, and sulphuric acid, potassium sulphate, or sodium sulphate on microcline, albite, and bytownite. Zeolites were formed by the action of water and potassium or sodium carbonate at 200° and 15 atm. on the felspars; cryolite by the action of water on aluminium fluoride and sodium fluosilicate at 350° and 1 atm., at 400° and 8 atm., and at 575° and 10 atm. Leverrierite was probably formed from felspars by the action of water and aluminium chloride (with or without sodium or potassium chloride) at 350° and 1 atm. or by water and potassium carbonate, or water, potassium fluoride, and sodium fluosilicate at 575° and 10 atm. Chemical Abstracts.

Hydrothermal formation of iron ores. R. Klemm (Zentr. Min. Geol., 1928, **A**, 90—94; Chem. Zentr., 1928, i, 1754).

Dumortierite. S. F. Glinka (Min. Resources and Tech., Moscow, 1927, No. 3, 189—191; Chem. Zentr., 1928, i, 2072).

Pigment of emerald. A. Fersmann (Compt. rend. Acad. Sci., U.S.S.R. [Russia], 1926, 24—25; Chem. Zentr., 1928, i, 2072).—Ural emeralds contained 0·11, 0·19% Cr_2O_3; vanadium was detected spectroscopically only in deeply-coloured specimens. A. A. Eldridge.

Pisekite. A. Krejči (Časopis min. geol., 1923, No. 1, 2—5; Chem. Zentr., 1928, i, 2073).—The radioactive mineral pisekite (qualitative analysis recorded) has d^{18} 4·0346, H 5½—6. A. A. Eldridge.

Slavikite. F. Ullrich and R. Jirkovsky (Vestn. stát. úst. Ceskoslov., 1926, **2**, 345—351; Chem. Zentr., 1928, i, 2073).—The mineral, from Mt. Valachov near Skřivaň, is trigonal, uniaxial negative, ε 1·506±0·002, ω 1·530±0·001; $d^{20·3}$ 1·905, and contains Fe_2O_3 20·08, Al_2O_3 4·29, CaO 0·01, Na_2O 1·63, K_2O 0·57, SO_3 34·06, H_2O (<110°) 3·10, (>110°) 35·66, insol., 0·52, corresponding with the formula $(Na,K)_2SO_4,Fe_{10}(OH)_6(SO_4)_{12},63H_2O$. A. A. Eldridge.

Liévrite (ilvaite) of the arsenic deposits at Dijmara, N. Caucasus. J. Kusnetzov (Bull. Com. Geol., 1925, **44**, 721—731; Chem. Zentr., 1928, i, 2073).—Analysis gave: SiO_2 29·18, Fe_2O_3 18·67, Al_2O_3 0·46, FeO 33·32, MnO 2·26, CaO 14·11, MgO 0·26, H_2O 1·53%; d^{18} 4·000. Type I has $a:b:c$ 0·6711 : 1 : 0·4469; 0·6586 : 1 : 0·4414; type II has $a:b:c$ 0·6843 : 1 : 0·4538. A. A. Eldridge.

Crystals of calcite from Voldelée. V. Billiet (Natuurwetensch. Tijdschr., 1928, **10**, 158—159).—

Examination of calcite crystals from the marble quarries of Vodelée, between the Sambre and the Meuse, has disclosed crystals with a form $70\bar{1}$ (Bravais $71\bar{8}6$), not hitherto observed in Belgium.

S. I. Levy.

The Whin sill and related dikes of the north of England. A. Holmes and H. F. Harwood (Min. Mag., 1928, **21**, 493—542).—Several detailed analyses of these quartz-dolerites show that the sill and the dikes are practically identical in composition, indicating a genetic connexion between the two.

L. J. Spencer.

Genesis of the jadeite of Burma. A. Lacroix (Compt. rend., 1928, **187**, 489—493).—The jadeite at Tawmaw, Upper Burma, occurs, as described by Bleeck (A., 1909, ii, 412), in the centre of a dike in serpentine, passing outwards into a jadeite-albite-rock (jadeitite) with some soda-amphibole, then into an amphibolite in which the amphibole is actinolite, and finally on the walls of the dike into a chloritic rock. The jadeite has been regarded as a dynamo-metamorphic product of a nepheline-syenite. The suggestion is now made that this is a case of desilicification of a granitic magma intruded into peridotite, but one in which the process has not proceeded so far as in the corundum-bearing rocks of South Africa.

L. J. Spencer.

Japanese minerals containing rarer elements. VI. Beryl from Ishikawa, Iwaki Province. T. Uemura (Japan. J. Chem., 1926, **2**, 117—121).—The beryl, analysed by a method previously adopted (A., 1926, 144), contained SiO_2 49·60, BeO 19·31, Fe_2O_3 0·11, Al_2O_3 24·09, CaO 0·79, MgO 0·14, ignition loss 2·81%, and the remainder alkali. Copaux's method (A., 1919, ii, 192) is not suitable for the analysis of Ishikawa beryl. A special molecular structure is suggested to account for this. The course of the analysis was followed spectroscopically. The green colour cannot be due to chromium, since no trace of the latter was observed.

M. S. Burr.

Clays. XII. Changes of certain clays into acidic ones through weathering. T. Okazawa (Abs. Bull. Inst. Phys. Chem. Res. Tokyo, 1928, **7**, 93—94; cf. this vol., 1110).—The so-called acidity of clays, supposed by the author to be the result of severe weathering, involves the production of aluminium salts and the corresponding acids when the clays are treated with solutions of neutral salts. The soluble free acid adsorbed by the clays is actually minute in quantity and ambiguous in nature. The behaviour of acid clays is analogous to that of the zeolites.

J. Grant.

Rare earths in the stellar atmospheres. L. Rolla and G. Piccardi (Gazzetta, 1928, **58**, 521—532).—An account of the occurrence and distribution of the rare-earth elements in the atmospheres of the various types of stars.

O. J. Walker.

Minerals. IV. H. Collins (Chem. News., 1928, **137**, 213—215).

Organic Chemistry.

[Cholesterol as parent of petroleum.] W. Steinkopf (Ber., 1928, **61**, [*B*], 1639).—A reply to Zelinski (B., 1927, 865; this vol., 865).

H. Wren.

Thermal decomposition of ethane, ethylene, propane, and propylene. F. E. Frey and D. F. Smith (Ind. Eng. Chem., 1928, **20**, 948—951).—The decomposition was carried out in silica vessels, which possess no appreciable catalytic activity. Decomposition of propane in the presence of a nickel catalyst at 200°, 350°, and 405° takes place: (1) $C_3H_8 \longrightarrow 2CH_4 + C$, (2) $C_3H_8 \longrightarrow C_3H_6 + H_2 \longrightarrow CH_4 + 2H_2 + C$, of which (1) takes place at all temperatures but (2) becomes important only at higher temperatures. Hydrogen has no effect on the reaction at 200°. A copper catalyst causes only slight decomposition of propane at 350° and 400°. Platinised (3%) and palladised (5%) asbestos at 568° have small but definite effects on the decomposition of propane, hydrogen, ethylene, ethane, and propylene being evolved and free carbon deposited. Silica has little catalytic effect at 575°, no carbon being formed, and the decomposition in unaffected by an increase in the surface area of the silica. Under these conditions the decomposition of propane may be explained thus: (1) $C_3H_8 \longrightarrow C_2H_4+CH_4$, (2) $C_3H_8 \longrightarrow C_3H_6+H_2$, (3) $2C_3H_8 \longrightarrow C_3H_6+C_2H_6+CH_4$, (1) and (2) having considerable velocities of the same order of magnitude, whilst (3) is a much slower reaction. The only products formed by the decomposition of ethane under the same conditions are ethylene and hydrogen, the reaction being of the first order over a considerable pressure range. The velocity of hydrogenation of ethylene at 575° in silica vessels is greater than that of dehydrogenation (cf. Wartenberg, A., 1908, ii, 26), greater than that of propylene under the same conditions, and is more dependent on the concentration of hydrogen than on that of ethylene, which suggests that an appreciable part of the reaction takes place at the surface of the vessel. Both cases are complicated by the tendency to polymerisation. Polymerisation of ethylene at 575° yields a relatively large amount of propylene, together with methane, ethane, and higher hydrocarbons, whilst under the same conditions propylene yields butylene, methane, ethylene, and higher hydrocarbons. Polymerisation in the presence of hydrogen results in the formation of less unsaturated products.

J. W. Baker.

Oxidation of *n*-hexane. M. Brunner (Helv. Chim. Acta, 1928, **11**, 881—897).—An extension of work already published (Brunner and Rideal, this vol., 731).

H. Burton.

Allyl transformations and additive products of erythrene hydrocarbons. C. Prévost (Ann. Chim., 1928, [x], **10**, 147—181).—Experimental details are given of work already published (this vol., 152, 613). Methylvinylcarbinol when boiled with 3·3% hydrochloric acid is converted into an equilibrium mixture containing 30% of Δ^{β}-buten-α-ol, b. p. 119—120°, d_4^{21} 0·8500, n_D^{21} 1·4260, together with a trace of α-chloro-Δ^{β}-butene and the three possible ethers. By the action of phosphorus pentabromide, methylvinylcarbinol is converted into α-bromo-Δ^{β}-butene, which is not hydrolysed with aqueous potassium hydroxide, but is converted by boiling aqueous alkali carbonate into a mixture of methylvinylcarbinol (60%) and Δ^{β}-buten-α-ol (40%), and with alcoholic potassium hydroxide into a mixture of ethyl Δ^{β}-butenyl ether, b. p. 99—100°, d_4^{22} 0·7870, n_D^{22} 1·4050, and probably ethyl α-methyl-Δ^{β}-propenyl ether. Esterification of methylvinylcarbinol with acetic acid yields only the corresponding acetate, but trichloroacetic acid behaves like the hydrogen halides and converts either methylvinylcarbinol or the isomeric Δ^{β}-buten-α-ol into a mixture of 50—55% of α-methyl-Δ^{β}-propenyl trichloroacetate, b. p. 74—74·5°/12 mm., d_4^{22} 1·2990, n_D^{22} 1·4588, and 40—45% of Δ^{β}-butenyl trichloroacetate, b. p. 89—89·5°/12 mm., d_4^{22} 1·3130, n_D^{22} 1·4710, together with a mixture of the ethers $(CH_2{:}CH{\cdot}CHMe)_2O$ and $CH_2{:}CH{\cdot}CHMe{\cdot}O{\cdot}CH_2{\cdot}CH{:}CHMe$. Hydrolysis of either of the trichloroacetates yields exclusively the corresponding alcohol. Physical data given are revised values (cf. Charon, A., 1899, i, 848).

J. W. Baker.

Relative reactivities of *n*-butyl bromide and bromobenzene towards magnesium in ether. H. Gilman and E. A. Zoellner (J. Amer. Chem. Soc., 1928, **50**, 2520—2523).—Determinations of the amount of Grignard reagent formed under standard conditions (cf. A., 1923, ii, 272; 1926, 535) in periods of 45 and 90 sec. after mixing show that *n*-butyl bromide reacts more rapidly than bromobenzene with magnesium in ether. H. E. F. Notton.

Action of metallic tin on methylene halides. K. A. Kozeschkov (Ber., 1928, **61**, [*B*], 1659—1663).—Methylene bromide, b. p. 97·5°/753 mm., d_4^{20} 2·4953, n_D^{20} 1·5420, is prepared in about 80% yield by the action of arsenious oxide dissolved in aqueous potassium hydroxide on bromoform. It is transformed by tin at 180—220° into tin methyl tribromide, m. p. 53°, and carbon: $3CH_2Br_2+2Sn=2MeSnBr_3+C$. If excess of methylene bromide is employed, tin tetrabromide results. Analogously, methylene chloride affords tin methyl trichloride, m. p. 42—43°, whereas tin tetraiodide is the main product from methylene iodide. H. Wren.

Rate of hydrolysis of esters of unsaturated alcohols. M. H. Palomaa and A. Juvala (Ber., 1928, **61**, [*B*], 1770—1776).—The velocity coefficients of acid (k_s) and alkaline (k_a) hydrolysis in aqueous solution at 25°±0·1° are recorded for the following esters of the general type $R{\cdot}CO_2{\cdot}[CH_2]_n{\cdot}CH{:}CH_2$. Allyl formate ($k_s$ 0·149); Δ^{γ}-*butenyl formate*, b. p. 112—113°, d^{20} 0·9267 (k_s 0·151); Δ^{δ}-*pentenyl formate*, b. p. 135—136°/777 mm., d^{20} 0·9124 (k_s 0·133); allyl acetate (k_s 0·00473, k_a 12·76); Δ^{γ}-butenyl acetate, b. p. 124—126°/753 mm. (k_s 0·00553, k_a 8·09); Δ^{δ}-*pentenyl acetate*, b. p. 144—146°/762 mm., d^{20} 0·9114 (k_s 0·00331, k_a 4·40). H. Wren.

Synthesis of butane-βγ-diol, its nature and odour. S. Maruyama and T. Higasi (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 934—939).—Butane-βγ-diol, b. p. 183—184°, prepared from *n*-butyl alcohol through Δ^{β}-butene, its dibromide, and diacetate, is a syrupy, colourless, almost odourless liquid, and hence, contrary to Taira (Rep. Dept. Ind. Govt. Res. Inst., Formosa, No. 8), the odour of "shoyu" is not due to this compound.

J. W. Baker.

Semisaturated derivatives of erythrenic hydrocarbons. C. Prévost (Bull. Soc. chim., 1928, [iv], **43**, 996—1018).—Polar considerations of published and unpublished results on the semisaturated derivatives of erythrenic hydrocarbons lead to the conclusion that these derivatives exist in three forms, a γ- or 1 : 4-form and two stereoisomeric α-(or 1 : 2- or 3 : 4)-forms. There is no evidence of *cis–trans*-isomerism among the γ-derivatives, and the two glycols, b. p. 108°/12 mm. and 126°/12 mm., previously described (A., 1926, 818) are now regarded as Δ^{β}-pentene-δε-diol and *trans*-Δ^{γ}-pentene-βε-diol, respectively; the physical constants of the six erythrene glycols are thus in harmony with one another and also with erythrol. According to the mobility of the additive group the α- and γ-isomerides can be desmotropic (with pseudomerism as the limiting case) or mesomeric. In any case, they are tautomeric, giving generally in double decomposition reaction mixtures of the three isomeric forms of the new compound. Desmotropism has been observed in the case of the dibromo-derivatives, but equilibrium between the α-(1 : 2- or 3 : 4-) and γ-(1 : 4-) forms is only very slowly attained, and at low temperatures the phenomena approximate to pseudomerism, the γ-form predominating. When this form is solid and in the absence of a solvent the γ-form alone is present at equilibrium. The α-isomerides are stable only when they are themselves solid. At the ordinary temperature the diacetins, glycols, and divinyl derivatives are mesomeric, and the reaction diacetins $\rightleftharpoons$ glycols is normal, multipolar ions playing no part. The reactions bromo-derivatives $\rightleftharpoons$ acetins, glycols, or divinyls are always abnormal, but the anomaly can be masked in some cases by one mesomeride greatly preponderating in the product. In these reactions of double decomposition, qualitatively the three mesomerides behave similarly, but quantitatively each tends to give mainly the derivative corresponding with itself. Secondary reactions may lead to the formation of substituted erythrenes. If this loss of hydrogen bromide occurs on erythrenes containing methyl groups in the 1 : 4-positions erythrylic derivatives may be formed.

Hydrolysis of the αδ-dibromo-Δ^{β}-pentenes, b. p. 85—86°/11 mm., obtained by bromination of crude $\Delta^{\alpha\gamma}$-pentadiene (A., 1926, 496) at 80°, with 10% sodium carbonate affords 15% of glycol of b. p. 92°/12 mm., 15% of glycol of b. p. 108°/12 mm., and 70% of glycol of b. p. 126°/12 mm. With dibromopentene, b. p. 60—80°/12 mm., these fractions are obtained in 25%, 20%, and 55% yield, respectively. With boiling 50% sodium carbonate solution the yield of glycols is poor, but the proportions are unchanged. The glycol of b. p. 92°/12 mm. has been separated by distillation into two fractions, b. p. 88—90°/12 mm., d^{21} 1·0074, n^{21} 1·4572, and

b. p. 93—95°/12 mm., d^{21} 1·0103, n^{21} 1·4585, consisting essentially of the two racemic forms of Δ^{α}-*pentene-γδ-diol*. In addition to the glycols, the product obtained by hydrolysis contains a little Δ^{β}-pentenal, b. p. 127°, d^{21} 0·858, n^{21} 1·4385 (semicarbazone, m. p. 177·5°), a substance, *d* 1·268, probably a pentenol, and a little *erythryl bromide*, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH_2Br$, b. p. 33—34°/16 mm., n^{21} 1·5205, d^{21} 1·335, which cannot be separated from the accompanying α-bromo-$\Delta^{\beta\delta}$-pentadiene. Erythryl bromide is prepared by the action of quinoline on αδ-dibromo-Δ^{β}-pentene; with bromine at 50° it affords αβγδε-*pentabromopentane*, m. p. 150°. R. Brightman.

Reactions relating to carbohydrates and polysaccharides. XV. The isomeric benzylideneglycerols. H. S. Hill, M. S. Whelen, and H. Hibbert (J. Amer. Chem. Soc., 1928, **50**, 2235—2242).—The work of Irvine, Macdonald, and Soutar (J.C.S., 1915, **107**, 337) indicated that the product of condensation of glycerol with benzaldehyde was αβ-benzylideneglycerol, but the possibility of formation of the αγ-derivative is suggested by the existence of a cyclic acetal of α-methylglucoside, which has an amylene-oxide structure. Condensation of benzaldehyde with glycerol by the method of Gerhardt (A., 1913, i, 47) or by heating with 40% sulphuric acid yielded products which were separable by crystallisation from light petroleum and benzene into *αγ-benzylideneglycerol*, m. p. 80·5° (*benzoate*, m. p. 103°), and *αβ-benzylideneglycerol*, b. p. 143—144°/2 mm. (*benzoate*, an oil), in the proportions of 1 : 7·5 and 1 : 3, respectively, in the two methods. The structure of these compounds was determined by Irvine's methylation–hydrolysis method. The αγ-derivative, with silver oxide and methyl iodide, yielded *αγ-benzylideneglyceryl β-methyl ether*, m. p. 52°, from which was obtained *glyceryl β-methyl ether*, b. p. 123°/13 mm., d_4^{17} 1·1306, n_D^{17} 1·4505. The products from the αβ-derivative were identical with those obtained by Irvine (*loc. cit.*). The two benzylideneglycerols were interconvertible, and an equilibrium mixture containing five parts of αβ- to one part of αγ-derivative was obtained when either isomeride was treated with a trace of dry hydrogen chloride and heated or kept for some time. R. K. Callow.

Dodecane-αμ-diol. Lespieau (Compt. rend., 1928, **187**, 605—607).—The action of magnesium on an ethereal solution of pentamethylene dibromide yields a mixture of magnesium compounds of the type $[(CH_2)_5]_n(MgBr)_2$, the proportion of each decreasing as *n* increases. From the products of the action of chloromethyl ether on these compounds are isolated: αμ-dimethoxyheptane, *methyl* n-*hexyl ether*, b. p. 124—125°, d^{19} 0·7897, n_D 1·4065; *αμ-dimethoxydodecane*, b. p. 156—156·5°/13 mm., m. p. 11·5°, d^{22} 0·8563, n_D 1·436. This last by the action of gaseous hydrogen bromide at 100° yields *αμ-dibromododecane*, m. p. 38·5—39°, converted by silver acetate and acetic acid into the *diacetate*, m. p. 36·5—37·5°, from which is obtained *dodecane-αμ-diol*, m. p. 80—81°.

J. W. Baker.

Configuration of pentaerythritol. II. Optically active compounds of pentaerythritol and pyruvic acid. J. Böeseken and B. B. C. Felix (Ber., 1928, **61**, [*B*], 1855—1857; cf. this vol., 616).—The action of pentaerythritol on ethyl pyruvate in alcoholic solution in presence of hydrochloric acid gives the *compound*, $C[C_2H_4O_2{>}CMe{\cdot}CO_2Et]_2$, m. p. 46°, hydrolysed to the corresponding *acid*, $C_{11}H_{16}O_8$, m. p. 238°. The acid is resolved by means of its *monostrychnine* salt into the corresponding l- and d-*acids*, $[\alpha]_D$ −3·98° and +3·72° in acetone ($[\alpha]_D$ +6·87° in water). The acids rapidly become racemised in boiling, aqueous solution. The tetrahedral configuration of pentaerythritol appears therefore established, at any rate in alcoholic solution. The assumption of pyramidal molecules is not immediately necessary.

H. Wren.

Identity of volemitol and α-sedoheptitol. F. B. La Forge and C. S. Hudson (J. Biol. Chem., 1928, **79**, 1—3).—The identity of volemitol and α-sedoheptitol (cf. La Forge, A., 1920, i, 595) is confirmed, the discrepancy in the m. p. of the benzylidene derivatives previously noted (A., 1917, i, 444) having been due to a mistaken reference. C. R. Harington.

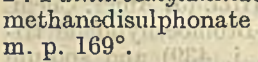
Mechanism of the acetal reaction; explosive rearrangement of hydroxyethyl vinyl ether to ethylidene glycol. H. S. Hill and L. M. Pidgeon (J. Amer. Chem. Soc., 1928, **50**, 2718—2725).—The mechanism suggested for the formation of ethylidene ethylene ether from acetylene and ethylene glycol (A., 1924, i, 133) is supported by the observation that this ether is produced quantitatively, and with explosive rapidity from β-hydroxyethyl vinyl ether, in presence of a trace of acid. Similarly, acetal formation probably consists of (*a*) formation of a semiacetal (cf. Adkins, this vol., 396), and (*b*) dehydration to a vinyl ether, which then undergoes inter- or intramolecular rearrangement. The application of this mechanism to sugar chemistry is discussed. β-Bromoethylidene ethylene ether (cf. A., 1923, i, 439), prepared by an improved method, yields with sodium in ether *β-hydroxyethyl vinyl ether*, b. p. 44—45°/10 mm., n_D^{17} 1·4564, the *benzoate*, b. p. 133°/9 mm., of which does not undergo rearrangement in presence of acid. H. E. F. Notton.

Vinyl derivatives: their relationship to sugars and polysaccharides. H. S. Hill (J. Amer. Chem. Soc., 1928, **50**, 2725—2731).—Bromoethylidene trimethylene ether (cf. A., 1923, i, 439) and sodium in ether give the *sodium* salt (I) of *γ-hydroxypropyl vinyl ether*, b. p. 64—65°/10 mm., which combines with bromine, and changes with violence in presence of a trace of hydrogen chloride into ethylidene trimethylene ether. This is also formed from the vinyl ether and 1 mol. of methyl alcohol in presence of acid, but with 3 mols. of alcohol the principal product is dimethylacetal (*a*). The sodium salt (I) and methyl iodide give *γ-methoxypropyl vinyl ether*, b. p. 75—76°/137 mm. In presence of a trace of hydrogen chloride this forms (*b*) with 1 mol. of methyl alcohol, mainly the mixed acetal, *α-methoxyethyl γ-methoxypropyl ether*, b. p. 153—155°; (*c*) with excess of alcohol, dimethylacetal; (*d*) with ethylene glycol, ethylidene ethylene ether and γ-methoxypropyl alcohol, and (*e*) with α-methylglucoside, ethylidene α-methylglucoside, but not the desired mixed acetal. Reaction (*b*) supports, by analogy, the suggestion (cf.

preceding abstract) that an unsaturated derivative (βγδζ-tetrahydroxy-Δ^{α}-hexene αε-oxide) is an intermediate in the formation of α-methylglucoside from dextrose; (*a*) and (*c*) show the lability of the alcohol residues in acetals, whilst (*d*) and (*e*) indicate a preference for the formation of cyclic derivatives rather than open-chain acetals. H. E. F. NOTTON.

Constitution of hexosediphosphoric acid. II. Dephosphorylated α- and β-methylhexosides. W. T. J. MORGAN and R. ROBISON (Biochem. J., 1928, **22**, 1270—1276).—By the action of the bone phosphatase on the α- and β-methylhexosidediphosphoric acids, α- and β-methylhexosides, $[\alpha]_{5461}$ $+55°$ and $-47°$, have been obtained as non-reducing syrups. The properties of these compounds agree with those expected for α- and β-methyl-γ-fructosides. They have been converted into fully methylated derivatives from which tetramethyl-γ-fructose, $[\alpha]_{5461}$ $+40°$, has been obtained. It is suggested that hexosediphosphoric acid is γ-fructose-1 : 6-diphosphoric acid. S. S. ZILVA.

Nitroamides of methionic [methanedisulphonic] acid. H. J. BACKER (Rec. trav. chim., 1928, **47**, 942—949).—Phenyl methanedisulphonate (Schroeter, A., 1919, i, 516) reacts with methylamine in benzene solution at 140°, forming *methanedisulphonmethylamide*, $CH_2(SO_2{\cdot}NHMe)_2$, m. p. 172·5°, which is nitrated at 0° to *methanedisulphon-nitromethylamide*, $CH_2(SO_2{\cdot}NMe{\cdot}NO_2)_2$, m. p. 118·5° (decomp.), also obtained by the action of nitric acid at 70—75° on *methanedisulphonacetmethylamide*, m. p. 174—175·5°. This nitroamide is decomposed by aqueous alkali hydroxides to methylnitroamine and alkali methanedisulphonate. The following are prepared similarly: methanedisulphonethylamide, m. p. 144—145° (*acetyl* derivative, m. p. 78°; *nitro*-derivative, m. p. 61—61·5°); *methanedisulphonpropylamide*, m. p. 171·5° (*nitro*-derivative, m. p. 47—48°); *methanedisulphonbutylamide*, m. p. 181—181·5° (*nitro*-derivative, m. p. 41—41·5°); *methanedisulphonamylamide*, m. p. 179·5—180° (*nitro*-derivative, m. p. 21°), and *methanedisulphonpiperidide*, m. p. 117—117·5°. Methanedisulphonethylanilide is nitrated to the corresponding 2 : 4-*dinitroethylanilide*, m. p. 219°, and phenyl methanedisulphonate affords the p-*nitrophenyl* ester, m. p. 169°. H. BURTON.

Organic cyclic polysulphides. Condensation of ethylene mercaptan with di- and tri-chloroacetic acids. G. C. CHAKRAVARTI and J. M. SAHA (J. Indian Chem. Soc., 1928, **5**, 453—458).—When ethylene mercaptan is boiled with dichloroacetic acid there is formed a *pentamethylene tetrasulphide* (I), m. p. 96°; in presence of xylene three *trimethylene disulphides*, m. p. 192—194°, m. p. 83—84°, and an oil, respectively, are obtained. Potassium dichloroacetate and monopotassium ethylene mercaptan react in alcohol solution, giving an oily *acid* (II),  $C_2H_4{<}\genfrac{}{}{0pt}{}{S}{S}{>}CH{\cdot}CO_2H$ (*potassium* salt), whilst ethyl dichloroacetate affords a mixture of the *ethyl* ester of (II) and a *compound*, $C_8H_{14}O_2S_4$. Trichloroacetic acid and ethylene mercaptan react in boiling xylene, forming (I) and polymerides of ethylene disulphide. H. BURTON.

Effect of structure of organic halides on their rate of reaction with inorganic halides. II. Effect of methylthiol group. New vesicant. W. R. KIRNER (J. Amer. Chem. Soc., 1928, **50**, 2446—2454).—The preparation of an anhydrous ethereal suspension of sodium methyl sulphide is detailed. This forms with chloromethyl acetate *methylthiolmethyl acetate*, b. p. 60—62°/20 mm., which gives on hydrolysis with methyl-alcoholic hydrogen chloride a *substance*, b. p. 70—71°/48 mm., and a sulphur-free product, but no hydroxydimethyl sulphide. Sodium methyl sulphide and ethylene chlorohydrin in boiling ether yield *methyl* β-*hydroxyethyl sulphide*, b. p. 80·5—81°/30 mm., d_{20}^{20} 1·0640, n_D^{20} 1·4867; *methyl* γ-*hydroxypropyl sulphide*, b. p. 105—105·5°/30 mm., d_{20}^{20} 1·0314, n_D^{30} 1·4832, is obtained similarly. These are respectively converted by thionyl chloride in chloroform into *methyl* β-*chloroethyl sulphide* (1·52), b. p. 44°/20 mm., d_{20}^{20} 1·1245, n_D^{30} 1·4902, which has a vesicant action similar to that of ββ′-dichloroethyl sulphide, and *methyl* γ-*chloropropyl sulphide* (2·52), b. p. 71·2°/29 mm., d_{20}^{20} 1·0863, n_D^{30} 1·4833, which is not a vesicant. The reactivities of the chlorine atoms in these derivatives (butyl chloride=1) given in parentheses are in accordance with results obtained in other series (cf. A., 1924, i, 273). They show no connexion with the vesicant effect (cf. Peters and Walker, A., 1923, i, 734), which appears in compounds of this type to be a specific property of β-chloroethyl derivatives. H. E. F. NOTTON.

Allyl derivatives. V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1927, **15**, 418—422).—Allyl acetate, b. p. 103—105°, was obtained by boiling allyl alcohol with acetic anhydride and a few drops of concentrated sulphuric acid. Bromination of allyl formate in carbon disulphide yielded βγ-*dibromopropyl formate*, b. p. 221—223°. The acetate was prepared similarly. R. K. CALLOW.

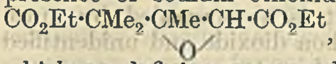
Preparation of pentadecoic acid. S. LANDA (Chem. Listy, 1928, **22**, 361—362).—Good yields of pentadecoic acid are obtained by the oxidation of cetene, using hot 1% potassium permanganate solution. R. TRUSZKOWSKI.

Three-carbon system. XVIII. Influence of alkyl substituents on the αβ–βγ change in unsaturated acids: reduction of sorbic acid, and a new synthesis of pyroterebic acid. A. A. GOLDBERG and R. P. LINSTEAD (J.C.S., 1928, 2343—2360).—The equilibrium between the following pairs of αβ- and βγ-unsaturated acids in the presence of aqueous potassium hydroxide has been investigated; the figures in brackets give the proportion of αβ-isomeride in the equilibrium mixture. (i) Δ^{α}-Pentenoic acid and Δ^{β}-pentenoic acid [75·4%], (ii) Δ^{α}-hexenoic acid (*anilide*, m. p. 109—110°) and Δ^{β}-hexenoic acid (hydrosorbic acid) [about 77%], (iii) γ-methyl-Δ^{α}-pentenoic acid (Δ^{α}-*iso*hexenoic acid) (*acid chloride*, b. p. 67°/20 mm.; *anilide*, m. p. 119°) and γ-methyl-Δ^{α}-pentenoic acid (pyroterebic acid) (*acid chloride*, b. p. 60°/15 mm.; *anilide*, m. p. 106°) [5·6%], (iv) α-methyl-Δ^{α}-pentenoic acid (*acid chloride*, b. p. 63°/16 mm.; *amide*, m. p. 80°) and α-methyl-Δ^{β}-pentenoic acid (*acid chloride*, b. p. 47°/17 mm.; *amide*,

m. p. 74°; *anilide*, m. p. 76°) [80·7%], (v) *cyclo*pentylideneacetic acid and Δ^1-*cyclo*pentenylacetic acid [13·7%]. Rules governing the effect of alkyl substituents on the equilibrium are formulated. The mobilities of the acids $10(k_1+k_2)$ (Linstead, A., 1927, 1167) are (i) 7, (ii) 7, (iii) 4·5, (iv) 7, and (v) 22. The equilibrium value of (iii) is so far on the βγ-side that equilibration of the αβ-isomeride (Δ^{α}-*iso*hexenoic acid) with aqueous potassium hydroxide affords a convenient method for the preparation of pyroterebic acid. Abnormal results were obtained with "hydrosorbic acid" and these were shown to be due to the presence of about 50% of the γδ-isomeride simultaneously produced in its preparation by the reduction of sorbic acid by sodium amalgam (cf. Fittig and Baker, A., 1895, i, 206). A. I. VOGEL.

Synthesis of certain γ-ketonic acids closely allied to Balbiano's acid. II. Syntheses of αββ- and ααβ-trimethyl-lævulic acids, of the lactone of α′-hydroxy-ααβ-trimethylglutaric acid, and of γ-keto-αββ-trimethylpropane-αγ-dicarboxylic acid (Balbiano's acid). J. C. BARDHAN (J.C.S., 1928, 2604—2621; cf. this vol., 1243).—Trimethylsuccinic anhydride was converted by sodium ethoxide into the acid ester; the latter on treatment with thionyl chloride followed by zinc methyl iodide gave a mixture of two ketonic esters which was hydrolysed to the acids with methyl-alcoholic potassium hydroxide. These were separated by fractional crystallisation of the semicarbazones from methyl alcohol, when two pure *semicarbazones*, m. p. 155° and 174°, respectively, were obtained. The former yielded αββ-*trimethyl-lævulic acid*, m. p. 65—66° (*ethyl* ester, b. p. 110°/14 mm., d_4^{19} 0·981537, n_D^{19} 1·43638; trimethylsuccinic acid was obtained on oxidation with potassium hypobromite), whilst the latter gave ααβ-trimethyl-lævulic acid, m. p. 77—78°, with dilute hydrochloric acid. The structure of the ααβ-acid was established by the following rational synthesis: methyl ethyl ketone was condensed with ethyl α-bromo*iso*butyrate and zinc to *ethyl* β-*hydroxy*-ααβ-*trimethyl*-n-*valerate*, b. p. 92°/11 mm., which was dehydrated with phosphoric oxide to *ethyl* ααβ-*trimethyl*-Δ^{β}-*pentenoate* (I), b. p. 100—102°/45 mm., $d_4^{16\cdot8}$ 0·906942, $n_4^{16\cdot8}$ 1·43878 (acetaldehyde was isolated on ozonolysis). Hydrolysis of (I) with methyl-alcoholic alkali furnished the corresponding acid, b. p. 113°/10 mm., $d_4^{19\cdot2}$ 0·963434, $n_D^{19\cdot2}$ 1·45283 (*silver* salt; p-*toluidide*, m. p. 71°), which when treated with a slight excess of bromine at 0° gave an unstable dibromide, decomposing on distillation with the elimination of hydrogen bromide and the production of the *lactone* of γ-*hydroxy*-ααβ-*trimethyl*-Δ^{β}-*pentenoic acid*, b. p. 80°/13 mm. Hydrolysis of the lactone with methyl-alcoholic potassium hydroxide yielded ααβ-*trimethyl-lævulic acid*, m. p. 77—78° (*semicarbazone*, m. p. 173°; p-*nitrophenylhydrazone*, m. p. 207°; *piperonylidene* derivative, m. p. 115°), identical with the acid obtained from the less fusible semicarbazone. Methyl mesityl oxide (*semicarbazone*, m. p. 186°), prepared from trimethylacrylyl chloride and zinc methyl iodide, when condensed with potassium cyanide gave chiefly a nitrogenous *substance*, $C_9H_{15}O_3N$, m. p. 238° (decomp.), probably  $\begin{matrix}\text{CMe}_2\cdot\text{CHMe}\\ \text{CO}\text{——}\text{NH}\end{matrix}>\text{CMe}\cdot\text{CO}_2\text{H}$ (A), and a very small quantity of the *semicarbazone* of ααβ-trimethyl-lævulic acid, m. p. 175°, insufficient for conversion into the solid acid.

By the oxidation of αββ-trimethyl-lævulic acid with alkaline permanganate γ-keto-αββ-trimethylglutaric acid, m. p. 119° (quinoxaline derivative, m. p. 223—224°), was obtained; this yielded αββ-trimethylglutaric acid when heated with hydriodic acid and red phosphorus, trimethylsuccinic acid and carbon monoxide when heated alone, and was identical in all respects with the acid $C_8H_{12}O_5$ prepared by Balbiano from camphoric acid (A., 1894, i, 614). This establishes the keto-formula first suggested by Mahla and Tiemann (A., 1895, i, 678) and disproves the original oxide formula of Balbiano.

Attempts to prepare γ-keto-ααβ-trimethylpropane-αγ-dicarboxylic acid by the oxidation of ααβ-trimethyl-lævulic acid or of the *lactone* of α′-*hydroxy*-ααβ-*trimethylglutaric acid*, m. p. 110° (synthesised by the action of hydrocyanic acid on the semi-aldehyde of trimethylsuccinic acid followed by the hydrolysis of the resultant lactonic nitrile with concentrated hydrochloric acid), with alkaline permanganate gave only trimethylsuccinic acid. Condensation of ethyl chloroacetate with ethyl dimethylacetoacetate in the presence of sodium ethoxide gave the oxidic *ester*,  $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\underset{\diagdown\text{O}\diagup}{\text{CMe}\cdot\text{CH}}\cdot\text{CO}_2\text{Et}$, b. p. 162°/26 mm., from which no definite compound was isolated on hydrolysis and distillation. I. VOGEL.

Synthesis of glyceric acid-monophosphoric acid. C. NEUBERG, F. WEINMANN, and M. VOGT (Biochem. Z., 1928, **199**, 248—252).—Glyceric acid-monophosphoric acid was prepared by the action of 2 mols. (*i.e.*, an excess) of ethyl metaphosphate on glyceric acid; it was isolated as the normal *barium* salt in a yield of 17% of the theoretical. The *monobarium* salt ($C_3H_5O_7PBa$) was prepared from the normal salt by acidification with hydrobromic acid. By means of the *brucine* salt the acid was resolved into its optical antipodes. J. H. BIRKINSHAW.

Walden inversion. H. N. K. RØRDAM (J.C.S., 1928, 2447—2453; cf. Holmberg, A., 1926, 384; 1927, 1169).—It is assumed that the inversion takes place in two steps, (*a*) a spontaneous elimination of one group and (*b*) the addition of another group X, during which period the remainder of the molecule is capable of rotation. The application of the activity factor of Brönsted (A., 1922, ii, 699) to this conception leads to the equation $n=kc_xf_1f_x/f_{1,x}$, where n is the fraction of the reaction product retaining its original steric configuration, c_x the mean concentration of X at the beginning and at the end of the reaction, f_1, f_x, and $f_{1,x}$, respectively, are the activity coefficients of the oscillating molecule, of X, and of the compound resulting from the union of these two, whilst k is a constant. The equation is applied to the reaction between salts of *l*-bromosuccinic acid and alkali xanthates (Holmberg, *loc. cit.*) and also to the reaction between hydrosulphides and salts of *l*-bromosuccinic acid (Holmberg, Arkiv Kemi, Min., Geol., 1915, 6, 1). Various assumptions are made as to the values of the activity coefficients and of k and fair agreement is obtained between theory and experiment.

I. Vogel.

Stereochemical studies. XVIII. Nitromalic acids. XIX. Diazotisation of aspartic acid and its ethyl ester. B. Holmberg (Ber., 1928, 61, [*B*], 1885—1892, 1893—1905).—XVIII. dl-*Nitromalic acid* [*nitro-oxysuccinic acid*], $CO_2H\cdot CH(O\cdot NO_2)\cdot CH_2\cdot CO_2H$, m. p. 132—133° (decomp.), is prepared by the action of sulphuric acid on a mixture of *dl*-malic acid and nitric acid (*d* 1·45) at 0°. Attempts to resolve it by *d*-phenylethylamine yielded only the corresponding *salt* ($+2H_2O$). l(—)-*Nitromalic acid*, m. p. 114—115° (decomp.), $[\alpha]_D$ −36·8°, −38·6°, −42·8°, −23·1° in alcohol, acetone, ethyl acetate, and water, respectively, is prepared similarly from *l*(—)-malic acid. The *sodium hydrogen*, $[\alpha]_D$ −26·7° in water, *di-sodium*, $[\alpha]_D$ −10·5° in water, *barium*, and *silver* salts are described. The ethyl ester has d_4^{20} 1·202, $[\alpha]_D^{20}$ −30·55°. Reduction of the acid by sodium amalgam or of the acid or ester by hydrogen sulphide affords almost homogeneous *l*-malic acid. The action of alkali hydroxide gives mainly fumaric acid. It could not be caused to react with sodium iodide in acetone or potassium xanthate in water. Racemisation under the influence of nitrates or formation of a lactone from normal nitromalates could not be established. Hydrolytic fission of *l*(—)-nitromalic acid does not proceed simply, since it is accompanied by auto-oxidation leading to carbon dioxide and unidentified products. The action of water appears to cause inversion and the production of *d*(+)-malic acid, whereas hydrolysis catalysed by hydrogen or copper ions gives *l*(—)-malic acid. Alkali bromosuccinates do not appear to react with nitrates, but the *l*(—)-acid, with the nitrate ion in presence of silver ions, affords *l*(—)-nitromalic acid; the interpretation of the change is uncertain with respect to the configuration of the acids.

XIX. The optical activity of the malic acid produced by diazotisation of (+)-aspartic acid varies greatly with the hydrogen-ion concentration of the solution. If this is sufficiently great, a change predominates which results in the formation of *l*(—)-malic acid, whereas with lower hydrogen-ion concentration the simultaneous occurrence of a reaction affording *d*(+)- or *r*-malic acid is obvious. If the aspartic acid is added to a moderately concentrated solution containing an excess of nitrite, an unexpectedly strongly lævorotatory malic acid is produced which is attributed to the production of β-nitronitrosopropionic acid and a nitrous ester of *l*-malic acid. Addition of sodium nitrate to the solution causes the production of *l*(—)-nitromalic acid in amount too small to influence the optical results. The yields decrease with decreasing acidity of the mixture, but a parallel diminution of the lævorotation of the acid is not observed. Similar results are obtained by the addition of chlorides with respect to the (—)-chlorosuccinic acid produced, but experiments with sulphates afford no conclusive evidence of the participation of the sulphate ion. Diazotisation of ethyl *d*(+)-aspartate gives an inactive or a very feebly dextrorotatory malic acid, according to the concentration of mineral acid in the solution. In presence of the corresponding normal salts, the esters of the nitromalic, chloro- and bromo-succinic acids show the same qualitative behaviour, but the halogen esters are much more strongly active than the nitro-compound.

The production of substituted succinic acids by the diazotisation of aspartic acid definitely involves two antipodal reactions in addition to the production of inactive materials through diazosuccinic ester. Experiments with the latter ester do not give support to the hypothesis of its existence in stereoisomeric forms. It is difficult to determine the extent to which inactive products arise from the corresponding diazosuccinic acid from aspartic acid.

The mechanisms of the diazo-reactions and of the conversion of halogenosuccinic into aminosuccinic acids are discussed in detail. It is concluded that the (+)-halogenosuccinic acids are configuratively related to the (—)-hydroxy-acids and are therefore *l*-forms and that natural (+)-aspartic acid has the *lævo*-configuration. With regard to the latter, the author is in agreement with Freudenberg and Noë (A., 1926, 53), but differs from Freudenberg and Lux (this vol., 735) in respect of the halogenosuccinic acids.

H. Wren.

Bromination of tetraethyl dicarboxyglutaconate and the constitution of glutaconic acids. Y. Urushibara (Bull. Chem. Soc. Japan, 1928, 8, 200—207; cf. A., 1927, 1059).—Addition of two atoms of bromine to ethyl αγ-dicarbethoxyglutaconate occurs almost instantaneously and is immediately followed by elimination of 1 mol. of hydrogen bromide, the removal of which is completed by treatment with pyridine, the final product being ethyl α-bromo-αγ-dicarbethoxyglutaconate, $CBr(CO_2Et)_2\cdot CH{:}C(CO_2Et)_2$ (Faltis and Pirsch, A., 1927, 856). This is hydrolysed by boiling aqueous-alcoholic hydrochloric acid for 3—4 hrs. to yield α-*chloroglutaconic acid*, m. p. 155°, in accordance with the scheme $>CBr\cdot CH{:}C< \longrightarrow >CBr\cdot CH_2\cdot CCl< \longrightarrow >C{:}CH\cdot CCl<$. Addition of bromine to ethyl α-methyl-αγ-dicarbethoxyglutaconate is not complete, the equilibrium $C_{16}H_{24}O_8+Br_2 \rightleftharpoons C_{16}H_{24}O_8Br_2$ being established, since in this case elimination of hydrogen bromide is not possible. The isolated dibromo-compound eliminates bromine spontaneously to re-establish this equilibrium. Since the equivalence of the α- and γ-positions in glutaconic acid derivatives (Thorpe, J.C.S., 1905, 87, 1669) depends on reactions involving hydrolysis with concentrated hydrochloric acid, the author doubts the validity of this evidence and regards the postulated existence of a normal form as unnecessary, only one form of glutaconic acid being considered stable.

J. W. Baker.

Constitution of aldehyde and ketone hydrogen sulphites. II. G. Schroeter [with M. Sulzbacher] (Ber., 1928, 61, [*B*], 1616—1627; cf. A., 1926, 1226).—The failure of Raschig and Prahl (this vol., 273) to repeat the author's quantitative hydrolysis of phenyl propane-ββ-disulphonate to phenol, barium sulphite, and barium β-hydroxypropane-β-sulphonate is attributed to the use of barium hydroxide containing barium chloride, which greatly affects the analytical results. Treatment of the barium salt with the requisite amount of sulphuric acid followed by neutralisation of the liberated acid with freshly-precipitated copper oxide readily yields homogeneous *copper* β-*hydroxypropane*-β-*sulphonate* (*anhydrous* and *trihydrate*). Raschig's purification of this compound by crystallisation from acetic acid is unfortunate, since it leads to *copper* β-*acetoxypropane*-β-*sulphonate*. The presence of the hydroxyl group in β-hydroxypropane-β-sulphonic acid is further established by the conversion of its sodium salt by an excess of phosphorus pentachloride into Δ^{α}-*propene*-β-*sulphonyl chloride*, b. p. 90—100°/17 mm., converted by methylaniline into Δ^{α}-*propene*-β-*sulphonmethylanilide*, m. p. 58—59°, regarded by Autenrieth as Δ^{α}-propene-α-sulphonmethylanilide. Gentle treatment of β-hydroxypropane-β-sulphonic acid or its sodium salt with 1 mol. of phosphorus pentachloride affords β-*hydroxypropane*-β-*sulphonyl chloride*, whence β-*hydroxypropane*-β-*sulphonethylanilide*, m. p. 44·5—45°. The difference between sodium β-hydroxypropane-β-sulphonate and "acetone sodium bisulphite" is therefore regarded as definitely established. Since the latter compound cannot be regarded as a sulphurous ester, its unitary formulation is no longer possible. It is therefore assumed that the known, labile, additive compounds of aldehydes and ketones with sulphur dioxide unite with water to more stable trimolecules $(R_2C{:}O),(SO_2),(H{\cdot}OH)$ which behave as monobasic acids, giving salts in which the character of the individual components is masked unless dissociation occurs, since their molecular valencies are mutually saturated.

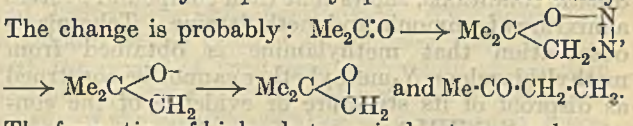
Phenyl propane-ββ-disulphonate with 1 mol. of barium hydroxide gives unchanged material, barium propane-ββ-disulphonate, phenol, sulphurous acid, and β-hydroxypropane-β-sulphonic acid, which is partly transformed into the lactide. Hydrolysis of propane-ββ-disulphonethylanilide with 1 mol. of barium hydroxide affords mainly ethylaniline and *barium propane*-ββ-*disulphonate* $(+2H_2O)$; with an excess of the hydroxide, barium β-hydroxypropane-β-sulphonate is also formed in considerable amount. Similarly, butane-ββ-disulphonethylanilide with equivalent amount and excess of barium hydroxide yields respectively *barium butane*-ββ-*disulphonate trihydrate* almost exclusively or mixed with *barium* β-*hydroxybutane*-β-*sulphonate*. Analogously, *barium* Δ^{δ}-*pentene*-ββ-*disulphonate* $(+3H_2O)$ and *barium* β-*hydroxy*-Δ^{δ}-*pentene*-β-*sulphonate* $(+3H_2O)$ are derived from Δ^{δ}-pentene-ββ-disulphonethylanilide. H. WREN.

Constitution of hydrogen sulphite compounds of aldehydes and ketones. O. STELLING (Cellulosechem., 1928, 9, 100—102; cf. A., 1925, ii, 935).—The absorption band of formaldehyde and acetone hydrogen sulphite compounds is at 4992·0 X., that of the sulphonic acids at 4992·2, whilst that of the metal alkyl sulphites is at 4996·0 and the dialkyl sulphites at 4997·7X. Hence it is concluded that the hydrogen sulphite compounds have the constitution $R_1R_2C(OH){\cdot}SO_3Na$. A critical review of the literature is given. J. W. BAKER.

Aldehydes from acetylenic carbinols. III. Two dimethylhexenals. H. RUPE, A. WIRZ, and P. LOTTER (Helv. Chim. Acta, 1928, 11, 965—971).—The action of acetylene on the sodium derivative of methyl *iso*butyl ketone furnishes *methyl*iso*butylethinylcarbinol*, b. p. 85—87°/80 mm. (*silver derivative*), which when heated with 70% formic acid gives a mixture of 4 parts of γε-*dimethyl*-Δ^{γ}-*hexenal* (I), b. p. 94—96°/80 mm. (*semicarbazone*, m. p. 178—179°; *oxime*, m. p. 53—54°), and 1 part of γε-*dimethyl*-Δ^{β}-*hexenal* (II) (*methyl*iso*butylacraldehyde*), b. p. 102—112°/80 mm. (*semicarbazones*, m. p. about 125° and 147°). Oxidation of (I) with cold alkaline potassium permanganate gives *iso*butyric and acetic acids, whilst (II) furnishes methyl *iso*butyl ketone and a small amount of an acid, m. p. 88—89°. Reduction of a mixture of (I) and (II) with hydrogen in presence of water and a nickel catalyst gives βδ-*dimethylhexaldehyde*, b. p. 93—94°/80 mm., when regenerated from its *semicarbazone*, m. p. 121—122°. H. BURTON.

Auto-oxidation of citronellal. J. ZIMMERMANN (Rec. trav. chim., 1928, 47, 940—941).—When citronella oil or pure citronellal is treated with zinc and then allowed to remain for some time in presence of light and air, zinc formate is produced. The oxidation is almost completely inhibited if the citronellal contains a small amount of phenolphthalein and is stored in brown bottles. H. BURTON.

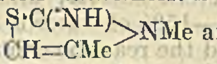
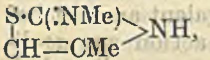
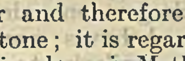
Action of diazomethane on ketones in presence of catalysts. H. MEERWEIN and W. BURNELEIT (Ber., 1928, 61, [*B*], 1840—1847).—The possibility of activating strictly homopolar compounds or atomic groups by complex formation is examined in the case of the carbonyl group. A solution of diazomethane in acetone scarcely undergoes decomposition at 0°. If 10—15% of water is added, nitrogen is freely evolved and the reaction continues as diazomethane is further added until about 80% of the equivalent amount has been used. The products of the action are *as*-dimethylethylene oxide (identified as *as*-dimethylethylene glycol), methyl ethyl ketone, probably diethyl ketone and methyl *n*-propyl ketone, and traces of *iso*butaldehyde probably produced secondarily. The change is probably:

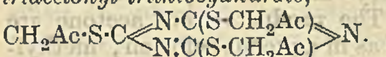
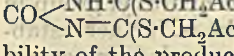
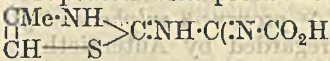
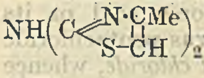


$$\mathrm{Me_2C{:}O} \longrightarrow \mathrm{Me_2C}\!\left<\begin{array}{l}\mathrm{O—N}\\ \mathrm{CH_2{\cdot}N}\end{array}\right. \longrightarrow \mathrm{Me_2C}\!\left<\begin{array}{l}\mathrm{O^-}\\ \mathrm{CH_2}\end{array}\right. \longrightarrow \mathrm{Me_2C}\!\left<\begin{array}{l}\mathrm{O}\\ |\\ \mathrm{CH_2}\end{array}\right. \text{ and } \mathrm{Me{\cdot}CO{\cdot}CH_2{\cdot}CH_3}.$$

The formation of higher ketones is due to an analogous reaction of diazomethane with methyl ethyl ketone. Water does not appear to be methylated. Its action cannot be attributed to hydrogen ions, since 0·1*N*-sodium hydroxide solution behaves analogously. Alcohols appear to behave similarly to but less energetically than water. Methyl alcohol is most active; with increase in mol. wt. and transition from primary to secondary and tertiary alcohols the activity decreases. The products from acetone are the same in alcoholic as in aqueous solution; methylation of the alcohols is scarcely appreciable. Lithium chloride (in 0·1*N*-solution) enhances the activity of acetone to about the same extent as 10% of water, but reaction ceases after about 70% of the theoretical amount of diazomethane has been introduced. The possible catalytic activity of acids cannot be preparatively tested, but comparison of the behaviour of diazomethane towards hydrochloric and oxalic acids dissolved in acetone and ether indicates that enhancement of the activity of acetone can be thus induced. H. WREN.

Preparation of acetonecyanohydrin. K. N. WELCH and G. R. CLEMO (J.C.S., 1928, 2629).—Acetonecyanohydrin is obtained in good yield by treatment of a mixture of acetone and aqueous potassium cyanide with 30% sulphuric acid (by wt.) below 20°; it is isolated by extraction with ether and rapidly distilled under diminished pressure (b. p. 81°/15 mm.) (cf. Urich, Annalen, 1872, **164**, 255; Bucherer and Grolée, A., 1906, i, 405). I. VOGEL.

Thiocyanoacetone, its isomerides and polymerides. A. HANTZSCH (Ber., 1928, **61**, [*B*], 1776—1788; cf. this vol., 187).—Mainly a reply to Tcherniac (J.C.S., 1919, **115**, 1071; this vol., 530). The conversion of thiocyanoacetone into hydroxymethylthiazole is effected by ebullition for 30 min. with 2*N*-hydrochloric acid. The action of bases on thiocyanoacetone has been examined by the author and by Tcherniac under considerably different conditions owing to the presence or absence of water. In anhydrous ether, thiocyanoacetone is converted by ammonia with partial resinification into aminomethylthiazole which is always accompanied by methylthiazolone, formed by the water liberated during closure of the ring. On the other hand, the action of methylamine proceeds without formation of resin or thiazolone, and the unstable, intermediate *compound*, $COMe\cdot CH_2\cdot S\cdot C(NHMe){:}NH$, passes at the atmospheric temperature into methylaminomethylthiazole, m. p. 70°. Aminomethylthiazole exhibits tautomerism in forming two methyl derivatives,  $\begin{array}{l}S\cdot C(:NH)\\ CH{=}CMe\end{array}\!>\!NMe$ and  $\begin{array}{l}S\cdot C(:NMe)\\ CH{=}CMe\end{array}\!>\!NH$, which, according to Traumann, yield exclusively ammonia and methylamine, respectively, when acted on by concentrated hydrochloric acid. Repetition of this work, possibly under more drastic conditions, shows that each compound evolves a mixture of ammonia and methylamine. Tcherniac's observation that methylamine is obtained from methylthiazolone *N*-methyl ether cannot be construed as disproof of its structure or evidence of the constitution  $\begin{array}{l}S\cdot C(:NMe)\\ CH{=}CMe\end{array}\!>\!O$.

Tcherniac's so-called "β-methylrhodim" is bimolecular and therefore not an isomeride of thiocyanoacetone; it is regarded as bimolecular hydroxymethylthiazole. *iso*Methylrhodim is termolecular thiocyanoacetone in which polymerisation is due to the thiocyano-group and hence is to be regarded as *triacetonyl trithiocyanurate*,  $CH_2Ac\cdot S\cdot C\!<\!\begin{array}{l}N\cdot C(S\cdot CH_2Ac)\\ N{:}C(S\cdot CH_2Ac)\end{array}\!>\!N$. Its ability to give a *diphenylhydrazone*, *di*-p-*tolylhydrazone*, *semicarbazone*, and *dioxime* is incompatible with Tcherniac's thiazolone formula, since compounds containing the ·CO·NH· group do not show ketonic properties. The production of cyanuric acid from "*iso*methylrhodim" in alkaline solution and of trimethylsulphonium iodide and cyanuric acid by the action of alcoholic methyl iodide is direct evidence of the pre-existence of the cyanuric ring in the molecule. The conversion of *iso*methylrhodim into dithiazylamine is simply explained as follows: partial hydrolysis causes removal of one $CH_2Ac\cdot S\cdot$ group as acetonylmercaptan which condenses to Tcherniac's dimethylthiene, $C_6H_8S_2$. The residual cyanuric derivative passes into its tautomeric, ketonic form,  $CO\!<\!\begin{array}{l}NH\cdot C(S\cdot CH_2Ac)\\ N{=}C(S\cdot CH_2Ac)\end{array}\!>\!N$, thereby giving the possibility of the production of the thiazole ring. Under further action of hydrochloric acid the cyanuric ring is ruptured with production of the carboxylic acid,  $\begin{array}{l}CMe\cdot NH\\ CH{-\!-}S\end{array}\!>\!C{:}NH\cdot C({:}N\cdot CO_2H)\cdot S\cdot CH_2Ac$, which loses water and carbon dioxide to produce dithiazylamine,  $NH\left(C\!<\!\begin{array}{l}N\cdot CMe\\ S{-}CH\end{array}\right)_2$. H. WREN.

Three-carbon system. XIX. Homomesitones. A. E. ABBOTT, G. A. R. KON, and R. D. SATCHELL (J.C.S., 1928, 2514—2524).—The four theoretically possible intermolecular condensation products from methyl ethyl ketone, $CH_2Me\cdot CMe{:}CH\cdot COEt$ (I), $CHMe{:}CMe\cdot CH_2\cdot COEt$ (II), $CH_2Me\cdot CMe{:}CMe\cdot COMe$ (III), $CHMe{:}CMe\cdot CHMe\cdot COMe$ (IV) have been synthesised and their mutual relationships elucidated. Alkaline condensing agents gave mixtures of I and II, whilst acid condensing agents gave mixtures of III and IV. Descudé's method (A., 1903, i, 735) after slight modification gave III only. The structures of I, III, and IV were confirmed by synthesis. Ketones I and II when treated with sodium ethoxide formed an equilibrium mixture (mobility high; equilibrium reached in 24 hrs. at the ordinary temperature; 67·5% of αβ-compound) identical with the crude homomesitone obtained by the action of sodium ethoxide on methyl ethyl ketone. Similar treatment with III and IV gave half equilibration after a fortnight at the ordinary temperature; complete equilibration was reached only after 9 hrs. at the b. p. of the reagent (mobility low; 17% of αβ-compound). The mobility differences are attributed to the α-methyl group in III and IV which favours the βγ-phase (cf. Kon and Narayanan, A., 1927, 873; Goldberg and Linstead, this vol., 1214).

Methyl ethyl ketone and ethyl α-bromopropionate in the presence of zinc gave *ethyl* β-*hydroxy*-αβ-*dimethyl*-n-*valerate*, b. p. 89—90°/13 mm., $d_4^{19\cdot5}$ 0·96457, $n_D^{19\cdot5}$ 1·4319. The liquid acid obtained by alkaline hydrolysis on dehydration with acetic anhydride gave poor yields of αβ-*dimethyl*-Δ^{α}-*pentenoic acid*, b. p. 116°/18 mm., $d_4^{17\cdot5}$ 0·97497, $n_D^{17\cdot5}$ 1·45952, $[R_L]_D$ 36·06 (p-*toluidide*, m. p. 123°), the *chloride*, b. p. 66°/17 mm., of which reacted with zinc methyl iodide to give γδ-*dimethyl*-Δ^{γ}-*hexen*-β-*one* (III), b. p. 65°/20 mm., $d_4^{17\cdot4}$ 0·86856, $n_D^{17\cdot4}$ 1·45283, $[R_L]_D$ 39·23. Ethyl β-hydroxy-αβ-dimethyl-*n*-valerate was readily dehydrated by phosphoryl chloride in benzene, giving *ethyl* αβ-*dimethyl*-Δ^{β}-*pentenoate*, b. p. 69°/13 mm., $d_4^{21\cdot1}$ 0·92379, $n_D^{21\cdot1}$ 1·43628, from which was prepared the *acid*, b. p. 116°/20 mm., $d_4^{18\cdot2}$ 0·97002, $n_D^{18\cdot2}$ 1·4498, $[R_L]_D$ 35·50 (p-*toluidide*, m. p. 56°), and the *acid chloride*, b. p. 52°/13 mm. The last-named compound with zinc (better magnesium) methyl iodide gave γδ-*dimethyl*-Δ^{δ}-*hexen*-β-*one* (IV), b. p. 48°/12 mm., 154°/750 mm., $d_4^{19\cdot2}$ 0·85385, $n_D^{19\cdot2}$ 1·43768, $[R_L]_D$ 38·74. Similarly, the chloride of β-methyl-β-ethylacrylic acid (Kon and Linstead, A., 1925, i, 506) and zinc ethyl iodide gave ε-*methyl*-Δ^δ-*hepten*-γ-*one* (I), b. p. 66°/18 mm., 53—54°/8 mm., $d_4^{21\cdot5}$ 0·85516, $n_D^{21\cdot5}$ 1·45073, $[R_L]_D$ 39·69.

Ethyl β-*keto*-α-*acetyl*-αδ-*dimethyl*-Δ^δ-n-*heptenoate*, CHMe:CMe·CH$_2$·CO·CMe(CO$_2$Et)·COMe, b. p. 158—168°/19 mm., obtained by condensation of β-methyl-Δ^β-pentenoyl chloride with ethyl sodiomethylacetoacetate in ethereal solution gave on alkaline hydrolysis an equilibrium mixture of I and II from which II was isolated by treatment with aluminium amalgam, whereby I became converted into a bimolecular reduction product and ε-*methyl*-Δ^ϵ-*hepten*-γ-*one* (II), b. p. 63°/19 mm., $d_4^{21\cdot2}$ 0·85244, $n_D^{21\cdot2}$ 1·43668, $[R_L]_D$ 38·73 (*semicarbazone*, m. p. 134°). Ketones IV, III, and I each gave a pair of *semicarbazones*, m. p. 203—204° and 163°, 186° and 166—167°, and 162° and 158° (Blaise and Maire, A., 1909, i, 85), respectively, indicating their possible existence in *cis*- and *trans*-forms. R. J. W. Le Fèvre.

Synthesis of acetylmethylcarbinol and its two homologues and their odour. T. Higasi and S. Marayama (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 940—947).—Acetylmethylcarbinol, prepared either by the reduction of diacetyl, or by hydrolysis of methyl α-bromoethyl ketone, or the corresponding acetate, has a faint agreeable odour, quite unlike that characteristic of Japanese saké and has no influence on the odour of these fermentation products. Its homologues have similar odours. J. W. Baker.

Hantzsch and Werner's stereochemical hypothesis in comparison with experimental facts and the constitution of isomeric oximes. G. Minunni (Gazzetta, 1928, 58, 504—521).—The constitution of isomeric oximes is discussed in relation to results published within the last few years, these emphasising the author's view that Hantzsch and Werner's hypothesis of geometrical isomerism is not only unnecessary, but also incapable of explaining the existence of known isomeric oximes. This hypothesis is not in accord with the author's observation that the acetyl and benzoyl derivatives of α-aldoximes undergo ready transformation into nitriles. The author's view that isomerism of the oximes is structural in character (A., 1891, 1354) is supported by the existence of five isomeric dioximes of *p*-methoxybenzil (cf. Ponzio and Bernardi, A., 1924, i, 293; Meisenheimer, Lange, and Lamparter, A., 1925, i, 1073) and by the fact that mesityl oxide and its isocyclic analogue, methyl*cyclo*hexenone, each form two isomeric oximes. T. H. Pope.

Action of alkali and carbon disulphide on xylan. E. Heuser and G. Schorsch (Cellulosechem., 1928, 9, 93—100).—Treatment of xylan with 4—14·5% sodium hydroxide solution and precipitation and washing the sodium *compound* three times with 20 c.c. of 96% alcohol in accordance with the technique of Karrer (A., 1921, i, 231) yields an alkali xylan containing the same proportion of sodium; the value closely approximates to that required by the compound $(C_5H_8O_4)_2$,NaOH, the alkali being determined either by titration or, for more trustworthy results, as sodium sulphate. Further washing with 96% alcohol causes a diminution in the sodium content, since the compound decomposes: $(C_5H_8O_2)_2\text{,NaOH} \rightleftharpoons (C_5H_8O_2)_2 + \text{NaOH}$. In the case of cellulose a compound containing the theoretical proportion of sodium is formed only with alkali concentrations between 15 and 30%; at lower concentrations the proportion of sodium in the product increases with increasing concentration of sodium hydroxide solution employed. Washing the alkali xylan with water causes a rapid decrease in the sodium content, whilst with varying concentrations of alcohol the loss of alkali is more rapid the more dilute is the alcohol, the sodium content tending to reach an equilibrium value. Washing with methyl alcohol or glycol gives results intermediate between those obtained with water and alcohol. A resinous product is obtained by the action of cold alcohol on xylan treated with 20% sodium hydroxide, or of alcohol at 70° on xylan treated with 12% sodium hydroxide solution. Similar treatment of xylan with sodium sulphide solution and washing until the filtrate is free from sulphur gives a product the sodium and sulphur content of which varies according to the concentration of alkali sulphide solution used. With potassium hydroxide the theoretical *compound* is obtained only with more concentrated alkali (8—12%), and then, like the sodium compound, the potassium content decreases if washed more than three times with alcohol. The lithium *compound* is more stable and requires ten washings to remove the excess of alkali, whilst the rubidium *compound* is stable only to four washings. Treatment of the unwashed alkali xylan (containing excess of alkali) with carbon disulphide yields a "xylan viscose," the viscosity of which, unlike that of cellulose viscose, decreases only slightly with time and is not coagulated after keeping for one month. A product free from combined sodium and sulphur compounds is obtained by neutralising the "viscose" with dilute acetic acid, precipitation and trituration of the product with alcohol, washing with ether, and drying over phosphoric oxide. The proportion of sulphur in the product so obtained varies slightly with the period of treatment with alkali and carbon disulphide, but is always much lower than that required by any of the possible cellulose xanthates, and, moreover, the proportion of sodium and sulphur present is less when xylan free from copper salts and ash is used. Hence the formation of the "xylan viscose" does not depend on xanthate formation, but involves merely a dissolution of sodium and sulphur compounds in the xylan. The action of alkali on xylan involves a chemical (hydrolysis) and not a physical degradation, since the proportion of xylan in the "viscose" compound determined as furfuraldehydephloroglucide is much less than that estimated from the carbon content determined by oxidation with potassium dichromate and sulphuric acid. Xylan regenerated from the "viscose" obtained by long keeping with alkali and carbon disulphide has a lower carbon and a higher hydrogen content than the original xylan. J. W. Baker.

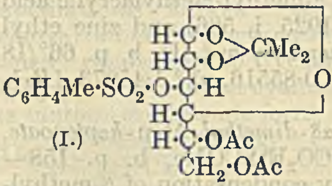
Colour tests for simple sugars. S. Y. Wong (Chinese J. Physiol., 1928, 2, 255—257).—By using glacial acetic acid instead of water or alcohol as solvent for the reagents of Molisch, Selivanov, and Tollens, their specificity and keeping power are enhanced. With 3 c.c. of such a 0·3% solution and 3 drops of a 1% sugar solution in the case of: (*a*) α-naphthol, 1 c.c. of sulphuric acid gives a pink to purple ring, which on heating, if the sugar be lævulose, gives a deep violet colour, or rhamnose an orange-red readily distinguished from the cherry-red of xylose and the much weaker reddish-violet of arabinose, whilst dextrose and galactose give only a faintly coloured solution; (*b*) resorcinol and 0·5 c.c. of hydrochloric acid when heated with lævulose, sucrose, or inulin give a red colour almost immediately, but scarcely any colour with the others after 1 min.; (*c*) phloroglucinol and 0·5 c.c. of hydrochloric acid on boiling with pentoses, gum-arabic, or yeast-nucleic acid readily give a cherry-red colour, whilst rhamnose gives only a yellow colour; (*d*) orcinol and 1 c.c. of hydrochloric acid (containing 5 drops of 10% ferric chloride per 100 c.c.), on boiling, give with pentoses, gum-arabic, and yeast-nucleic acid, but not with rhamnose, a greenish-blue colour. L. C. BAKER.

Colour reactions of carbohydrates. L. EKKERT (Pharm. Zentr., 1928, **69**, 597—600).—Colour reactions of arabinose, xylose, rhamnose, dextrose, mannose, galactose, lævulose, sucrose, lactose, maltose, dextrin, glycogen, and soluble starch with resorcinol, α- and β-naphthol, morphine, codeine, phenacetin, and α-naphthylamine in presence of sulphuric acid are described. E. H. SHARPLES.

Rotatory dispersion of sugars. T. WAGNER-JAUREGG (Helv. Chim. Acta, 1928, **11**, 786—789).—Solutions of αβ-glucose, αβ-galactose, αβ-fructose, αβ-arabinose, α-methylglucoside, α-phenylglucoside, and β-pentamethylglucose in water, and β-pentaacetylglucose in chloroform, show simple dispersion, whilst β-pentamethylglucose in chloroform exhibits complex dispersion. H. BURTON.

Degradation of dextrose by oxidation. III. B. BLEYER and W. BRAUN (Biochem. Z., 1928, **199**, 186—194).—In the oxidation of dextrose with chloroamine in alkaline solution the end-products are acetic acid and carbon dioxide. The full acidity (or decrease in alkalinity) is produced before the oxidation is complete. The evidence points to pyruvic acid as the intermediate product; this is supposed to arise from the hydrolysis of gluconic acid, the first step in the oxidation. The other intermediate product should be methylglyoxal; however, an attempt to oxidise this in alkaline solution with chloroamine was not successful. It is suggested that the hydrolysis product is a more active labile form. J. H. BIRKINSHAW.

Acetone [*iso*propylidene] derivatives of sugars and their transformation products. XII. Displacement of the oxygen bridge during the action of hydrogen bromide–glacial acetic acid on acyl derivatives of monoacetoneglucose [glucose *iso*propylidene ether]. H. OHLE and H. ERLBACH (Ber., 1928, **61**, [*B*], 1870—1875; cf. A., 1926, 1126).—3-*p*-Toluenesulphonyl*iso*propylideneglucose is converted by acetic anhydride in the presence of pyridine into 3-p-*toluenesulphonyl*-5 : 6-*diacetyl*iso*propylidene*-d-*glucose* (I), m. p. 85—86°, $[\alpha]_D^{20}$ −16·96° in chloroform; indications of the production of an isomeride, m. p. 78·5°, $[\alpha]_D^{20}$ −16·17° in chloroform, are obtained. Its constitution is deduced from its mode of production and from its alkaline hydrolysis to *iso*propylideneglucose. It is transformed by hydrogen bromide in glacial acetic acid into 1-*bromo*-3-p-*toluenesulphonyl*-2 : 5 : 6-*triacetyl*-d-*glucose*, m. p. 140° after darkening at 115° and softening at 135°, $[\alpha]_D^{20}$ −198·9° in chloroform, converted by methyl alcohol and silver carbonate into 3-p-*toluenesulphonyl*-2 : 5 : 6-*triacetyl*-β-*methylglucoside*, m. p. 128°, $[\alpha]_D^{20}$ −64·25° in chloroform, which differs from the analogous compound obtained by Freudenberg and Ivers from 3-*p*-toluenesulphonyldi*iso*propylideneglucose and by Ohle and Spencker from 3-*p*-toluenesulphonyl*iso*propylideneglucose. If too much acetone is used in the crystallisation of 1-bromo-3-*p*-toluenesulphonyl-2 : 5 : 6-triacetylglucose, the compound loses hydrogen bromide and forms 3-p-*toluenesulphonyl*-2 : 5 : 6-*triacetyl*-α-*glucose*, m. p. 129·5°, $[\alpha]_D^{20}$ +62·97° to +40·65° in chloroform. 3-p-*Toluenesulphonyl*-2 : 4 : 6-*triacetylglucose* has m. p. 178·5—179°, $[\alpha]_D^{20}$ +40·11° to +51·48° in chloroform.



(I.)

The applicability of hydrogen bromide and glacial acetic acid for the examination of the relative stability of the ring structure of a sugar and its derivatives is examined theoretically. H. WREN.

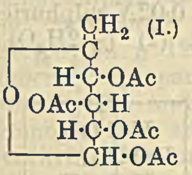
Acetone [*iso*propylidene] derivatives of sugars and their transformation products. XIII. Behaviour of completely acylated derivatives of monoacetoneglucose [glucose *iso*propylidene ether] towards hydrogen bromide–glacial acetic acid. K. OHLE, H. ERLBACH, and H. VOGL (Ber., 1928, **61**, [*B*], 1875—1885; cf. A., 1926, 1126).—The acyl derivative of *iso*propylideneglucose can be divided into two groups according to their behaviour towards hydrogen bromide–glacial acetic acid. 3-Benzoyl*iso*propylidene-, 3-benzoyldi*iso*propylidene-, 3-*p*-toluenesulphonyl-mono- and -di-*iso*propylidene-, 6-benzoyl*iso*propylidene-, 6-*p*-toluenesulphonyl-mono- and -*iso*di-*iso*propylidene-, 6-benzoyl-5-*p*-toluenesulphonyl*iso*propylidene-, 5 : 6-di-*p*-toluenesulphonyl*iso*propylidene-, triacetyl- and tribenzoyl-*iso*propylidene-glucose give characteristic colour reactions and compounds with firmly-combined bromine, whereas 3-*p*-toluenesulphonyl-5 : 6-dibenzoyl-, 3 : 5-di-*p*-toluenesulphonyl-6-benzoyl-, tri-*p*-toluenesulphonyl-, 5-*p*-toluenesulphonyl-3 : 6-anhydro-, and [3-*p*-toluenesulphonyl-5 : 6-diacetyl]-*iso*propylideneglucose do not exhibit this behaviour. Examination of the optical data of related derivatives of furoid glucose in the light of Hudson's rules shows that the principle of optical superposition is limited to compounds of similar constitution which exhibit only steric differences.

*iso*Propylideneglucose is converted with difficulty by *p*-toluenesulphonyl chloride in pyridine and chloroform at 36° into *tri*-p-*toluenesulphonyl*iso-

propylidene-α-glucose, m. p. 95—96°, $[\alpha]_D^{19}$ −5·15° in chloroform, which is transformed by hydrogen bromide and glacial acetic acid into the unstable 1-*bromo*-3 : 5 : 6-*tri*-p-*toluenesulphonyl-2-acetyl*-d-*glucose*, m. p. 124—125°, $[\alpha]_D^{19}$ +124·5° in chloroform, conveniently isolated as the additive *product* with 1 mol. of benzene, m. p. 106·5—108° (decomp.), $[\alpha]_D^{20}$ +114·5° in chloroform. The latter compound is converted by methyl alcohol and silver carbonate into 3 : 5 : 6-*tri*-p-*toluenesulphonyl-2-acetyl-β-methylglucoside*, m. p. 129·5°, $[\alpha]_D^{20}$ −8·9° in chloroform. Successive treatment of tri-*p*-toluenesulphonyl*iso*propylideneglucose with hydrogen bromide and acetic acid and with acetone and silver carbonate affords 2-*acetyl*-3 : 5 : 6-*tri*-p-*toluenesulphonylglucose*, m. p. 117—118°, $[\alpha]_D^{20}$ +51·09° to +37·2° in chloroform. 3 : 5-Di-*p*-toluenesulphonyl-6-benzoyl*iso*propylideneglucose similarly affords 1-*bromo*-3 : 5-*di*-p-*toluenesulphonyl-2-acetyl-6-benzoyl*-d-*glucose*, m. p. 159—160°, $[\alpha]_D^{20}$ +156·6° in chloroform, 3 : 5-*di*-p-*toluenesulphonyl-2-acetyl-6-benzoyl-β-methylglucoside*, m. p. 105°, $[\alpha]_D^{20}$ −4·16°, and 3 : 5-*di*-p-*toluenesulphonyl-2-acetyl-6-benzoyl*-d-*glucose*, m. p. 139°, $[\alpha]_D^{20}$ +69·2° to +46·33° in chloroform. 3-*p*-Toluenesulphonyl-5 : 6-dibenzoyl*iso*propylideneglucose is transformed into a very unstable acetylated bromide which yields 3-p-*toluenesulphonyl-2-acetyl*-5 : 6-*dibenzoyl-β-methylglucoside*, m. p. 132·5°, $[\alpha]_D^{20}$ −74·3° in chloroform, and 3-p-*toluenesulphonyl-2-acetyl*-5 : 6-*dibenzoyl*-d-*glucose*, m. p. 122°, $[\alpha]_D^{20}$ +3·55° to −20·52° in chloroform.

H. Wren.

New unsaturated anhydroglucose. B. Helferich and E. Himmen (Ber., 1928, **61**, [*B*], 1825—1835).—Acetyldibromoglucose dissolved in acetic anhydride is converted by concentrated sulphuric acid into *α-tetra-acetyl*-d-*glucose-6-bromohydrin*, m. p. 172—173° (corr.) after softening at 171°, $[\alpha]_D^{25}$ +108·5° in ethyl acetate, $[\alpha]_D^{24}$ +110·6° in chloroform, transformed by sodium iodide in acetone at 100° into *α-tetra-acetyl*-d-*glucose-6-iodohydrin*, m. p. 182° (corr.), $[\alpha]_D^{24}$ +102·0° in chloroform. The latter compound is converted by technical silver fluoride (containing subfluoride and oxide) in presence of pyridine into the unsaturated anhydroglucose derivative (I), for which the name *α-tetra-acetyl*-d-*glucoseen* is proposed; it has m. p. 115—116° (corr.), $[\alpha]_D^{23}$ +110·9° in chloroform. β-Tetra-acetyl-*d*-glucose-6-iodohydrin similarly affords β-*tetra-acetyl*-d-*glucoseen*, m. p. 119° (corr.), $[\alpha]_D^{22}$ −35·0° in chloroform. 2 : 3 : 4-Triacetyl-α-methyl-*d*-glucoside is converted by *p*-toluenesulphonyl chloride in pyridine into the corresponding 6-p-*toluenesulphonate*, m. p. 77—78·5° (corr.), hydrolysed by Zemplén's method to *p*-toluenesulphonyl-*d*-methylglucoside and converted by sodium iodide in acetone at 130° into *triacetyl-α-methyl*-d-*glucoside-6-iodohydrin*, m. p. 150—151° (decomp.), $[\alpha]_D^{24}$ +116·3° in chloroform. From the latter compound *triacetyl-α-methyl*-d-*glucoseenide*, m. p. 100—101° (corr.) after softening at about 98°, $[\alpha]_D^{18}$ +123·8° in chloroform (also +0·5MeOH), is derived. Ozonisation of triacetyl-α-methyl-*d*-glucoseenide in glacial acetic acid followed by reduction of the ozonide and peroxide with zinc dust yields *triacetyl-α-methyl*-d-*xyluronic acid*, $C_{12}H_{16}O_9$, m. p. 83—84°, $[\alpha]_D^{18}$ +92·0° in chloroform. *Triacetyl-β-methyl*-d-*glucoseenide*, prepared from triacetyl-β-methyl-*d*-glucoside-6-iodohydrin, has m. p. 92—93° (corr.), $[\alpha]_D^{20}$ −34·8° in chloroform; silver fluoride in its preparation may be replaced by silver sulphate or, less advantageously, by silver acetate and pyridine by acetonitrile or methyl alcohol (which causes some production of the 6-methoxy-derivative). The compound readily absorbs 1 mol. of hydrogen in acetic acid in presence of spongy platinum. It instantaneously decolorises bromine, giving an unstable additive product, whereas the corresponding *dichloride*, $C_{13}H_{18}O_8Cl_2$, m. p. 129·5—132° (corr.), is readily isolated. Triacetyl-β-methyl-*d*-glucoseenide is hydrolysed by sodium methoxide to β-*methyl*-d-*glucoseenide*, $C_7H_{12}O_5$, m. p. 109—110° (corr.), $[\alpha]_D^{25}$ 115·5° in aqueous solution. The compound does not reduce Fehling's solution. It is very sensitive to acids and is easily re-acetylated to the original compound. Solutions of hydrolysed β-methyl-*d*-glucoseenide give with phloroglucinol and hydrochloric acid, orcinol, pyrogallol, aniline, and *m*-nitroaniline colorations very closely resembling those of certain components of wood or of lignin itself. Since unsaturated substances are present in wood, it is possible that glucoseen is related to the transition products between dextrose and lignin or the compounds from which lignin arises biologically.


(I.)

H. Wren.

New *h*-fructose anhydride. H. H. Schlubach and H. Elsner (Naturwiss., 1928, **16**, 772).—From the syrup obtained by the action of acetone on lævulose (Irvine and Garrett, J.C.S., 1910, **97**, 1282) is isolated, in addition to 2 : 3-*iso*propylidenefructose, a 1 : 2-h-*fructose anhydride*, which by methylation is converted into 3 : 4 : 6-trimethyl-*γ*-fructose, identical with that obtained by Haworth and Learner (this vol., 510) from inulin, and a *di*-h-*fructose* which readily yields a *difructose anhydride*.

J. W. Baker.

Halogenohydrins of gentiobiose and dextrose. B. Helferich and H. Collatz (Ber., 1928, **61**, [*B*], 1640—1646; cf. A., 1926, 386).—Acetodibromoglucose is converted by tetra-acetylglucose and silver oxide in the presence of chloroform into *hepta-acetylgentiobiose-ζ′-bromohydrin*, $C_{26}H_{35}O_{17}Br$, m. p. 240° (corr.), $[\alpha]_D^{17}$ +2·38° in chloroform, from which the hygroscopic *gentiobiose-ζ′-bromohydrin*, m. p. 125—130° (decomp.) after softening at about 100°, $[\alpha]_D^{18}$ −12·8° in water after addition of sodium borate, is obtained by hydrolysis with the requisite amount of sodium methoxide and removal of sodium as the sulphate. *Acetodibromogentiobiose*, from the ζ′-bromohydrin in chloroform and acetic acid saturated with hydrogen bromide, has m. p. about 193° (decomp.), $[\alpha]_D^{21}$ +109·5° in chloroform; it is converted by silver carbonate in moist acetone into *hexa-acetylgentiobiose-ζ′-bromohydrin*, $C_{24}H_{33}O_{16}Br$, m. p. 264° (corr.), $[\alpha]_D^{22}$ +40·97° in pyridine (final value; the substance is highly mutarotatory and appears initially lævorotatory).

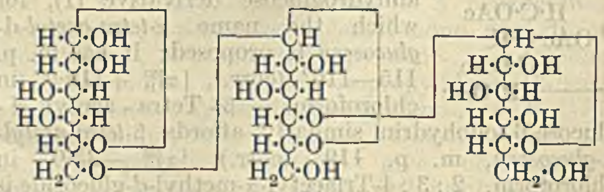
β-Tetra-acetylglucose-6-bromohydrin (cf. Fischer, A., 1920, i, 529) is transformed by sodium iodide in acetone at 100° into β-*tetra-acetylglucose-6-iodohydrin*, m. p. 152° (corr.), $[\alpha]_D^{23}$ +9·34° in chloroform. The latter substance with hydrogen bromide in glacial acetic acid affords *triacetylglucose*-1-*bromo*-6-*iodohydrin*, m. p. 168—177° (decomp.) according to the rate of heating, $[\alpha]_D^{21}$ +178·9° in chloroform, converted by silver carbonate in moist acetone into β-*triacetylglucose*-6-*iodohydrin*, m. p. 159—160° (decomp.), $[\alpha]_D^{21}$ +32·23° to +81·25° in 6 days. *Acetyl*-1 : 6-*di-iodoglucose*, $C_{12}H_{18}O_7I_2$, decomp. about 150° after darkening at 130°, $[\alpha]_D^{21}$ +205·9° in chloroform, is obtained from β-tetra-acetylglucose-6-iodohydrin and hydrogen iodide in glacial acetic acid. H. Wren.

Mechanism of carbohydrate oxidation. X. Action of potassium hydroxide on mannose; comparison with that of dextrose and lævulose. W. L. Evans and D. C. O'Donnell (J. Amer. Chem. Soc., 1928, **50**, 2543—2556).—The action of aqueous potassium hydroxide on mannose at 25°, 50°, and 75° has been studied by the methods previously employed with dextrose, for which revised results are given, and lævulose (cf. this vol., 397, 741). The amounts of pyruvaldehyde, lactic, acetic, and formic acids obtained vary with the alkali concentration in the same general manner with each sugar, although at 25° and 50° the results differ quantitatively. At 75°, however, the proportions of lactic, acetic, and formic acids formed at a given alkalinity are independent of the hexose used. This supports the view that alkaline solutions of these sugars contain equilibrium mixtures which become identical in composition at 75°, but contain different proportions of the same components at lower temperatures. H. E. F. Notton.

Acetone [*iso*propylidene] sugars. XIII. Hydrolysis of certain disaccharides, glucosides, and *iso*propylidene sugars. K. Freudenberg, W. Dürr, and H. von Hochstetter [with H. vom Hove, W. Jacobi, A. Noë, and E. Gärtner] (Ber., 1928, **61**, [*B*], 1735—1743; cf. A., 1927, 230).—The inversion constants of glucosido-β-6-galactose, cellobiose, turanose, maltose, lactose, galactosido-β-6-galactose, melibiose, α- and β-methyl-, α- and β-phenyl-, β-benzyl-glucoside, α- and β-methylgalactoside, and 1 : 2-*iso*propylideneglucose by sulphuric acid at 70° have been determined polarimetrically. Among disaccharides, the two β-glucosides have the smallest and the β-galactosides the highest constants corresponding with the relationship of β-methylglucoside to β-methylgalactoside. Maltose and turanose are more rapidly hydrolysed than cellobiose and glucosido-β-6-galactose, whereas the order is inverted with α- and β-methylglucoside. *iso*Propylideneglucose is much more rapidly hydrolysed than the disaccharides or glucosides. Hydrolysis of the other *iso*propylidene sugars occurs so rapidly that it must be measured in a boiling aqueous, buffered solution followed by titrimetric determination of acetone in the distillate. *iso*Propylideneglucose is most stable. The constants of di*iso*propylidenegalactose are of the same order of magnitude, so that it is impossible to prepare mono*iso*propylidenegalactose by partial hydrolysis of the di-derivative. *iso*Propylidenerhamnose is hydrolysed about ten times as rapidly as *iso*propylideneglucose. With di*iso*propylidenemannose marked progression is observed in the values of the "constant," which is even more obvious with di*iso*propylideneglucose.

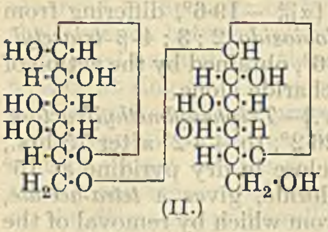
The dependence of the production of di*iso*propylideneglucose on the quality of the acetone employed is shown to be due to the high accelerating action of acetaldehyde and acetals. Removal of the εζ-acetone group of di*iso*propylideneglucose is best effected with acetic acid. The sodium derivative of *iso*propylideneglucose is transformed by benzyl chloride into γ-benzyl*iso*propylideneglucose. The benzyl ethers of the sugars appear very stable towards acid and alkali, but may be decomposed by hydrogenation in presence of platinum metals or of sodium amalgam. The crude di*iso*propylidenemethylmannoside of Freudenberg and Hixon (A., 1923, i, 1179) contains a crystalline component, m. p. 40—41°, $[\alpha]_D$ −42°, which appears to belong to the β-series. Levene and Meyer's product (A., 1924, i, 616) and the liquid component of Freudenberg's preparation are regarded as mixtures of the α- and β-forms. The unstable hepta-acetylchloromaltose (A., 1922, i, 524; 1925, i, 635) is a probable intermediate compound in the conversion of octa-acetylmaltose into the ordinary acetylchloromaltose. The following new compounds are described incidentally: γ-*benzyl*iso*propylideneglucose diacetate*, m. p. 119—119·5°, $[\alpha]_D$ −53° in *s*-tetrachloroethane; γ-*methyl*iso*propylideneglucose*, b. p. 173—175°/1 mm. (*dibenzoate*, m. p. 81—82°); iso*propylidenemannose triacetate*, m. p. 59°, $[\alpha]_D$ +49·9° in *s*-tetrachloroethane. H. Wren.

Acetone [*iso*propylidene] sugars. XIV. Syntheses of further di- and tri-saccharides from galactose, dextrose, and mannose. K. Freudenberg, A. Wolf, E. Knopf, and S. H. Zaheer (Ber., 1928, **61**, [*B*], 1743—1750; cf. A., 1927, 230).—The initial value $[\alpha]_D^{18}$ +1·6° (±0·5°) and final value $[\alpha]_D^{18}$ +13·9° (±0·5°) in water for β-galactosido-6-β-galactose are now recorded. Acetylbromocellobiose and di*iso*propylidenegalactose are converted by silver oxide in the presence of chloroform into *hepta-acetylcellobiosidodi*iso*propylidenegalactose*, m. p. 227°, $[\alpha]_D^{18}$ −47·1° in *s*-tetrachloroethane, hydrolysed by aqueous barium hydroxide to the syrupy *cellobiosidodi*iso*propylidenegalactose*, converted by 0·02*N*-sulphuric acid into β-*cellobiosido*-6-α-*galactose* (I) (+$2H_2O$),


(I.)

$[\alpha]_D^{19}$ +24·6° to +9·9° in water during 3 hrs. (calculated for anhydrous substance) [*osazone*, m. p. 207° (decomp.)].

Acetylbromolactose and di*iso*propylidenegalactose afford the non-crystalline *hepta-acetyl-lactosidodi*iso*propylidenegalactose*, converted successively into *lactosidodi*iso*propylidenegalactose*, m. p. 117°, $[\alpha]_D^{18}$ −39·8° in water, and β-*lactosido*-6-*galactose*, $[\alpha]_D^{18}$ +22·2° in water [osazone, m. p. 211° (decomp.)]. Di*iso*propylidenegalactose and acetylbromogalactose yield successively *tetra-acetylgalactosidodi*iso*propylidenegalactose*, m. p. 101—102°, $[\alpha]_D^{16}$ −44·7° in *s*-tetrachloroethane, non-crystalline *galactosidodi*iso*propylidenegalactose*, and β-*galactosido*-6-β-*galactose* (II), $[\alpha]_D^{17}$ +23·2° to +34·1° in water during 48 hrs. (*osazone*, m. p. 207° (decomp.)]. Chlorodi*iso*propylidenemannose and di*iso*propylidenegalactose afford *di*iso*propylidenemannosidodi*iso*propylidenegalactose*, b. p. 205—210°/1 mm., $[\alpha]_D^{18}$ −44·6° in *s*-tetrachloroethane, and thence 6-*mannosidogalactose*, $[\alpha]_D^{20}$ +144° to +134° in aqueous solution during 3 hrs. *Di*iso*propylidenemannosidodi*iso*propylidenemannose*, m. p. 180—181°, $[\alpha]_D^{18}$ +84° in *s*-tetrachloroethane, from chlorodi*iso*propylidenemannose and di*iso*propylidenemannose, is converted into the non-crystalline l-*mannosidomannose*, $[\alpha]_D^{17}$ +53° in water. H. Wren.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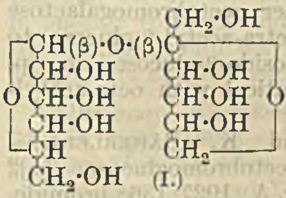
Acetone [*iso*propylidene] sugars. XV. Syntheses of disaccharides. K. Freudenberg, H. Toepffer, and C. C. Andersen (Ber., 1928, **61**, [*B*], 1750—1760).—Acetyldibromoglucose is converted into triacetylglucose-ζ-bromohydrin (cf. Fischer and Zach, A., 1912, i, 239), which is hydrolysed by 5% hydrobromic acid to *glucose-ζ-bromohydrin*, m. p. 134° (decomp.), $[\alpha]_D^{17}$ +86·9° to +48·95° in water after 18 hrs. The latter compound is converted by acetone in the presence of concentrated sulphuric acid into a mixture of *di*iso*propylideneglucose-ζ-bromohydrin*, $C_{12}H_{19}O_5Br$, b. p. 146°/1—2 mm., $[\alpha]_D^{18}$ +42·0° in alcohol, and iso*propylideneglucose-ζ-bromohydrin*, m. p. 87°, $[\alpha]_D^{20}$ −13·1° in water. *Diacetyl*iso*propylideneglucose-ζ-bromohydrin*, m. p. 115°, $[\alpha]_D^{20}$ −7·11° in *s*-tetrachloroethane, from the latter compound and acetic anhydride in pyridine, is converted by thallium acetate in a mixture of acetic anhydride and acetic acid into triacetyl*iso*propylideneglucose, m. p. 72°. The bromine atom of the di*iso*propylidene derivative could not be smoothly removed by silver acetate or toluenesulphonate, whereas sodium methoxide causes the production of iso*propylideneanhydroglucose*, $C_9H_{14}O_5$, m. p. 126°, $[\alpha]_D^{18}$ −27·1° in water, more conveniently prepared from *iso*propylideneglucose-ζ-bromohydrin and silver oxide in acetone. Acetobromoglucose and *iso*propylideneglucose-ζ-bromohydrin in chloroform are transformed by silver carbonate into *tetra-acetylglucosidomonoacetylmono*iso*propylideneglucose-ζ-bromohydrin*, m. p. 161°, $[\alpha]_D^{17}$ −63·6° in *s*-tetrachloroethane, in which the bromine atom could not be replaced by the acetoxy-group. Di*iso*propylideneglucose-ζ-bromohydrin is transformed by sodium iodide in acetone at 100° into *di*iso*propylideneglucose-ζ-iodohydrin*, m. p. 58°, $[\alpha]_D^{18}$ +30·9° in alcohol, and, similarly, the above bromo-compound is converted into *tetra-acetylglucosidomonoacetylmono*iso*propylideneglucose-ζ-iodohydrin*, m. p. 186°, $[\alpha]_D$ −80·8° in *s*-tetrachloroethane, from which *tetra-acetylglucosido*iso*propylideneanhydroglucose*, m. p. 126°, is obtained by means of thallium acetate. Treatment of the α- and β-methylglucosides with zinc chloride and benzaldehyde gives benzylidene-α-methylglucoside, m. p. 161—162°, and benzylidene-β-methylglucoside, m. p. 205°. Methylation of these products affords dimethylbenzylidene-α-methylglucoside, m. p. 122—123° (cf. Irvine and Scott, J.C.S., 1913, **103**, 575), and *dimethylbenzylidene-β-methylglucoside*, m. p. 134°, $[\alpha]_D^{22}$ −61·0° in alcohol. 3-Methylglucose is converted by methyl-alcoholic hydrogen chloride into a syrupy mixture of its α- and β-methylglucosides, from which two *benzylidene-3-methyl*(*methylglucosides*), m. p. 133°, $[\alpha]_D^{22}$ +49·1° in *s*-tetrachloroethane, and m. p. 164°, $[\alpha]_D^{22}$ −39·1° in *s*-tetrachloroethane, respectively, are derived. Further methylation affords two benzylidenedimethylmethylglucosides identical with the product of methylation of the benzylidene-α-methylglucoside, m. p. 161—162°, and with that of benzylidene-β-methylglucoside. It follows therefore that the 3-hydroxy-group is unsubstituted in the monobenzylidene derivatives of α- and β-methylglucoside. Benzylidene-α-methylglucoside is readily converted by hydrogen in the presence of spongy platinum into α-methylglucoside. A mixture of acetobromoglucose and benzylidene-α-methylglucoside is converted by silver carbonate in presence of chloroform into *tetra-acetylglucosidobenzylidene-α-methylglucoside*, m. p. 232°, $[\alpha]_D^{25}$ +47° in chloroform, converted by sodium methoxide into *glucosidobenzylidene-α-methylglucoside*, m. p. 245°, whence β-glucosido-2(or 3)-α-methylglucoside, m. p. 252° (decomp.), $[\alpha]_D^{20}$ +62·7° in water, is derived. H. Wren.

Sucrose *B*. A. Pictet and H. Vogel (Helv. Chim. Acta, 1928, **11**, 901—905).—When sucrose is crystallised from aqueous-acetone, -pyridine, -*iso*propyl alcohol, -ethylene glycol, -glycerol, and -acetaldehyde the *A* form, m. p. 185°, is obtained. The *B* modification, m. p. 171°, is obtained only from aqueous methyl alcohol. The analytical composition, rotation, and octa-acetate of the *B* form are identical with those of the *A* modification, and the conversion of *B* into *A* appears to be instantaneous in water, but is only slow in alcohol. The differences in the two modifications appear to be purely physical (cf. Helderman, A., 1927, 1174). H. Burton.

Sucroses *C* and *D*. A. Pictet and H. Vogel (Helv. Chim. Acta, 1928, **11**, 905—909).—A chloroform solution of equal parts of β-tetra-acetylglucose and tetra-acetylfructose is treated during 14 hrs. with phosphoric anhydride, and the residual product after repeated dissolution in water gives a 15% yield of the *octa-acetate*, m. p. 113—114°, $[\alpha]_D$ −60·8° in chloroform, of *sucrose* C (I), m. p. 104°, $[\alpha]_D$ −24·6° in water. This new sugar is decomposed by warming with traces of alkali, this being the probable cause of its ability to reduce Fehling's and potassium permanganate solutions, but is more resistant to acids than sucrose *A*. Inversion by hot 10% hydrochloric acid gives ordinary invert-sugar.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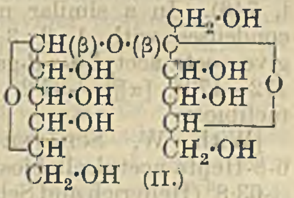
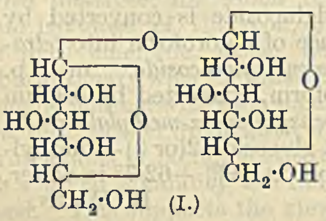

(II.)

When octa-acetylsucrose *A* is triturated with concentrated hydrochloric acid, neutralised with barium carbonate, extracted with alcohol, and finally treated with silver carbonate, a mixture of tetra-acetylglucose and -fructose is obtained. When this is treated with phosphoric oxide in chloroform solution the *octa-acetate*, m. p. 125°, $[\alpha]_D$ +20·3° in chloroform, of *sucrose* D (II), m. p. 127°, $[\alpha]_D$ +19·0° in water, is obtained. This sugar is readily hydrolysed by acids giving ordinary invert-sugar, does not reduce Fehling's or potassium permanganate solution, and does not yield an osazone. H. BURTON.

New sugars of trehalose type. H. VOGEL and H. DEBOWSKA-KURNICKA (Helv. Chim. Acta, 1928, **11**, 910—915).—A solution of β-tetra-acetylglucose in pure toluene is heated for 2·5 hrs. with a small amount of zinc chloride, and then for a further 6 hrs. with phosphoric anhydride. Trituration of the resulting product with alcohol gives the *octa-acetate*, m. p. 68—70°, $[\alpha]_D$ +68·1° in chloroform, of αβ-*trehalose* (I), m. p. 85°, decomp. 97°, $[\alpha]_D$ +67·1° in water. This sugar is not a reducing agent, and when hydrolysed yields dextrose.

Treatment of a chloroform solution of β-tetra-acetylgalactose with phosphoric oxide gives the *octa-acetate*, m. p. 82—83°, $[\alpha]_D$ +51·7° in chloroform, of a *galactobiose*, m. p. 122°, $[\alpha]$ +67·8° in water, which is hydrolysed to galactose.


(I.)

Similar treatment of hepta-acetylmaltose affords the *tetradeca-acetyl* derivative, m. p. 105°, $[\alpha]_D$ +105·4° in chloroform, of a *maltotetrose*, $C_{24}H_{42}O_{21}$, m. p. 120—122°, $[\alpha]_D$ +113·5° in water, readily hydrolysed to dextrose. H. BURTON.

Sugar syntheses. VIII. Synthesis of vicianose, melibiose, and cellobiosidogentiobiose acetate, and a new tetra-acetylfructose. B. HELFERICH and H. BREDERECK (Annalen, 1928, **465**, 166—184; cf. Helferich and Rauch, A., 1927, 44, 859).—1 : 2 : 3 : 4-β-Tetra-acetylglucose is condensed with *l*-(+)-acetobromoarabinose (Gehrke and Aichner, A., 1927, 544) in chloroform in presence of silver oxide to give *hepta-acetyl*-6-β-l-*arabinosidoglucose*, m. p. 158—160°, $[\alpha]_D^{14}$ +7°, which by hydrolysis (cf. Helferich and Collatz, this vol., 1221) yields 6-β-*l*-arabinosidoglucose, m. p. 210°, $[\alpha]_D^{14}$ +56·6°, to +40·5°, identical with vicianose.

α-Acetobromo-*d*-galactose, when melted with phenol and quinoline, yields a mixture of α- and β-galactosides, from which is isolated *tetra-acetyl-α-phenol*-d-*galactoside*, m. p. 131—132°, $[\alpha]_D^{20}$ +175·5° (in chloroform), differing thus from the β-isomeride prepared from sodium phenoxide (Fischer and Armstrong, A., 1902, i, 746). In a similar manner acetobromogalactose condenses with 1 : 2 : 3 : 4-tetra-acetyl-β-glucose to give octa-acetyl-6-α-*d*-galactosido-β-glucose, m. p. 172—173°, $[\alpha]_D^{20}$ +97·2°, identical with octa-acetylmelibiose.

[With W. SCHÄFER and K. BÄUERLEIN.]—6-β-Hepta-acetylcellobiosidoacetobromoglucose, $[\alpha]_D^{19}$ +63·8° (Helferich and Schäfer, A., 1927, 136; bromide, m. p. 209°, not 231°), condenses with 1 : 2 : 3 : 4-β-tetra-acetylglucose in chloroform in presence of silver oxide to form 6′-β-*cellobiosido*-β-*gentiobiose tetradeca-acetate*, m. p. 239—240°, $[\alpha]_D^{15}$ −19·6°, differing from the *hepta-acetyl*-6-β-*cellobiosido*-2 : 3 : 4-β-*triacetylglucose*, m. p. 233°, $[\alpha]_D^{15}$ −6°, obtained by the action of silver oxide on the trisaccharide alone.

[With T. MODROW.]—*Triphenylmethylfructose*, m. p. 160—165°, $[\alpha]_D^{15}$ −26·2°, to +4·2° after 75 hrs., obtained by treating lævulose in dry pyridine at 15° with triphenylmethyl chloride, gives a *tetra-acetate*, m. p. 146°, $[\alpha]_D^{20}$ +42·4°, from which by removal of the triphenylmethyl residue with hydrobromic and acetic acids at 5° there is obtained a new *tetra-acetylfructose*, m. p. 112°, $[\alpha]_D$ +51·0°. This yields α-penta-acetylfructose and thus contains the usual 2 : 6-oxygen bridge. It is extraordinarily unstable, even esterification with toluenesulphonyl chloride in pyridine leading only to decomposition products. It condenses, however, with acetobromoglucose to give an octa-acetyl-β-*d*-glucosidofructose, m. p. 80°, $[\alpha]_D^{20}$ +14·1°, probably identical with Pictet and Vogel's compound (this vol., 1224).

All the above m. p. are corrected. C. HOLLINS.

Synthesis of raffinose. H. VOGEL and A. PICTET (Helv. Chim. Acta, 1928, **11**, 898—900).—When a mixture of sucrose and galactose or sucrose and α-galactosan (A., 1922, i, 811) is heated at 160—165°/13—15 mm. for 1¼ hrs. and the resulting product extracted with methyl alcohol, about 1% of raffinose, m. p. (hydrated) 80—81°, $[\alpha]_D$ +104·9° in water, is obtained. This is hydrolysed by hot 10% acetic acid to melibiose and lævulose, and on acetylation gives an acetate, m. p. 98—100°, $[\alpha]_D$ +91·9° in alcohol (cf. Scheibler, A., 1887, 306). H. BURTON.

Methyl salicylate glucoside of *Gaultheria procumbens*, L., identical with monotropitin. M. BRIDEL and (MLLE.) S. GRILLON (Compt. rend., 1928, **187**, 609—611).—Contrary to the suggestion of Procter (1844), *Gaultheria procumbens*, L., does not contain methyl salicylate in the free state but combined in the form of a glucoside, m. p. 179·5°, α_D −57·91° (in water), containing 3·85% of water, which is isolated (yield, 4 g./kg. of fresh plant) and shown to be identical with monotropitin, isolated from *Monotropa hypopitys* (A., 1923, i, 1275). J. W. BAKER.

Ameliaroside, a new glucoside from *Amelanchier vulgaris*, Moench. M. BRIDEL, C. CHARAUX, and G. RABATÉ (J. Pharm. Chim., 1928, [viii], 8, 345—357, and Bull. Soc. Chim. biol., 1928, **10**, 1111—1122).—A more detailed account of work already published (this vol., 992).

Röntgen diagram of native starch. S. VON NÁRAY-SZABÓ (Annalen, 1928, **465**, 299—304).—The Debye–Scherrer method of *X*-ray analysis has been applied to starch from different sources (cf. Herzog and Jancke, A., 1921, i, 308; Sponsler, A., 1923, i, 999; Ott, A., 1926, 460). A copper–potassium anticathode is used, and the starch is contained in a glass capillary. Starches may be divided into the potato group (from potato, *Curcuma angustifolia*, *Canna indica* and *C. edulis*, *Musa paradisiaca*, *Dioscorœa alata*, *Arracalia esculenta*, *Jatropha manihot*, and *Araucaria brasiliensis*) and the rice group (from rice, wheat, millet, *Maranta arundinacea*, *Ipomœa tjalappa*, *Arum esculentum*, and *Batatas edulis*). The former are characterised by a strongly-marked ring 1 (not observed by Sponsler or by Ott, *loc. cit.*), from which the distance between planes of the crystal lattice is calculated as 16·0 Å.; there is a second strong interference at ring 5. In the rice group ring 1 is absent, and rings 5 and 8 are present.

The variations in strength of the rings from groups I and II cannot be due to contamination or deformation; the amount of amylopectin has no influence on the diagrams, and swelling by absorption of water has only normal effects. It is therefore suggested that the parameters of the unit cell (of which the volume is calculated to be $2 \cdot 524 \times 10^{-21}$ cm., *i.e.*, 16 $C_6H_{10}O_5$ groups) vary, through either physical or chemical differences between the different starches.

E. W. Wignall.

Starch. I. Potato starch. K. Hess, H. Friese, and F. A. Smith (Ber., 1928, **61**, [*B*], 1975—1982).—Potato starch, dried in air and thus containing 18% of moisture, is readily acetylated without suffering acetolysis if first swollen with pyridine and then treated with acetic anhydride and pyridine at 50—70° for 4 days, yielding thereby *starch triacetate*. Under similar conditions, starch which has been dehydrated over phosphoric oxide at 100°/1 mm. reacts only superficially if at all. Undried " amylose " and " amylopectin " are acetylated in a similar manner. The starch triacetate is a white, granular powder with a phosphoric acid content corresponding with that of the starch previous to acetylation. It is not dissolved by chloroform, acetone, glacial acetic acid, or other usual solvents. It is hydrolysed by methyl-alcoholic ammonia or sodium hydroxide to a carbohydrate which, like natural starch, does not reduce Fehling's solution. "*Amylopectin*" *triacetate* is identical in solubility with starch triacetate. The disruption of starch into amylose and amylopectin might be expected to find its counterpart in the division of starch triacetate by solvents into the more soluble amylose triacetate and less soluble amylopectin triacetate. This cannot, however, be effected and it is therefore probable that starch suffers partial hydrolysis when treated with water at 80°. When treated with water at 55°, 69% of the starch passes into solution, whilst, on raising the temperature to 80°, 31·8% of the residue is dissolved, making 80% in all. Microscopical examination of the most soluble portion shows it to retain the structure of the original material but to be composed of smaller particles so that water has merely removed the outer layers of carbohydrate. The final residue is, however, completely de-organised. It must therefore be assumed that, at most, that portion of the starch which is removed by water at 80° corresponds with a particular nucleus material of the starch granule and even this assumption is somewhat uncertain since the swelling temperature has been exceeded. The final residue is completely insoluble in water and may be designated " amylopectin " if the differentiation of starch into chemically different carbohydrates ultimately proves to be practicable. Amylopectin cannot be the " integument substance " of starch. The portion of the starch granules dissolved by water contains reducing components. Its non-homogeneity is further established by fractionation experiments with acetic anhydride and pyridine. Reducing fractions have a higher acetyl content than starch triacetate. With increasing reducing power the fractions exhibit diminishing rotation in chloroform and negatively increasing mutarotation of their hydrolytic products. Non-reducing carbohydrates which give a triacetate have the same specific rotation in alkali hydroxide as starch. The acetate, in contrast to those of starch and amylopectin, is soluble in chloroform ($[\alpha]_D^{20}$ +169·41°). The final residue from the extraction of starch (corresponding with " amylopectin ") has $[\alpha]_D^{20}$ +153·37° in *N*-sodium hydroxide and gives a triacetate; it possibly represents the purest form of starch yet isolated.

Apart from the solubility of the purest " amylose " fractions in organic media, there appear to be no reasonable grounds for supposing that amylose, amylopectin, and natural starch are chemically different substances.

H. Wren.

Starch. XXI. Constitution of glycogen. H. Pringsheim and G. Will (Ber., 1928, **61**, [*B*], 2011—2017).—Glycogen triacetate is rendered sufficiently soluble in chloroform by treatment during 20 min. with boiling naphthalene and is then heated with a solution of benzenesulphonic acid in chloroform whereby partial removal of the acetyl groups is effected; hydrolysis is completed by alcoholic potassium hydroxide or aqueous barium hydroxide, the ultimate product being *glycogesan*, which has the same optical activity and identical iodine coloration as glycogen. Cryoscopic examination of the product in water establishes its trisaccharide character, independent of details of its mode of preparation. In boiling water glycogesan passes into the colloidal state. Under the influence of pancreatic amylase, glycogesan is degraded to maltose, fission being approximately quantitative if yeast complement is added. The kinetics of fermentation are exactly parallel when glycogen or glycogesan is used as substrate, thus establishing the constitutional similarity of the polysaccharide with its structural element. Towards glycolysis the behaviour of glycogen and glycogesan is quantitatively identical. Re-acetylation of glycogesan affords a *triacetate*, identical in optical activity with glycogen triacetate. Determination of mol. wt. of glycogesan triacetate in glacial acetic acid gives the values of a triacetylhexosan at concentrations up to 0·3%; with more highly concentrated solutions association is observed.

H. Wren.

Inulin. VII. H. Pringsheim and J. Reilly (Ber., 1928, **61**, [*B*], 2018—2019).—Inulin acetate is converted by treatment with benzenesulphonic acid in boiling toluene and subsequently with alcoholic potassium hydroxide into inulan, identical with inulin in specific rotation and behaviour towards inulinase but having the mol. wt. of a disaccharide anhydride (cf. Pringsheim and Fellner, this vol., 742). H. Wren.

Cellulose. K. Hess and C. Trogus (Ber., 1928, **61**, [*B*], 1982—1996).—Attempts are made to establish relationships between the results of preparative chemical research and *X*-ray investigation in the sugar group. In the examination of the diagrams of cellulose it is not valid to assume that the compound is composed of cellobiose residues. The production of cellobiose from cellulose and dextrose from cellobiose is governed by a completely different chemical mechanism. The fact that dextrose, under the condition of acetolysis, does not pass into cellobiose is not evidence that the latter exists preformed in cellulose. Attempts to interpret the *X*-ray diagrams of cellulose on the basis of a cellobiose unit are of very doubtful value. Observations on cellulose and its derivatives, molten and in solution, indicate that it does not contain glucosidic disaccharide linkings. The disentanglement of the structural factors of cellulose from its *X*-ray diagram is rendered difficult by lack of knowledge of the corresponding diagrams of carbohydrates of known structure. The following diagrams are reproduced in the original: hexa-acetylbiosans of Hess and Friese and of Bergmann and Knehe, acetates II and I, biosan of Hess and Friese, cellulose hydrate, hexamethylbiosan, trimethylcellulose, dextrose, mannose, cellobiose, lactose, βγζ-trimethylglucose, trimethylcellulose, "amorphous" cellulose, and amorphous cellulose after dissolution and re-precipitation from ammoniacal copper solution. The most striking feature of a comparison of the individual diagrams is the very close similarity between those of biosan, which is certainly a substance of low mol. wt. ($C_{12}H_{20}O_{10}$), and cellulose. It is therefore considered that the mass distribution of the atoms in the molecule of cellulose does not differ widely from that in biosan. The diagrams of dextrose, mannose, cellobiose, maltose, and lactose all show a maximal intensity the identity period of which differs within narrow limits in the individual cases. This intensity corresponds with net-plane distance of about 4·5 Å. The same intensity is observed in the case of cellulose hydrate and biosan which hence have a mass distribution in a hydropyran ring analogous to that in known sugars. The same general concordance is noted in the cases of βγζ-trimethylglucose, βγζ-triethylglucose, octamethylcellobiose, octaethylcellobiose, trimethylcellulose, trimethylbiosan, and penta-acetylglucose. The relatively indistinct interferences of cellulose and its derivatives may be attributed to an arrangement of masses of a glucosan-like complex held together by directed associative forces. The sharpening of the interference lines in the transition from cellulose to biosan depends on the transition from this "diffuse" force to exact oxygen bridges whereby the mass distribution remains approximately the same. The effect of substitution on mass distribution is exhaustively discussed. The noteworthy result is obtained that tristearylcellulose gives an *X*-ray diagram with only one marked ring corresponding with a hydropyran ring instead of the probable thread diagram.

Cellulose which has been cautiously nitrated (13·5% N) and then denitrated by ammonium sulphide gives only a moderately strong line and thus appears amorphous; when dissolved in ammoniacal copper solution and re-precipitated, it shows the *X*-ray diagram of cellulose hydrate.

It is concluded that a model with greater mass concentration explains more closely the present knowledge of cellulose than that deduced by Sponsler and Dore or by Meyer and Mark (cf. this vol., 621, 939). H. WREN.

New degradation of cellulose. I. H. PRINGSHEIM, E. KASTEN, and E. SCHAPIRO (Ber., 1928, **61**, [*B*], 2019—2025).—If a 4% solution of cellulose acetate ("agfa") in chloroform is heated with 0·1% of anhydrous benzenesulphonic acid, the acetyl groups are partly removed and the particles become smaller. The process continues so far that the acetate loses its power of dissolving in chloroform and becomes soluble in water for the most part. After 3 or 6 days, 25—28% or 9% of acetyl is retained. If hydrolysis is completed with aqueous barium hydroxide and barium is quantitatively removed by sulphuric acid from the dilute, aqueous solution, the clear filtrate deposits a gelatinous precipitate *A* when evaporated in a vacuum. In ammoniacal copper solution the material has $[\alpha]_{Hg}$ −1·7° to −1·95° under conditions for which cellulose has −2·6°; its *X*-ray diagram is not distinguishable from that of cellulose hydrate. Addition of alcohol to the filtrate from *A* gives a preparation *B*, corresponding analytically with $C_6H_{10}O_5,H_2O$ or $C_6H_{10}O_5$ after intensive desiccation. It does not reduce Fehling's solution. In water, sodium hydroxide, or 95% pyridine it has $[\alpha]_D$ +38°. It is converted quantitatively into dextrose by boiling, dilute hydrochloric acid or by aqueous malt extracts. It is strongly associated in aqueous solution. It is converted by acetylation into a *triacetate*, $C_6H_7O_5Ac_3$, which, in 0·5% solution in glacial acetic acid, gives the mol. wt. required for a hexose anhydride acetate. In 1% solution it is associated. It is hydrolysed to the preparation *B*, [α] +38°.

Degradation by benzenesulphonic acid is not a specifically catalytic action, but is due to the acidity of the reagent; a similar effect is not produced by ethyl benzenesulphonate. H. WREN.

Action of highly concentrated nitric acid on cellulose. K. R. ANDRESS (Z. physikal. Chem., 1928, **136**, 279—288).—By *X*-ray examination native cellulose may be referred to the monoclinic system with a unit having the constants $a = 8{\cdot}35$ Å., $b = 10{\cdot}28$ Å., $c = 7{\cdot}96$ Å., $\beta = 78°$. The additive compound prepared by Knecht by the action of nitric acid (*d* 1·415) is formed with a distortion of the cellulose lattice, the new unit having the dimensions $a = 12{\cdot}20$ Å., $b = 10{\cdot}28$ Å., $c = 9{\cdot}73$ Å., $\beta = 53° 7'$.
F. G. TRYHORN.

Cellulose formate. II. Formation of cellulose formate. Y. UEDA and K. KATO (J. Cellulose Inst. Tokyo, 1928, **4**, 203—205; cf. this vol., 399).—Cellulose formate is prepared from regenerated cellulose, 100% formic acid, and sulphuric acid. The formic acid content of the ester increases with the reaction period to a maximum and subsequently decreases. Similar variations occur with increasing proportions of sulphuric acid. In both cases the maximum figures are slightly below the theoretical for the triformate. A. G. POLLARD.

Sulphuric esters from cellulose. E. GEBAUER-FÜLNEGG, W. H. STEVENS, and O. DINGLER (Ber., 1928, **61**, [*B*], 2000—2003).—Carefully dried cotton wool or filter-paper is converted by chlorosulphonic acid in excess of pyridine at 100° into a homogeneous, gelatinous product which gives with water a transparent, colloidal solution. The cellulose derivatives are precipitated (i) by alcohol with or without addition of ether, (ii) by alcohol and sodium chloride, (iii) by sodium hydroxide with or without alcohol, and (iv) by hydrochloric acid in presence of alcohol. Products, i, ii, and iii are white, very hygroscopic solids which have no reducing power and give optically inactive, colloidal solutions in water. Product i is a *pyridine* salt, whereas ii and iii are composed of a *sodium* salt of a cellulose hydrogen sulphate. Solutions of the freshly-prepared products, i, ii, and iii, give a precipitate with barium salts which dissolves in hydrochloric acid but is again formed by addition of a further quantity of barium salt. When isolated, the *barium* salt is insoluble in water or other media, very little affected by boiling alkali hydroxide, and only very slowly decomposed by boiling hydrochloric acid. Aqueous solutions of i, ii, and iii give sparingly soluble *precipitates* with lead, iron, calcium, and benzidine salts. Analyses of the barium salt gives the ratio C : S : Ba=6 : 2·78 : 1·48, but, after further treatment, a substance with the composition of a trisulphate is obtained.

Attempts to decide whether the sulphate is actually a derivative of cellulose are hindered by the impossibility of removing the sulphuric acid residues by acids or alkalis without considerable decomposition of the cellulose components; this can, however, be effected by methyl-alcoholic hydrogen chloride. H. Wren.

Structural matter of the leaves of white cabbage. H. Pringsheim, K. Weinreb, and E. Kasten (Ber., 1928, **61**, [*B*], 2025—2028).—The material is converted by 6—8% sodium hydroxide into a white, swollen mass which is treated further with chlorine dioxide and sodium hydroxide. The removal of those components which yield a furfuraldehyde–phloroglucinol precipitate is not completely effected by 18% sodium hydroxide. The remaining substance definitely contains only a small proportion of cellulose and represents a polysaccharide or mixture of polysaccharides extraordinarily resistant to hydrolytic agents. It is only slightly soluble in Schweizer's reagent. It is converted by treating the wet (but not dried) material with glacial acetic acid and acetic anhydride in the presence of a little sulphuric acid into a *triacetate*, $C_6H_7O_5Ac_3$, $[\alpha]_D^{20} > +1°$ in chloroform, from which the polysaccharide is regenerated. The substance now appears almost free from pentosans, since the differences given in the determination of furfuraldehydes by the phloroglucinol and barbituric acid methods indicate the production of hydroxymethylfurfuraldehyde, probably derived from decomposition products of the polysaccharide. The acetate is heated with a solution of benzenesulphonic acid and subsequently with 2% hydrochloric acid, thus giving a material which, in reducing power and optical activity, is not identical with any of the common hexoses; the temperature of decomposition of its osazone is identical with that of galactosazone.

H. Wren.

Lignin and cellulose. VII. Lignin. K. Freudenberg, M. Harder, and L. Markert (Ber., 1928, **61**, [*B*], 1760—1765).—The variation in the amounts of protocatechuic acid (20—30%) recorded as derivable by the action of molten potassium hydroxide on lignin is due to the difficulty of purifying the acid, particularly when oxalic acid is also present, and to the untrustworthiness of the colorimetric process. Experiments in which protocatechuic acid is determined colorimetrically in ferric chloride solution and gravimetrically after transformation into veratric acid indicate about 5% of this substance; if unavoidable losses are taken into consideration, it appears that about 9—10% of protocatechuic acid and traces of pyrocatechol are obtained from lignin. Since eugenol gives similar results, it remains possible that the actual content of pyrocatechol derivatives in lignin greatly exceeds 8%.

Use of "dimedon" in the determination of formaldehyde obtained by distillation of wood with 12% hydrochloric acid indicates not more than 1%, although the actual amount is estimated to be 2%. Comparison of the behaviour of triformalmannitol, piperonylic acid, narceine, and narcotine with that of lignin towards acidic hydrolysis indicates that the formaldehyde group in lignin is present as a methylenedioxy-group attached to the pyrocatechol nucleus. Appreciable quantities of formaldehyde are not present in wood except in the lignin component.

The lignin and cellulose in wood are readily separable from one another by repeated alternate treatment with hot 1% sulphuric acid and ammoniacal copper solution; even 0·1% sulphuric acid can be successfully used. Apparently the union between lignin and cellulose is resolved by removal of wood gum, pentosans, and hemicelluloses. This hypothesis is supported by the observation that wood thus treated and then methylated yields considerable amounts of methylcellulose to chloroform or acetic acid. The lignin preparations contain about 16% OMe.

H. Wren.

Beech wood. Acetylation of beech wood and hydrolysis of the acetylated product. H. Suida and H. Titsch (Ber., 1928, **61**, [*B*], 1599—1604; cf. Fuchs, this vol., 743, and following abstract).—Attempts are described to protect the active groups of wood in such a manner as not to disturb the union of the wood components and subsequently to hydrolyse the products without removal of the groups thus introduced. Powdered beech wood is extracted with alcohol and benzene (1 : 1) and degummed by 5% sodium hydroxide. Acetylation with boiling acetic anhydride followed by treatment with acetic anhydride and pyridine affords a product containing 37% OAc which does not react with aniline sulphate or phloroglucinol and hydrochloric acid. Hydrolysis is effected with boiling glacial acetic acid containing 0·25% of hydrogen chloride, whereby deacetylation is not completely avoided. The residue, which still contains a small proportion of lignin, consists mainly of partly acetylated cellulose containing 25·8% OAc. The lignin fraction, isolated by dilution of the filtrate from the acetylcellulose with water, contains 28·9% OAc and 14·1% OMe; the latter datum shows that it corresponds closely with primary lignin. H. Wren.

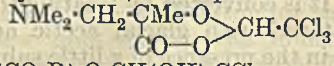
Methylation of beech wood and hydrolysis of the methylated product. A. von Wacek (Ber., 1928, **61**, [*B*], 1604—1609; cf. preceding abstract).—Repeated treatment of powdered beech wood, free from resin and gum, with methyl sulphate yields a product containing 39—39·4% OMe which is unchanged by the customary solvents for methylcellulose and lignin. The product is hydrolysed with cold 17% hydrochloric acid and subsequently treated with boiling alcohol or, preferably, acetone. The lignin fraction precipitated from the acetone solution contains 26·5% OMe. The residue is repeatedly extracted with cold water and the extracts are heated, whereby a mixture of di- and tri-methylcellulose (mainly the latter) is precipitated. Treatment of the portion insoluble in cold water with chloroform allows a further separation of it into methylcelluloses and, probably, non-hydrolysed initial material. Even if it is assumed that cellulose is not uniformly united in wood, it follows that the linking of a part of it does not involve one or more of its three hydroxyl groups. H. WREN.

Formation of bases from carbonyl compounds. II. A. SKITA and F. KEIL [with E. BAESLER and L. BOENTE] (Ber., 1928, **61**, [*B*], 1682—1692; cf. this vol., 1120).—Ketones react generally with aliphatic amines and ammonia, even in aqueous suspension, giving intermediate *N*-substituted imines which are reduced to secondary amines in the presence of platinum. On the other hand, if nickel is used as catalyst, ketones and ammonia give substantially primary amines, which are also obtained from aldehydes. If, however, the conditions used for nickel are followed (temperature 90°) but the amount of platinum is greatly diminished, the production of primary amines becomes marked, but always subordinate to that of secondary amines. At the atmospheric temperature, secondary amines are produced exclusively. In confirmation, mixtures of acetone, methyl ethyl ketone, diethyl ketone, or *cyclo*hexanone with *cyclo*hexylamine do not form secondary amines in the presence of nickel, whereas they readily do so under the influence of platinum at 90° or at atmospheric temperature. Similarly, benzaldehyde and acetophenone in aqueous suspension are transformed into secondary bases in presence of platinum. Palladium appears to have an action intermediate between those of platinum and nickel. The production of tertiary bases from certain aldehydes occurs in accordance with the scheme: $\longrightarrow$ $R{\cdot}CH_2{\cdot}NH{\cdot}CH_2R \xrightleftharpoons[+H_2O]{+R{\cdot}CHO} [(R{\cdot}CH_2)_2NR{:}CH{\cdot}OH] \xrightarrow{+H_2} (R{\cdot}CH_2)_3N$. Reduction of diketones in the presence of primary amines affords amino-alcohols in very satisfactory yield; these compounds are also derived from hydroxyaldehydes and hydroxyketones in presence of bases. The method can be applied in the sugar group.

The following data appear new. N-*Phenyl*cyclo*hexylamine*, b. p. 146—148°/16 mm. (non-hygroscopic *hydrochloride*, m. p. 204—205°), apparently differing from the compound thus designated by Sabatier and Senderens (A., 1904, i, 305); N-iso*propyl*cyclo*hexylamine*, from acetone and *cyclo*hexylamine, b. p. 169—171° (*hydrochloride*, m. p. 204—205°; *picrate*, m. p. 142°); N-sec.-*butyl*cyclo*hexylamine*, from methyl ethyl ketone and *cyclo*hexylamine, b. p. 193° (*hydrochloride*, m. p. 211°; *picrate*, m. p. 118°); N-α-*ethyl*-n-*propyl*cyclo*hexylamine*, from diethyl ketone, b. p. 208—209° (*hydrochloride*, m. p. 178°; *picrate*, m. p. 124°); *di-α-ethyl*-n-*propylamine*, b. p. 172—174° (*hydrochloride*, m. p. 115—117°); benzyldiethylamine from benzaldehyde, acetaldehyde, and ethylamine, or benzylethylamine and acetaldehyde; β-cyclo*hexylaminopentan-γ-ol*, from acetylacetone and *cyclo*hexylamine, b. p. 123—125°/13 mm. (*hydrochloride*, m. p. 157—158°; *diacetyl* derivative, b. p. 183°/13 mm.); β-cyclo*hexylaminopropan-α-ol*, b. p. 116—117°/13 mm. (*hydrochloride*, m. p. 148—149°); N-cyclo*hexylarabinamine*, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}NH{\cdot}C_6H_{11}$, from arabinose and *cyclo*hexylamine, m. p. 135—137° (*hydrochloride*, m. p. 167°; N-cyclo*hexylmannamine hydrochloride*, m. p. 165—167°. H. WREN.

Action of anhydrous chloral on amino-alcohols and on hydroxy-amino-ethers containing a tertiary amino-group. E. FOURNEAU and (MLLE.) W. BRYDOWNA (Bull. Soc. chim., 1928, [iv], **43**, 1023—1027). — Methyldimethylaminomethylethylcarbinol reacts with anhydrous chloral with evolution of heat, giving a *semi-acetal*, which at 56—58°/10 mm., dissociates into chloral and the base, with formation of the acetal on cooling. With hydrogen chloride in ether it affords a *hydrochloride*, m. p. 128—130° (decomp.), decomposed by sodium hydroxide, giving chloroform. Benzoyl chloride in benzene gives a *benzoate hydrochloride*, m. p. 196—198° (decomp.), possessing powerful anæsthetic properties which are of no value on account of its strong acidic nature, and a little stovaine. Acetyl chloride in acetone gives the *hydrochloride* of the *acetate*, m. p. 193°, from which the *acetyl* derivative, b. p. 158—160°, is obtained on treatment with sodium carbonate, the dissociation of the acetal being thus prevented by acetylation of the hydroxy-group.

Since both ethyl and propyl γ-dimethylamino-β-hydroxy-β-methylpropionate with anhydrous chloral afford the same product, b. p. 140—142°/22 mm., m. p. 66—67° (hydrochloride, m. p. 180—186°), yielding on hydration in moist air γ-dimethylamino-β-hydroxy*iso*butyric acid, this product must have the structure



$$NMe_2{\cdot}CH_2{\cdot}\underset{\displaystyle CO{-}O}{\overset{|}{C}Me{\cdot}O}{>}CH{\cdot}CCl_3$$

and not $NMe{\cdot}CH_2{\cdot}CMe(CO_2R){\cdot}O{\cdot}CH(OH){\cdot}CCl_3$ as originally suggested in the patent. It may thus be considered an ether or semi-acetal of chloral hydrate or a chloralide. R. BRIGHTMAN.

Structure of chitin. K. H. MEYER and H. MARK (Ber., 1928, **61**, [*B*], 1936—1939).—A review of the literature on chitin combined with examination of Gonell's *X*-ray diagrams of the compound leads the author to assume that the 1 : 5-rings are joined by 1 : 4-oxygen bridges and oriented at an angle of 180° round a screw axis; the main valency chains thus produced are linked with one another to micellæ. Eight acetylglucosamine anhydride residues appear present in the unit. Nothing quantitative is known with respect to the size of the micellæ in chitin, but the general similarity of the chitin and cellulose diagrams indicate that it is of the same order as in cellulose or silk. H. WREN.

Action of acetic anhydride and pyridine on amino-acids. P. A. LEVENE and R. E. STEIGER

(J. Biol. Chem., 1928, 79, 95—103).—Further study of the reaction previously observed (this vol., 61) leads to conclusions similar to those reached by Dakin and West (this vol., 874). C. R. Harington.

Structure of silk fibroin. K. H. Meyer and H. Mark (Ber., 1928, 61, [*B*], 1932—1936; cf. Brill, A., 1924, i, 102).—The conception that the structural unit of fibroin is composed of one or two alanylglycyl residues as peptide or peptide anhydride is not compatible with the known properties of the known, open tetrapeptides. The assumption of four main-valency chains which connect the elementary bodies is in harmony with all experimental data. The identity period is identical with the length of a glycylalanyl residue. The length of the micelles and hence the mean length of the main-valency chain corresponds with a polypeptide containing at least twenty glycylalanyl residues. The distances of the main-valency chains from one another amount to 4·6 Å. in one direction and 5·2 Å. in the other, these values being observed frequently with molecules attached to one another by subsidiary valencies. The close attachment of the chains is attributed to the high associating power of the –CO·NH– group.

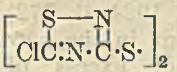
The diagrams of different silks indicate that the proportion of crystalline material is less than in the case of cellulose and is estimated to be about 40—60%. H. Wren.

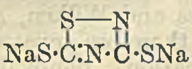
Determination of carbamide. J. M. Luck (J. Biol. Chem., 1928, 79, 211—219).—Carbamide is precipitated with xanthydrol; the precipitate is dissolved in dilute sulphuric acid, and the resulting yellow solution is warmed to 70—75° and titrated with potassium permanganate until colourless; 0·1 mg. of carbamide may be determined with an error of ±5%. C. R. Harington.

Nitroaminoguanidine. R. Phillips and J. F. Williams (J. Amer. Chem. Soc., 1928, 50, 2465—2470).—Hydrazine and nitroguanidine in dilute aqueous solution at 50—60° probably yield first an additive compound which then decomposes into nitrous oxide, aminocyanamide which is hydrolysed, and *nitroaminoguanidine*, $NO_2·NH·C(:NH)·NH·NH_2$, m. p. 190° with explosion. The nitrogen in this compound can be determined only by a special procedure. It reduces copper and silver solutions with formation of explosive metallic derivatives and quantitatively precipitates nickel as the *salt*, $NiO[NO_2·NH·C(:NH)·NH·NH_2]_2$, the blue solution of which in alkali hydroxide affords a delicate test for nickel. Nitroaminoguanidine gives characteristic colour tests and forms with aldehydes and ketones crystalline hydrazones which may be detonated. It is reduced by zinc dust and acetic acid to diaminoguanidine. H. E. F. Notton.

Ureides of bromovaleric acids. III. Influence of the position of the halogen atom in the acid on physiological properties. E. Fourneau and G. Florence (Bull. Soc. chim., 1928, [iv], 43, 1027—1040).—Examination of the ureides of the bromo-*n*-valeric acids and of bromo-α-methylbutyric acids has confirmed the conclusions reached from earlier work (this vol., 401) that the α-bromine atom is not a condition of hypnotic action, ureides containing β- and γ-bromine atoms being also active. Branching of the chain produces a marked increase in the solubility in water and in the partition coefficient, and in this series of compounds the partition coefficient and the hypnotic action are closely parallel. The following data are recorded (percentage figures indicate solubility in water, and ordinary figures partition coefficients): α-bromo-*n*-valerureide, 0·83%, 0·44; β-*bromo*-n-*valerureide*, m. p. 184°, 0·78%, 0·35; γ-*bromo*-n-*valerureide*, m. p. 160—161°, 0·97%, 0·29; α-bromo-α-methylbutyrureide, 5·3%, 1·99; β-*bromo*-α-*methylbutyrureide*, m. p. 125—126°, 3·2%, 1·7; α-*bromomethyl*-n-*butyrureide*, m. p. 108°, 4·01%, 0·84; γ-*bromo*-α-*methylbutyrureide* (yield, 30%), m. p. 147·5°, 1·05%, 0·90. Attempts to obtain the ureide of δ-bromo-*n*-valeric acid, m. p. 39—40°, from the chloride in the usual way were unsuccessful. γ-Bromo-α-methylbutyryl chloride, b. p. 128°/18 mm., is obtained in good yield by the action of phosphorus trichloride or pentachloride on the methylbutyrolactone. R. Brightman.

Tetrathiocyanogen dichloride and thiodiazoles obtainable therefrom. E. Söderbäck (Annalen, 1928, 465, 184—210; cf. A., 1920, i, 219).—The "thiocyanogen monohydrochloride," m. p. 60—70°, previously described is shown by analysis and mol. wt. determinations to be tetrathiocyanogen dichloride, its preparation from thiocyanogen and hydrogen chloride in absolute ether being represented by the equation $3(SCN)_2+2HCl=(SCN)_4Cl_2+2HSCN$. It forms with metallic mercury a *compound*, $C_4N_4Cl_2S_4Hg$, m. p. 168—169°, from which the dichloride is regenerated by the action of bromine or iodine. This behaviour distinguishes it from aliphatic and aromatic disulphides, but is analogous to the reaction of diantipyryl disulphide and the disulphides from 5-thiol-3-phenyl-1 : 2 : 4-thiodiazole and 5-thiol-2-thioketo-3-phenyl-1 : 3 : 4-thiodiazoline with metallic mercury, and suggests a heterocyclic disulphide structure. By the action of hydrogen bromide in benzene the dichloride is converted, with liberation of bromine, into thiocyanogen dihydrobromide, which is entirely analogous to the dihydrochloride (*loc. cit.*) and is therefore 3 : 3-dibromo-5-imino-1 : 2 : 4-dithioazolidine. The dichloride hence contains S–C–N groupings and must be 5-chloro-1 : 2 : 4-thiodiazolyl 3 : 3′-disulphide (I). Reduction with sodium amalgam gives the sodium salt of the 3-thiol, "*sodium chlorodithiocyanate*," much more readily obtained by the action of sodium sulphide on the mercury compound; a white *polythiocyanogen*, decomp. above 300°, is obtained as a by-product in the preparation of sodium chlorodithiocyanate, or by decomposition of the latter at 15° in acetone solution. The *lead*, *cuprous*, and *silver* salts are described, but the free thiol is obtained only in solution. Sodium chlorodithiocyanate is converted by hot sodium sulphide solution into sodium perthiocyanate (II), which is obtained crystalline from hot acetone. Sodium hydroxide similarly yields "*sodium hydroxydithio-*


(I.)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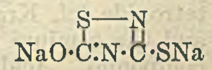
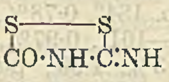
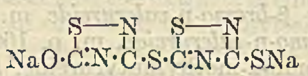

(III.)

cyanate" (III), m. p. 108° (+$4H_2O$; *lead* salt described), which is easily hydrolysed in aqueous solution to thiocarbamide, sulphur, and sodium carbonate. Acidification of the ice-cooled aqueous solution of sodium hydroxydithiocyanate gives "thiocyanogen hydrate" (3-imino-1 : 2 : 4-dithioazolidone; IV) by isomerisation of the hydroxydithiocyanic acid transiently formed. By the action of iodine on

(IV.)



$$\begin{array}{l} S\text{———}S \\ |\qquad\quad\ | \\ CO{\cdot}NH{\cdot}C{:}NH \end{array}$$



$$\begin{array}{l} \qquad\ \ S\text{—}N\quad S\text{—}N \\ \qquad\ \ |\quad\ \ \|\quad\ |\quad\ \ \| \\ NaO{\cdot}C{:}N{\cdot}C{\cdot}S{\cdot}C{:}N{\cdot}C{\cdot}SNa \end{array}$$

(V.)

sodium hydroxydithiocyanate the corresponding *disulphide*, "sodium dihydroxydithiocyanate," $C_4O_2N_4S_4Na_2,5H_2O$, is obtained, which on acidification gives the free acid, 5 : 5′-*dihydroxy*-3 : 3′-*di*-1 : 2 : 4-*thiodiazolyl disulphide*, decomp. 160°. The acid and its sodium salt react with metallic mercury to give 5-hydroxy-3-mercurithiol-1 : 2 : 4-thiodiazole and its sodium salt, respectively.

In the preparation of sodium hydroxydithiocyanate there is also produced "*sodium hydroxytetrathiocyanate*" [disodium salt of 5-hydroxy-3′-thioldi-1 : 2 : 4-thiodiazolyl sulphide (V)], the aqueous solution of which gels even at 0·02 molar concentration. The "*acid*" is precipitated on acidification. The sodium salt reacts with iodine to give a *disulphide* containing four thiodiazole residues. C. HOLLINS.

Determination of cyanides and basic cyanides of mercury. A. IONESCO-MATIU and (MLLE.) A. CARALE (J. Pharm. Chim., 1928, [viii], **8**, 258—263).—Mercuric cyanide and basic mercuric cyanide, $Hg(CN)_2,HgO$, can be accurately determined by transforming the mercury into the sulphate, adding sodium nitroprusside, and titrating the mixture with sodium chloride solution until the turbidity just disappears (cf. Votoček, A., 1923, ii, 184).

E. H. SHARPLES.

Cyanogen compounds of the platinum metals. IV. Cyano-oxo-salts of osmium. F. KRAUSS and G. SCHRADER (J. pr. Chem., 1928, [ii], **120**, 36—40).—Addition of excess of potassium cyanide to an aqueous solution of osmium tetroxide furnished an orange-red solution containing the complex salt $K_2[OsO_2(CN)_4]$, which could not be isolated in a pure state. The amount of iodine liberated on treatment of the solution with concentrated hydrochloric acid and potassium iodide was half that liberated by osmium tetroxide (cf. Krauss and Wilken, A., 1924, ii, 772) and the osmium is therefore sexavalent in the new compound. Acidification, removal of excess of hydrogen cyanide, and addition of copper sulphate or silver nitrate yielded, respectively, precipitates of the *compounds* $Cu[OsO_2(CN)_4]$, grey, and $Ag_2[OsO_2(CN)_4]$, yellow. Digestion of these with ammonia yielded the *compounds* $[Cu(NH_3)_4][OsO_2(CN)_4]$, black, and $[Ag_2(NH_3)_4][OsO_2(CN)_4]$, dark reddish-brown, respectively, which lost ammonia slowly in air.

R. K. CALLOW.

Organic compounds of arsenic. XIV. Tenacity of hydrocarbon residue to arsenic. W. STEINKOPF, H. DUDEK, and S. SCHMIDT (Ber., 1928, **61**, [*B*], 1911—1918; cf. A., 1922, i, 994, and previous abstracts).—Methyldichloroarsine is converted by magnesium *iso*amyl chloride in ether into *methyldi*iso*amylarsine*, b. p. 95—99°/11 mm., transformed by chlorine in light petroleum into the corresponding *dichloride*, which decomposes at 186—210° into methyl*iso*amylchloroarsine, b. p. 68—72°/11 mm., *di*iso*amylchloroarsine*, b. p. 114—122°/11 mm., methyl chloride, and *iso*amyl chloride; the methyl and *iso*amyl groups are therefore attached to arsenic with almost equal firmness. Arsenic trichloride and magnesium *cyclo*hexyl chloride in ether afford *tri*cyclo*hexylarsine*, b. p. 208—215°/11 mm., solidif. pt. 41—40°. The corresponding *dichloride* decomposes at 200°/vacuum into *di*cyclo*hexylchloroarsine*, b. p. 168—171°/10 mm., from which the *oxide*, $[As(C_6H_{11})_2]_2O$, is obtained by means of aqueous sodium carbonate. The monochloride is converted successively into the corresponding *trichloride*, decomp. 80—90°, and cyclo*hexyldichloroarsine*, b. p. 122—125°/15 mm. Di*cyclo*hexylphenylarsine (cf. Roberts, Turner, and Bury, A., 1926, 852), obtained in 93% yield from phenyldichloroarsine and magnesium *cyclo*hexyl chloride, is transformed into the *trichloride*, m. p. 167° (decomp.), and cyclo*hexylphenylchloroarsine*, b. p. 183—184°/15 mm., from which the *oxide*, $C_6H_{11}{\cdot}AsPh{:}O$, is derived. Phenyl*cyclo*hexylmethylarsine and cyanogen bromide in ether give a solid *bromocyanide* which decomposes when heated into cyclo*hexylphenylcyanoarsine*, b. p. 156·5°/about 2 mm., also derived from *cyclo*hexylphenylchloroarsine and potassium cyanide. The bromocyanide is converted by moisture into the *hydroxybromide*, $C_6H_{11}{\cdot}AsMePh(OH){\cdot}Br$, characterised as the *picrate*, $C_6H_{11}{\cdot}AsMePh(OH){\cdot}O{\cdot}C_6H_2(NO_2)_3$, m. p. 132·5—133°. n-*Propyldi-iodoarsine*, b. p. 136—137°/11 mm., is prepared in 55% yield by the action of sulphur dioxide on an aqueous solution of magnesium propylarsinate, potassium iodide, and concentrated hydrochloric acid. n-*Propylarsine oxide*, b. p. 142—145°/1 mm., is described. The di-iodide and propyl bromide afford *di*-n-*propyliodoarsine*, b. p. 103·5—106°/12·5 mm., converted by magnesium *cyclo*hexyl chloride into cyclo*hexyldi*-n-*propylarsine*, b. p. 126·5—129·5°/12 mm. The latter compound yields a solid *bromocyanide* which is decomposed by heat into propyl bromide and cyclo*hexyl*-n-*propylcyanoarsine*, b. p. 108·5—110°/1 mm. The action of moisture on the bromocyanide affords the corresponding *hydroxybromide*, $C_{12}H_{26}OBrAs$, m. p. 64—67°, converted into the *picrate*, $C_{18}H_{28}O_8N_3S$, m. p. 110—111°. *cyclo*Hexyldipropylarsine is converted by chlorine in light petroleum into the corresponding *dichloride*, m. p. about 40°, which decomposes at 200° into *n*-propyl chloride and cyclo*hexyl*-n-*propylchloroarsine*, b. p. 131—132°/16 mm. The *cyclo*hexyl group is therefore more firmly united to arsenic than the methyl or *n*-propyl groups and less firmly than the phenyl radical. H. WREN.

β-Chlorosubstituted compounds of arsenic. V. V. NEKRASSOV and A. S. NEKRASSOV (Ber., 1928, **61**, [*B*], 1816—1821).—β-Chloroethyldichloroarsine, b. p. 89—90°/12 mm., d^{15} 1·573, is prepared in very modest yield by passing a current of dry ethylene through a mixture of arsenic trichloride and aluminium chloride at 0°. Preferably, ethylene chlorohydrin is converted by sodium arsenite into β-hydroxyethylarsinic acid, $OH\cdot CH_2\cdot CH_2\cdot AsO_3H_2$, which is reduced by sulphur dioxide to the corresponding *oxide*, $OH\cdot CH_2\cdot CH_2\cdot AsO$, a colourless, viscous liquid which could not be distilled without decomposition; it does not evolve ethylene when treated with cold alkali hydroxide and is re-converted by hydrogen peroxide into the syrupy arsinic acid. Hydrogen chloride converts the oxide into the corresponding dichloride without affecting the hydroxyl group, whereas phosphorus trichloride in chloroform converts it into β-chloroethyldichloroarsine in moderately good yield. Aqueous alkali hydroxides immediately decompose β-chloroethyldichloroarsine into ethylene chloride and arsenite. Since this behaviour is shared by β-chlorovinylarsines, the explanation of the reaction put forward by Lewis and Stiegler (A., 1925, i, 1470) can scarcely be maintained, since it fails to cover both cases. Oxidising agents convert β-chloroethyldichloroarsine into β-*chloroethylarsinic acid*, m. p. 133°, which is monobasic towards methyl-orange but dibasic in presence of phenolphthalein.

H. Wren.

β-Substituted alkylarsinic acids and their derivatives. S. M. Scherlin and G. Epstein (Ber., 1928, 61, [*B*], 1821—1825).—Ethylene chlorohydrin is converted by sodium arsenite into β-hydroxyethylarsinic acid, which is reduced to the corresponding oxide and thence converted by hydrogen chloride into β-hydroxyethyldichloroarsine; isolation of the products in the homogeneous state could not be effected. Treatment of the dichloro-compound with 95—96% acetic acid and hydrogen chloride affords β-*acetoxyethyldichloroarsine*, $OAc\cdot CH_2\cdot CH_2\cdot AsCl_2$, b. p. 120—121°/9—10 mm., d_{20}^{20} 1·6766, which evolves ethylene when boiled with water or alkali hydroxide. β-Hydroxyethyldichloroarsine is transformed by phosphorus pentachloride or, preferably, by a small excess of phosphoryl chloride into β-*chloroethyldichloroarsine*, b. p. 90·8°/12·5 mm., d_{20}^{20} 1·8401, oxidised by hydrogen peroxide to β-*chloroethylarsinic acid*, m. p. 134°. Carbonyl chloride transforms β-hydroxyethyldichloroarsine into a *compound* with a pronounced odour of ethyl chloroformate, which loses carbon dioxide and gives β-chloroethyldichloroarsine when distilled under diminished pressure.

H. Wren.

Trypanocidal action and chemical constitution. VIII. Derivatives of β-aminoethyl- and γ-aminopropyl-arsinic acids. G. A. C. Gough and H. King (J.C.S., 1928, 2426—2447).—A series of amphoteric acids, $R_1R_2N\cdot[CH_2]_n\cdot AsO_3H_2$, where R_1 and R_2 are hydrogen, aliphatic, or alicyclic radicals, have been synthesised by the action of the appropriate amines on the chloro-acids, $Cl\cdot[CH_2]_n\cdot AsO_3H_2$. The reaction proceeds normally when $n=3$, but when $n=2$, unless alkalinity be avoided when exhaustive substitution of the amine takes place, the arsinic acid decomposes with the formation of ethylene and the corresponding arsenate and hydrochloride of the base. Of all the compounds described only triethylamine-ββ′β″-triarsinic acid and γ-piperidinopropylarsinic acid were found to have any curative action when tested on experimental trypanosomiasis in mice.

β-Hydroxyethylarsinic acid (*calcium* salt) on dissolution in hydrochloric acid and treatment with sulphur dioxide in the presence of hydrogen iodide followed by thionyl chloride in petroleum was converted into β-chloroethyldichloroarsine, b. p. 92—93°/32 mm., which on oxidation with chlorine water gave β-*chloroethylarsinic acid*, m. p. 134—135°. Similarly γ-*hydroxypropylarsinic acid* (*calcium* salt) (from trimethylene chlorohydrin and sodium arsenite) gave γ-*chloropropyldichloroarsine*, b. p. 120—122°/16 mm., and γ-*chloropropylarsinic acid*, m. p. 146—148° (*barium* and *calcium* salts). From the reaction between γ-hydroxypropylarsinic acid and sulphur dioxide in hydrochloric acid solution, the *di-ester* of γ-*hydroxypropyldichloroarsine* and γ-*hydroxypropylarsinous acid*, b. p. 35°/0·16 mm., was isolated. β-Chloroethylarsinic acid gave with carbamide in aqueous solution *triethylamine*-ββ′β″-*triarsinic acid*, m. p. 184—185° (*calcium*, *barium*, and *magnesium* salts); with methylamine, *methyldiethylamine*-ββ′-*diarsinic acid*, m. p. 192—194°; with dimethylamine, *dimethyldiethylammonium chloride*-ββ′-*diarsinic acid*, m. p. 178°, and β-*dimethylaminoethylarsinic acid hydrochloride*, m. p. 138—145°; with trimethylamine, β-*dimethylaminoethylarsinic acid methochloride*, m. p. 187—188° (decomp.); with piperidine, β-*piperidinoethylarsinic acid hydrochloride*, m. p. 155—157° (β-*piperidinoethyl-dichloroarsine hydrochloride*, m. p. 126—127°; -*di-iodoarsine hydriodide*, m. p. 158—159°); with piperazine hydrate, NN′-*piperazinodi*-ββ′-*ethylarsinic acid dihydrochloride*. *Methyl*-β-*chloroethyldiethylammonium iodide*, m. p. 219—220°, was obtained from β-chloroethyldiethylamine (*chloroaurate*, m. p. 68—71°) and methyl iodide and was converted into the *chloride* (*chloroaurate*, m. p. 202—204°) with silver chloride. A small yield of methylarsinic acid was obtained from the reaction between methyl *p*-toluenesulphonate and sodium arsenite. From the interaction between *p*-toluenesulphonyl chloride and β-diethylaminoethanol *tetraethylpiperazinium di*-p-*toluenesulphonate*, m. p. 300—301° (decomp.) (*di-iodide*; *dichloroaurate*), was isolated, whilst with trimethylene glycol the chief products were *trimethyleneglycol di*-p-*toluenesulphonate*, m. p. 93—94°, and *propane*-αγ-*dipyridinium di*-p-*toluenesulphonate*, m. p. 118—120° (*dichloride*; *dichloroaurate*; *dipicrate*, m. p. 176°; *tetramercurichloride*). γ-Chloropropylarsinic acid gave with ammonia, γ-*aminopropylarsinic acid*, m. p. 212—214° (decomp.); with dimethylamine, γ-*dimethylaminopropylarsinic acid hydrochloride*, m. p. 108—110°; with trimethylamine, γ-*dimethylaminopropylarsinic acid methochloride*, m. p. 174—176°; with *n*-propylamine, γ-n-*propylaminopropylarsinic acid*, m. p. 222—224° (*hydrochloride*, m. p. 210—212°; m-*nitrobenzoyl* derivative, m. p. 132—134°; γ-n-*propylaminopropyldichloroarsine hydrochloride*, m. p. 195—196°); with *n*-hexylamine, γ-n-*hexylaminopropylarsinic acid hydrochloride*, m. p. 221—223° (m-*nitrobenzoyl* derivative, m. p. 118—120°; with ethyl chloroformate, γ-*carbethoxy*-n-*hexylaminopropylarsinic acid*, m. p. 58—60°; *phenylcarbamyl* derivative, m. p. 118—124°; γ-n-*hexylaminopropyldichloroarsine hydrochloride*, m. p. 190—192°); with *l*-α-phenylethylamine, l-α-*phenylethylaminopropyldichloroarsine hydrochloride*, m. p. 194—196°;

with piperidine, γ-*piperidinopropylarsinic acid hydrochloride*, m. p. 162—164° (γ-*piperidinopropyldichloroarsine hydrochloride*, m. p. 194—196°; γ-4-*hydroxy-2 : 2 : 6-trimethylpiperidinopropylarsinic acid*, m. p. 162°, with vinyl diacetonealkamine); with 2 : 2 : 6-*trimethylpiperidine* (prepared by reduction of 4-bromo-2 : 2 : 6-trimethylpiperidine hydrochloride with zinc and acetic acid), b. p. 138—139° (*hydrochloride*, m. p. 236—237°; *chloroaurate*, m. p. 127—129°; *picrate*, m. p. 195—196°), γ-2 : 2 : 6-*trimethylpiperidinopropylarsinic acid*, m. p. 150—160°; with piperazine hydrate, γ-*piperazinopropylarsinic acid dihydrochloride* (*benzoyl* derivative, m. p. 204—206°); with ethyl nipecotinate, γ-3-*carbethoxypiperidinopropylarsinic acid*. A. I. VOGEL.

Auto-oxidation of Grignard's magnesium compounds. J. MEISENHEIMER and W. SCHLICHENMAIER (Ber., 1928, **61** [*B*], 2029—2043).—The determination of the content of solutions of magnesium aryl or alkyl halides by addition of water followed by titration of magnesium oxide and magnesium halide with nitric acid and silver nitrate (cf. this vol., 624) gives inaccurate results when solutions of the iodides are greatly diluted with ether before decomposition. The incidence of "etherolysis," $MeMgI+Et_2O=MeMg{\cdot}OEt+EtI$, is excluded by the absence of formation of considerable amounts of alkyl iodide and the phenomenon is traced to auto-oxidation. Experiments with magnesium methyl iodide show that dilution in absence of oxygen has no effect on the analytical results. Even in the diluted solutions, methyl iodide is exclusively produced (recognised as tetramethylammonium iodide); the absence of ethyl iodide proves that the ether is not oxidised. With increasing dilution the ratio OH′ : I′ at first increases rapidly, but ultimately attains a limiting value which does not exceed 2 : 1. The net reaction may therefore be expressed: $3MeMgI+3O=MeI+MgO+2MeO{\cdot}MgI$. Solutions of magnesium methyl iodide in amyl ether behave similarly to those in ethyl ether, the greatest observed displacement being OH′ : I′=1·92 : 1 with 10 vols. of the ether. Magnesium ethyl iodide behaves similarly.

Auto-oxidation of solutions of magnesium phenyl iodide affords iodobenzene, phenol, phenylmethylcarbinol, and benzene. The effect of dilution is less marked than with alkyl iodides, the highest observed value for the ratio OH′ : I′ being 1·67 : 1, which corresponds with the reaction $4PhMgI+3O+Et{\cdot}O{\cdot}Et=PhI+MgO+CHPhMe{\cdot}O{\cdot}MgI+C_6H_6+EtO{\cdot}MgI+PhO{\cdot}MgI$. Direct measurement of the absorption of oxygen by solutions of magnesium alkyl halides indicates that the ratio Grignard compound : oxygen=1 : 0·95. With magnesium phenyl iodide the corresponding observed ratio is 1 : 0·66, but, in view of the results with the alkyl compounds, the true ratio is regarded as 1 : 0·75. Magnesium alkyl and aryl bromides are less sensitive to atmospheric oxidation, but the ratio OH′ : I′ increases with dilution. Measurement of the oxygen consumed by magnesium phenyl bromide gives the ratio mols. of Grignard compound : atoms of oxygen=1 : 0·69. The production of diaryls during the auto-oxidation of aromatic Grignard compounds is considered doubtful.

The primary reaction between magnesium methyl iodide and oxygen is considered to be the formation of a complex $[MeMgI \cdots 3O \cdots MeMgI{\cdot}Et_2O]$ which subsequently decomposes according to (*a*) a unimolecular reaction in which the two iodine atoms are replaced by oxygen, giving iodine, which reacts immediately with unchanged magnesium methyl iodide, and the complex $[MeMg \cdots 3O \cdots MgMe,Et_2O]$, giving MgO and $Mg(OMe)_2$, and (*b*) a bimolecular change in which the complex oxidises 1 mol. of MeMgI to $MeO{\cdot}MgI$; in the residue $[MeMgI \cdots 2O \cdots MeMgI,Et_2O]$, the oxidation potential is so diminished that expulsion of the iodine atoms does not occur and the methyl groups become oxidised to methoxy-residues. In concentrated solutions (*a*) and (*b*) are concurrent, whereas at greater dilutions (*b*) disappears. Under all conditions (*b*) preponderates with bromides on account of the greater affinity of bromine for magnesium. Similar views may be developed for the auto-oxidation of magnesium aryl halides, the essential difference lying in the oxidation of the ether, which is not explained.

The gradual decomposition of magnesium methyl iodide at 75° (*loc. cit.*) is not a thermal action but is due to insufficient exclusion of air. H. WREN.

Monomagnesium derivative of acetylene. V. GRIGNARD, L. LAPAYRE, and T. FAKI (Compt. rend., 1928, **187**, 517—520).—The magnesium acetylenyl bromide obtained by the action of acetylene on magnesium phenyl bromide (Oddo, A., 1904, i, 862; 1908, i, 748; Zalkind and Rosenfeld, A., 1924, i, 1291) affords with carbon dioxide 15% of propiolic acid and with *n*-butyl bromide at 80—90°, 29% of true hexinene and nearly as much dibutylacetylene. When the magnesium phenyl bromide is prepared with excess of magnesium and ether yields of 39% of true hexinene and 30% of *s*-decinene can be obtained. If the acetylene is passed in under pressure (0·5 atm.) the product on treatment with carbon dioxide affords 28% of propiolic acid and 13% of acetylenedicarboxylic acid. Gentle heating and special agitation (cf. A., 1913, ii, 1046) similarly give a product yielding 62% of propiolic acid and only 10% of the acetylenedicarboxylic acid. Further evidence that the product is an equilibrium mixture of the mono- and di-magnesium acetylenyl derivatives, in proportions depending on the temperature and pressure, is afforded by experiments with magnesium ethyl bromide. Excess of acetylene under normal pressure gives a solution containing 95% of the dimagnesium derivative. When the ether is partly replaced by benzene, and acetylene is passed in at 65° and 0·5 atm., after 4 hrs. the solution contains 80—81% of monomagnesium derivative, and with benzyl bromide affords 70% of γ-phenyl-Δ^{α}-propinene, b. p. 71—73°/17 mm., n_D^{23} 1·53481, d_4^{28} 0·931, 8% of dibenzylacetylene, m. p. 80°, and 12% of acetylene (by hydrolysis). In ether at 45° the absorption is more rapid, and after 50 min. the solution contains 70% of monomagnesium derivative, and after 4 hrs. 85%. With carbon dioxide, 78% of propiolic acid, 8% of acetylenedicarboxylic acid, and 5% of acetylene are obtained. At −10° absorption is theoretical in

45 min. and with allyl bromide the product gives in 75% yield *allylacetylene*, b. p. 41—42°, n_D^{22} 1·3653, d_{22}^{22} 0·777, and a small fraction, b. p. 120—125°, probably *γ-allylallylacetylene* (*γ-allyl-*Δ^{α}*-penten-*Δ^{δ}*-inene*), b. p. 29°/17 mm. The absence of *s*-diallylacetylene is attributed to the acidic nature of the central $\cdot CH_2\cdot$ group of allylacetylene, which probably decomposes the dimagnesium acetylenyl derivative, giving $CH_2\colon CH\cdot CH(MgBr)\cdot C\vdots CH$. *n*-Butyl bromide similarly affords butylacetylene, b. p. 71—72°, d_4^{17} 0·720, n_D^{19} 1·402, in 72% yield. Allylacetylene, γ-allylallylacetylene, and *γγ-diallylallylacetylene*, b. p. 49°/17 mm., have been obtained by Lespieau (private communication) by the action of allyl halides on monosodium acetylide in liquid ammonia.

R. BRIGHTMAN.

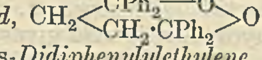
Action of acetylene on aryl-hydrocarbons in presence of a mercury catalyst. II. J. A. REILLY and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1928, 50, 2564—2566; cf. A., 1924, i, 156).—*αα-Diarylethanes* containing the following aryl radicals have been prepared: n-*propylphenyl-*, b. p. 192—194°/42 mm.; iso*propylphenyl-*, b. p. 240—245°/15 mm.; n-*butylphenyl-*, b. p. 244—248°/37 mm.; tert.-*butylphenyl-*, m. p. 94°, b. p. 212—214°/16 mm.; *α-methyl-*n-*propylphenyl-*, b. p. 250—252°/11 mm.; *α-ethylpropylphenyl-*, b. p. 234—236°/29 mm., and *α-methyl*iso*butylphenyl-*, b. p. 225—228°/13 mm. Di- and tri-phenylmethane, diphenyl, dibenzyl, and naphthalene fail to react, but tetrahydronaphthalene gives *αα-di-*ar-*tetrahydronaphthylethane*, b. p. 261—263°/16 mm., and a trace of a cyclic product. The yields of diarylethanes decrease with increasing mol. wt. and, among isomeric compounds, with increasing length of side-chain.

H. E. F. NOTTON.

Ring strain and radical formation. II. G. WITTIG and F. VON LUPIN (Ber., 1928, 61, [*B*], 1627—1634; cf. this vol., 642).—Unsuccessful attempts to prepare 1 : 1 : 2 : 2-tetraphenyl-*cyclo*butane and -*cyclo*butene are recorded.

Treatment of ααδδ-tetraphenylbutane-αδ-diol with boiling acetic and hydrochloric acids, or saturation of its solution in acetic acid with hydrogen bromide, affords *ααδδ-tetraphenyl-*$\Delta^{\alpha\gamma}$*-butadiene*, m. p. 201°, also obtained from the glycol and thionyl chloride in chloroform. The hydrocarbon is converted by the successive action of chlorine in carbon tetrachloride and methyl alcohol into *βγ-dichloro-αδ-dimethoxy-ααδδ-tetraphenylbutane*, m. p. 183° (decomp.), which is reduced by sodium in amyl alcohol to ααδδ-tetraphenylbutane, converted by heat into *β-chloro-ααδδ-tetraphenyl-*$\Delta^{\alpha\gamma}$*-butadiene*, m. p. 246—247°, and oxidised by chromic acid to 3 : 4-*dichloro*-2 : 2 : 5 : 5-*tetraphenyltetrahydrofuran*, m. p. 280—281°; 3-*chloro*-2 : 2 : 5 : 5-*tetraphenyl*-2 : 5-*dihydrofuran*, from the last compound, sodium, and amyl alcohol, has m. p. 168—169°. ααδδ-Tetraphenylbutadiene is converted by sodium–potassium alloy in the presence of ether into the strongly coloured *dipotassium* derivative which, with alcohol and carbon dioxide, respectively, affords *ααδδ-tetraphenyl-*Δ^{β}*-butene*, m. p. 132—133°, and *ααδδ-tetraphenyl-*Δ^{β}*-butene-αδ-dicarboxylic acid*, m. p. 260—261°. In ethereal suspension, the metallic derivative is immediately decolorised by iodine, methylene iodide, tetramethylethylene dibromide, benzoyl chloride, oxygen, and sulphur, but in all cases only more or less pure ααδδ-tetraphenylbutadiene is obtained after addition of water.

as-Diphenylethylene gives a potassium derivative when shaken with sodium–potassium alloy in presence of ether, which is converted by alcohol into ααδδ-tetraphenylbutane; treatment of the metallic compound with iodine, methylene iodide, or tetramethylethylene bromide unexpectedly affords *as*-diphenylethylene; with dry oxygen the potassium derivative yields the *compound*,



$CH_2<\begin{matrix}CPh_2—O\\CH_2\cdot CPh_2\end{matrix}>O$, m. p. (indef.) 171—180°. as-*Didiphenylylethylene*, m. p. 204—205·5°, prepared by the action of magnesium methyl iodide on didiphenylyl ketone and dehydration of the product by glacial acetic acid, similarly yields a *potassium* derivative converted by alcohol into *ααδδ-tetradiphenylylbutane*, m. p. 234—235°; attempts to prepare 1 : 1 : 4 : 4-tetradiphenylyl*cyclo*butane were unsuccessful.

H. WREN.

Oxidation in the benzene series by gaseous oxygen. IV. Mechanism of slow oxidation of saturated hydrocarbons. H. N. STEPHENS (J. Amer. Chem. Soc., 1928, 50, 2523—2529).—Oxidation of xylene at 102—104° in presence of acetic anhydride gives no xylyl acetate, but much more tolualdehyde than is obtained from xylene alone, on account of the removal of traces of water. Xylyl acetate does not yield tolualdehyde under these conditions. Similarly, ethylbenzene and acetic anhydride give an increased yield of acetophenone but no α-phenylethyl acetate. In parallel oxidations at 122—124° more acetophenone is formed from ethylbenzene in 11 days than from phenylmethylcarbinol. These and other facts (cf. A., 1926, 1028; 1927, 48; this vol., 285) indicate that alcohols are not intermediates in the formation of aldehydes and ketones in the oxidation of hydrocarbons. All the known facts are explained by assuming that the following series of reactions occurs: (*a*) reversible formation of a molecular aggregate from 1 mol. of hydrocarbon and 1 mol. of oxygen, (*b*) reversible decomposition of the aggregate into 1 mol. of water and an unsaturated residue, and (*c*) irreversible transformation of the unsaturated residue into an aldehyde or a ketone. The second stage accounts for the inhibitory action of water and also for the absence of inhibition in the oxidation of the *iso*propyl group, since in this case methyl alcohol is eliminated in (*b*). Oxidation to alcohols under exceptional conditions is explained by the formation of termolecular aggregates.

H. E. F. NOTTON.

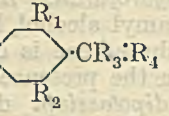
Alternating reactive positions in the nucleus of *tert.*-butylbenzene. J. B. SHOESMITH and A. MACKIE (J.C.S., 1928, 2334—2340).—Malherbe (A., 1919, i, 261) and the present authors were unable to confirm Senkowski's observation (A., 1890, 1296) that both *ortho-* (b. p. 247—248°/738 mm.; acetyl derivative of amino-compound, m. p. 159°) and *para-tert.*-butylbenzenes are produced by direct nitration. By the further nitration of *p*-nitro-*tert.*-butylbenzene to 2 : 4-dinitro-*tert.*-butylbenzene, reduction of the latter with ammonium hydrogen sulphide in alcohol to 2-*nitro*-4-*amino*-tert.-*butylbenzene*, m. p. 55°, and elimination of the amino-group *o*-nitro-*tert.*-butylbenzene, b. p. 114—115°/10 mm. or 250·5°/765 mm., was obtained; reduction with iron and hydrochloric acid gave *o*-amino-*tert.*-butylbenzene (acetyl derivative, m. p. 161°). This, together with the observation that only *o*- and *p*-iodo-*tert.*-butylbenzenes react with hydrogen iodide in glacial acetic acid, the *meta*-compound being unaffected, are examples of the alternations of the reactive positions in the nucleus of *tert.*-butylbenzene. *p*-Nitro-*tert.*-butylbenzene with bromine and finely-divided iron at 90° is converted into o-*bromo*-p-*nitro*-tert.-*butylbenzene*, m. p. 94·5°, which with iron and hydrochloric acid gives 2-*bromo*-4-*amino*-tert.-*butylbenzene*, b. p. 153—155°/11 mm. [*hydrochloride*, m. p. 235° (decomp.); *acetyl* derivative, m. p. 142—143°]; o-*bromo*-tert.-*butylbenzene*, b. p. 96—98°/12 mm., was obtained from the last-named by elimination of the amino-group. Both o-*iodo*- (prepared from the corresponding amino-compound) and o-*bromo*-tert.-*butylbenzene* react with magnesium and carbon dioxide to give o-tert.-*butylbenzoic acid*, m. p. 68·5° (cf. Tschitschibabin, Elgasine, and Lengold, this vol., 404). A. I. VOGEL.

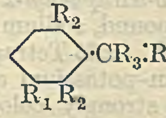
Micro-identification of isomerides and homologues in mixtures. I. Three isomeric xylenes. M. MAGITA (Bull. Chem. Soc. Japan, 1928, 8, 191—199).—2 : 4 : 6-Trinitro-*m*-xylene in alcoholic solution gives an instant intense bluish-green coloration (changing to dull yellow on keeping) on addition of a drop of potassium hydroxide solution, whilst 2 : 3 : 5-trinitro-*p*-xylene slowly develops an orange colour, the solution becoming turbid on keeping and a reddish-brown deposit is formed. In acetone solution the colours produced are respectively dark green and reddish-brown, both appearing instantaneously, but the trinitro-*m*-xylene is almost insoluble in hot acetone, whilst the trinitro-*p*-xylene is freely soluble. These colour reactions may, therefore, be used to detect the presence of *m*- and *p*-xylenes in mixtures if compounds such as trinitro-*ψ*-cumene, 2 : 4-di- and 2 : 4 : 6-tri-nitrotoluenes which give similar colour reactions are first removed by extraction with ether, alcohol, or acetone, in which the trinitroxylenes are only sparingly soluble. Identification of the three isomeric xylenes has been attempted by the polarisation-microscope method (Ernich, "Lehrbuch der Mikrochemie," 2nd Ed., 1926, 21). For this purpose the tetrabromo-compounds are unsuitable, but *m*- and *p*-xylenes may be distinguished by examination of their trinitro-compounds, 2 : 4 : 6-trinitro-*m*-xylene in α-bromonaphthalene having $n_1<N<n_2$ (n_1, n_2, and N representing the refractive indices for the faster and shorter rays in the crystal, and that of the medium, respectively) and positive elongation, and 2 : 3 : 5-trinitro-*p*-xylene having $n_1>N$ and negative elongation. Similar examination of sodium *o*- and *m*-xylene-4-sulphonates and *p*-xylene-2-sulphonate enables the last to be distinguished from *o*- and *m*-compounds by its refractive indices in cedar oil ($n_1>N$), but the *o*- and *m*-compounds can be distinguished only by their crystalline form, prismatic and rhombic plates, respectively, the value of n_1 for the former being lower than that of the cedar oil. Application of these methods to a sample of commercial xylene shows the absence of any appreciable quantity of the *o*-compound. Contrary to the principle of the technical separation of *p*-xylene, this hydrocarbon is readily absorbed by concentrated sulphuric acid. J. W. BAKER.

Introduction of the benzyl group into the benzene nucleus by means of sulphonic esters. Z. FÖLDI (Ber., 1928, 61, [*B*], 1609—1616; cf. A., 1927, 453).—The introduction of the benzyl group into the benzene nucleus of hydrocarbons, phenols, phenolic ethers, carboxylic esters, and aldehydes is readily effected when a considerable excess of them is heated with benzyl benzenesulphonate in the absence of solvent, usually at 110—140°. The yields of mono-substituted derivatives are somewhat restricted by the pronounced tendency towards the production of di-derivatives and by the formation of *cyclo*paraffins from the eliminated benzylidene group. The change is considered to consist in the primary decomposition of the sulphonate into benzenesulphonic acid and benzylidene, followed by union of the latter with the benzenoid compound, giving an intermediate dicyclic *cyclo*propane which passes into the benzyl derivative. Benzene yields diphenylmethane (80%) and a mixture of *o*- and *p*-dibenzoylbenzenes. Toluene affords 85% of phenyl-*p*-tolylmethane (3 : 4′-dinitro-4-methyldiphenylmethane, m. p. 142—143°) and dibenzyltoluenes. Diphenylmethane gives a small yield of *o*-dibenzylbenzene, m. p. 77—79°, but the reaction is complicated by the production of much *cyclo*paraffin. Nitrobenzene and benzyl benzenesulphonate give a very dark product from which (?) 3 : 5-*dinitrodiphenylmethane*, m. p. 183—185°, is isolated in small amount (due to the presence of dinitrobenzene in the nitrobenzene used). Phenol yields *p*-benzylphenol, m. p. 83°, o-*benzylphenol*, b. p. 303—307°, and a small amount of benzyl phenyl ether, b. p. 284—286°. Anisole affords p-*benzylanisole*, b. p. 288—295°, in 77% yield. A benzylated benzaldehyde could not be obtained. Methyl salicylate is converted into *methyl* 6-*hydroxy*-3-*benzylbenzoate*, m. p. 79—80°, b. p. 134—138°/1 mm., and probably, methyl 2-hydroxy-3-benzylbenzoate. Tiglic acid does not appear to unite with the benzylidene group. Ethyl cinnamate is transformed into a mixture of the α-benzylcinnamate and (?) αβ-dibenzylcinnamate. H. WREN.

Possible isomerism of analogues of resolvable diphenyl compounds. J. F. HYDE and R. ADAMS (J. Amer. Chem. Soc., 1928, 50, 2499—2506).—If the forces preventing free rotation in the resolvable diphenyl compounds are entirely mechanical in nature, derivatives of types I and II might exist in

(I.)





(II.)

enantiomorphic forms providing R_4 is sufficiently large to interfere with the *o*-substituents. Attempts to resolve derivatives of these types (R_4 being oxygen) have been unsuccessful. Bromomesitylene, benzoyl chloride, and aluminium chloride in carbon disulphide yield 2-*bromo*-4-*benzoylmesitylene*, m. p. 48—49°, the ketonic group of which does not react with zinc and ethyl bromoacetate, or magnesium phenyl bromide. 2-*Bromo*-4-p-*nitrobenzoylmesitylene*, m. p. 154—155°, prepared similarly, is hydrogenated (platinum) in alcohol to 2-*bromo*-4-p-*aminobenzoylmesitylene*, m. p. 138° (*hydrochloride*), an *azo*-derivative, m. p. 203—205°, being formed as a by-product in ethyl acetate. The d-*camphorsulphonate*, m. p. 175—200° (decomp.), of this amine has $[\alpha]_D$ +13·7°, changing in several hours to +7·1°, in chloroform. This is probably not due to stereoisomeric change (cf. Pope and Read, J.C.S., 1914, **105**, 800), since aniline *d*-camphorsulphonate shows a still greater variation ($[\alpha]_D$ +33·3° to $[\alpha]_D$ +6·6° in chloroform). 2-*Bromo*-4-mm′-*dinitrobenzoylmesitylene*, m. p. 160—161·5°, is hydrogenated to 2-*bromo*-4-mm′-*diaminobenzoylmesitylene*, m. p. 168—169°, which yields a d-*camphorsulphonate*, m. p. 216—218°, $[\alpha]_D$ +21·2° or 20·2° in chloroform, decreasing on keeping. Fractionation of these camphorsulphonates gave no indications of resolution and the regenerated amines were inactive. Attempts to obtain an optically active acid from the *brucine* salt, m. p. 90—95° (decomp.), $[\alpha]_D$ −21·3° or 19·9° in chloroform, of *iso*propyl 2-nitro-6-carboxybenzoate, or from *brucine* 3-*nitro*-2-(2′-*hydroxy*-p-*toluoyl*)*benzoate*, m. p. 160—165° (decomp.), $[\alpha]_D$ +18·3°, were unsuccessful. The anomalous rotation of the latter salt and that of quinine 4 : 4′-dinitrodiphenate (Kuhn and Albrecht, A., 1927, 876) is probably not due to asymmetric transformation, but to effects such as those observed by Hilditch (J.C.S., 1911, **99**, 224).

H. E. F. Notton.

Hydrogenation of fluorene under pressure in the presence of nickel or osmium with addition of cerium and thorium. V. S. Sadikov and A. K. Michailov (Ber., 1928, **61**, [*B*], 1792—1796).—Hydrogenation of fluorene in the presence of osmium at 300° and 165 atm. original pressure proceeds much more rapidly than in the presence of nickel (cf. Ipatiev, A., 1909, i, 466) and gives a small proportion of dodecahydrofluorene in addition to decahydrofluorene, which is the sole product when nickel is used. Addition of cerium dioxide to the osmium catalyst causes an extraordinary enhancement of its activity, the yield of dodecahydrofluorene attaining about 93% at 300° with a maximal pressure of 153 atm. With thorium dioxide in place of cerium dioxide a still greater activation is observed, and dodecahydrofluorene is the sole product. With nickel oxide hydrogenation proceeds slowly and yields decahydrofluorene and unchanged fluorene; addition of cerium dioxide enormously increases the activity and causes almost exclusive production of dodecahydrofluorene. Thorium dioxide, on the other hand, greatly diminishes the activity of the nickel oxide catalyst.

H. Wren.

α-Chloronaphthalene. II. Nitration. P. Ferrero and C. Caflisch (Helv. Chim. Acta, 1928, **11**, 795—812).—Mononitration of α-chloronaphthalene with nitric (*d* 1·4; 1·01 mols.) and sulphuric acids (2 mols.) gives a mixture of 1-chloro-4-, -5-, and -8-nitronaphthalenes. The proportion of the 1 : 5-derivative diminishes with rise of the reaction temperature (at 0—5°, 18·5%; at 95°, nil), whilst the 1 : 4-derivative increases (47%; 63·5%). The amount of the 1 : 8-compound is approximately constant (about 36·5%). A detailed study of numerous methods of nitration has been carried out and the results show that the isomerides can be obtained in varying amounts: 1 : 4-, 34·4—63·5%; 1 : 5-, 0—21·5%; 1 : 8-, 30·6—65·2%.

Determination of the amounts of the above isomerides in a mixture is not possible by physical methods. The following method was used. Treatment of the mixture with a 10% solution of ammonia in ethylene glycol at 150—160° removes the 1 : 4-isomeride as the corresponding amine. Sulphonation of the residue with sulphuric acid monohydrate at 95° for 3 hrs. effects the removal of the major part of the 8-nitro-derivative, the 5-nitro-compound being unaffected.

H. Burton.

Chlorodecalin [chlorodecahydronaphthalene]. P. Ferrero and M. Fehlmann (Helv. Chim. Acta, 1928, **11**, 763—776).—A modified Gysin apparatus (A., 1926, 389) is described for chlorinating decahydronaphthalene in an atomised state. The maximum yield of 2-chlorodecahydronaphthalene (about 40%) is obtained in presence of 0·5% of iodine and by repeated and rapid passage of the hydrocarbon through the chlorinating chamber. 2-Chlorodecahydronaphthalene is converted by fusion with potassium hydroxide at 150—160° into decahydro-β-naphthol, but does not give recognisable products when heated with amines. Condensation of 2-phenyldecahydronaphthalene, b. p. 163—164°/13 mm., d^{14} 0·9799, n^{12} 1·5419 (2-*p*-tolyl derivative, b. p. 178—180°/12 mm.), with phthalic anhydride in presence of aluminium chloride and carbon disulphide gives a small amount of 2 : 3′-β-*decahydronaphthylbenzoylbenzoic acid*, m. p. 184—186°; with *p*-chlorophenol, quinol, or benzoic acid and chlorodecahydronaphthalene, or with benzoyl- and chlorobenzoylbenzoic acids and decahydronaphthalene, no recognisable products were obtained.

Chlorination of benzene by the above process gives a mixture of polyhalogenated benzenes, whilst naphthalene in carbon tetrachloride solution gives under favourable conditions a 65% yield of α-chloronaphthalene.

H. Burton.

Attempt to prepare *p*-diphenylene. A. C. Sircar and J. N. Majumdar (J. Indian Chem. Soc., 1928, **5**, 417—418; cf. A., 1927, 50).—When 4 : 4′-di-iododiphenyl is heated with copper powder at 300—310° for 15 hrs. in a sealed tube, *tetraphenylene*, $C_{24}H_{16}$, m. p. 304—305°, is formed. If the reaction is carried out at 280—300° for 5—6 hrs. in presence of a small quantity of water diphenyl is obtained.

H. Burton.

Constitution and synthesis of rubicene. W. Schlenk and M. Karplas (Ber., 1928, **61**, [*B*], 1675—1680).—9 : 10-Diphenylanthracene, m. p. 240°, is obtained by the action of calcium hydride on boiling benzophenone, the product, $CHPh_2\cdot O\cdot Ca\cdot O\cdot CHPh_2$, being probably formed intermediately. Phenyl diphenylyl ketone under similar conditions at 300° affords 9 : 10-didiphenylylanthracene (I), m. p. considerably above 300°, identical with rubicene obtained by the distillation of diphenic acid with alkali hydroxide (cf. Pummerer, A., 1912, i, 182). The hydrocarbon is prepared synthetically by converting anthraquinone by means of magnesium *p*-diphenyl iodide into 9 : 10-*dihydroxy*-9 : 10-*didiphenylyldihydroanthracene*, m. p. 29°, which is reduced by boiling formic acid. Boiling fluorenone and calcium hydride also yield rubicene. The reaction does not, however, appear generally applicable, since anthracene derivatives are not obtained from Michler's ketone or 4 : 4′-dimethoxybenzophenone. Acetophenone and calcium hydride afford 1 : 3 : 5-triphenylbenzene, m. p. 171—172°, and a *substance*, $C_{24}H_{20}O$, m. p. 165—165·5°.


(I.)

H. Wren.

Arylamine salts of the naphthalenesulphonic acids. V. Acetylation of Peri, Laurent, and Brönner acids and the arylamine salts of their acetyl derivatives. R. B. Forster, T. H. Hanson, and R. Watson (J.S.C.I., 1928, 47, 155—157T).—Peri acid (α-naphthylamine-8-sulphonic acid), Laurent acid (α-naphthylamine-5-sulphonic acid), and Brönner acid (β-naphthylamine-6-sulphonic acid) behave in the same manner towards arylamines as naphthionic acid. They do not form arylamine salts unless the amino-group is acetylated first, showing that the inhibiting action of the amino-group on arylamine salt formation is independent of the relative positions of the sulphonic groups.

All these acids are acetylated readily by acetic anhydride in the presence of pyridine. The free acetamidosulphonic acids are easily hydrolysed, especially in the presence of dilute mineral acid; the sodium and potassium salts are quite stable and may be purified by recrystallisation from water. The pure naphthylaminesulphonic acids may be obtained by hydrolysing the alkali salts of the pure acetyl derivatives with dilute hydrochloric acid. The acetyl derivatives readily yield arylamine salts, most of which are well-defined crystalline substances with definite m. p. They are easily hydrolysed by either alkali hydroxide or mineral acid, but may be purified by recrystallisation from dilute acetic acid.

1-Acetamidonaphthalene-8-sulphonic acid forms arylamine *salts*, with m. p. as follows: aniline, 273°; *o*-toluidine, 198°; *p*-toluidine, 207°; ψ-cumidine, 257°; α-naphthylamine, 242°; benzidine, 287° (decomp.); tolidine, 267° (decomp.); dianisidine; *p*-chloroaniline; *p*-nitro-*o*-toluidine, 277° (decomp.).

1-Acetamidonaphthalene-5-sulphonic acid gives *salts* with m. p. as follows: aniline, 344° (decomp.); *o*-toluidine, 259°; *p*-toluidine, 255°; α-naphthylamine, indef.; β-naphthylamine, 280°; benzidine, 322° (decomp.); tolidine, 307° (decomp.); dianisidine, 328° (decomp.); ψ-cumidine, *p*-chloroaniline, and *p*-nitro-*o*-toluidine, no m. p.

2-Acetamidonaphthalene-6-sulphonic acid forms *salts* with m. p. as follows: aniline, 256°; *o*-toluidine, 262°; *p*-toluidine, 243°; ψ-cumidine, 277°; α-naphthylamine, 258°; β-naphthylamine, 262°; benzidine, 246°; tolidine, 315° (decomp.); *p*-chloroaniline, 275°; *p*-nitro-*o*-toluidine, 287° (decomp.); *o*-anisidine, 230°; *o*-phenetidine, 225°; *m*-bromoaniline, 249°; *p*-bromoaniline, 267° (decomp.).

Arylamine salts of the naphthalenesulphonic acids. VI. Salts of Koch acid, "H" acid, and chromotropic acid. R. B. Forster and D. H. Mosby (J.S.C.I., 1928, 47, 157—159T).—Koch acid (α-naphthylamine-3 : 6 : 8-trisulphonic acid) forms salts with arylamines, containing 1 mol. of Koch acid to 2 mols. of monoamine or 1 mol. of a diamine. The third sulphonic acid group forms an inner salt with the amino-group. In "H" acid (1-amino-8-naphthol-3 : 6-disulphonic acid) only one of the sulphonic acid groups takes part in arylamine salt formation. The salts with diamines, therefore, consist of 2 mols. of "H" acid and 1 mol. of the diamine, and those with monoamines of 1 mol. of "H" acid and 1 mol. of the monoamine. In chromotropic acid (1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid), which contains no basic group, both sulphonic acid groups are free to take part in arylamine salt formation.

The majority of the arylamine salts of Koch acid and chromotropic acid are extremely soluble in water and to a smaller extent in alcohol. Those of "H" acid are only sparingly soluble in either water or alcohol. It is pointed out that the capability of a sulphonic acid group to take part in arylamine salt formation depends on the stability of its sodium salt in dilute mineral acid solution.

The *salts* of Koch acid described have the following m. p.: aniline, 312°; *o*-toluidine, 304°; *p*-toluidine, 292°; *m*-xylidine, 284°; *o*-anisidine, 290°; *p*-anisidine, 287°; α-naphthylamine, 312°; β-naphthylamine, 322° (all decomp.); benzidine, decomp. 348°; tolidine, decomp. 345°; dianisidine, decomp. 339°.

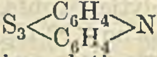
The corresponding *salts* of "H" acid all decompose without melting between 320° and 345° (*p*-nitro-*o*-toluidine *salt*, 286°). The *salts* of chromotropic acid have the following m. p. (decomp.): aniline, 300°; *o*-toluidine, 290°; *p*-toluidine, 308°; *m*-xylidine, 307°; α-naphthylamine, 311°; β-naphthylamine, 293°; benzidine, decomp. 312°.

Nitration of substituted tertiary aromatic amines. G. R. Clemo and J. M. Smith (J.C.S., 1928, 2414—2422).—*p*-Chloro- and *p*-bromo-dimethylaniline when nitrated in concentrated sulphuric acid give a good yield of almost pure *m*-nitro-derivative (purity improved by the presence of carbamide), but when nitrated in dilute sulphuric acid yield the pure *o*-nitro-compound; the latter reaction is inhibited in the presence of carbamide. It is found that the change-over from *o*- to *m*-nitration is not a gradual process, but occurs between the sulphuric acid concentrations of 86% and 90%. *p*-Methyldimethylaniline, tetramethylbenzidine, *pp*′-tetramethyldiaminodiphenylmethane, and p-*dimethylaminobenzyl alcohol* (see this vol., 1239) are nitrated in the *m*-position in concentrated sulphuric acid, but readily yield *o*-nitro-derivatives with dilute sulphuric acid in the presence of carbamide. Further nitration and the ultimate effect of fuming nitric acid on *p*-bromodimethylaniline are recorded. The following are described: 4-chloro-2-nitrodimethylaniline, m. p. 56°, converted by iron and hydrochloric acid into *4-chloro-2-aminodimethylaniline*, b. p. 158°/22 mm. (*acetyl* derivative, m. p. 90°); 4-chloro-3-nitrodimethylaniline, m. p. 79°; *4-chloro-3-aminodimethylaniline*, m. p. 54° (*acetyl* derivative, m. p. 97°); 4-bromo-2-nitrodimethylaniline, m. p. 64° (lit. 72°); *4-bromo-2-aminodimethylaniline*, b. p. 165°/23 mm. (*acetyl* derivative, m. p. 111°); *4-bromo-3-nitrodimethylaniline*, m. p. 93·5°; 3 : 3′-dinitro-4 : 4′-tetramethyldiaminodiphenylmethane, m. p. 121°; 3 : 3′-dinitrotetramethylbenzidine, m. p. 188°. Nitration of 4-bromo-2-nitrodimethylaniline with dilute nitric acid yields *4-bromo-2 : 6-dinitrodimethylaniline*, m. p. 118°, together with *4-bromo-2 : 6-dinitrophenylmethylnitrosoamine*, m. p. 124° (preferably prepared by direct dinitration of 4-bromodimethylaniline in dilute sulphuric acid), converted by alcoholic hydrogen chloride into *4-bromo-2 : 6-dinitromethylaniline*, m. p. 104—105°, and by fuming nitric acid into 4-bromo-2 : 6-dinitrophenylmethylnitroamine, m. p. 113—114° (lit. 110°); treatment with fuming nitric acid for a longer period yields 2 : 4 : 6-trinitrophenylmethylnitroamine (tetryl), m. p. 127°. 4-Bromodimethylaniline when nitrated in concentrated sulphuric acid at 40° yields 4-bromo-3 : 6-dinitrodimethylaniline, m. p. 107° (lit. 108°), and with fuming nitric acid 4-bromo-2 : 3 : 6-trinitrophenylmethylnitroamine, m. p. 158° (lit. 165°).

C. W. Shoppee.

Nitro-derivatives of dibenzylaniline. R. D. Desai (J. Indian Chem. Soc., 1928, 5, 425—431).—Nitration of dibenzylaniline with nitric and acetic acids at 5° gives mainly *p*-nitrodibenzylaniline together with a small amount of the *o*-nitro-derivative. If an excess of nitric acid is used some *2 : 6-dinitrodibenzylaniline*, m. p. 107°, accompanies the 2 : 4-dinitro-derivative, m. p. 103—104° (cf. Pinnow and Wiskott, A., 1899, i, 500). These dinitro-compounds are decomposed by heating with acetic anhydride and concentrated hydrochloric acid to the corresponding dinitroanilines. Reduction of *p*-nitrodibenzylaniline with zinc dust and hydrochloric acid in alcohol solution gives *p*-aminodibenzylaniline, m. p. 89—90° (*acetyl* derivative, m. p. 137—138°; *benzoyl* derivative, m. p. 166°), which condenses normally with benzaldehyde to give the corresponding *benzylidene* derivative, m. p. 166—167° [*hydrochloride*; *dibromide*, m. p. 220—225° (decomp.)], and not the substituted amino-carbinol (cf. Matzudaira, A., 1887, 812). *m*-Nitroaniline condenses with benzyl chloride in presence of sodium acetate and a trace of iodine at 125—130° to give m-*nitrodibenzylaniline*, m. p. 73—74° (*hydrochloride*, m. p. 140—142°), reduced to m-*aminodibenzylaniline* (*acetyl* derivative, m. p. 143—144°; *benzoyl* derivative, m. p. 171—172°), which affords a *benzylidene* derivative, m. p. 156—158° [*hydrochloride*, m. p. 195° (decomp.); *dibromide*, m. p. 196—198° (decomp.)]. *p*-Aminobenzylaniline (*acetyl* derivative, m. p. 141—142°; *benzoyl* derivative, m. p. 182—183°) yields a *benzylidene* derivative, m. p. 92—93° [*hydrochloride*, m. p. 170—172°; *dibromide*, m. p. 210° (decomp.) after sintering at 200°]. *o*-Aminodibenzylaniline (*acetyl* derivative, m. p. 121—122°; *benzoyl* derivative, m. p. 155—156°) is described.

H. Burton.

Action of sulphur monochloride on diphenylamine, and the preparation of trithiodiphenylamine and of other diphenylamine derivatives from diphenylamine. E. I. Orlov (Ukraine Chem. J., 1928, 3, 171—175).—Sulphur monochloride reacts at the ordinary temperature with diphenylamine to yield a precipitate of trithiodiphenylamine,  $S_3\!<\!{}^{C_6H_4}_{C_6H_4}\!>\!NH$, whilst dithiodiphenylamine remains in solution. The former product, when nitrated, yields *di*-(p-*hydroxy*-o-*nitrophenyl*)*amine*, which is reduced to the corresponding amino-compound. The nitro-derivative forms a tetrammine salt with ammonia, which dyes wool a red colour.

R. Truszkowski.

Manufacture of 2 : 3- and 2 : 5-dichloroaceto-*p*-toluidides and -*p*-toluidines. I. G. Farbenind. A.-G.—See B., 1928, 704.

Ring formation. II. Constitution of monophthalylbenzidine. III. Condensation of benzidine with dibasic acid anhydrides. A. C. Sircar and P. R. Sen-Gupta (J. Indian Chem. Soc., 1928, 5, 397—399, 401—404).—II. When monophthalylbenzidine is treated with benzaldehyde, salicylaldehyde, or *m*-nitrobenzaldehyde in boiling nitrobenzene the corresponding benzylidene, m. p. above 300°, salicylidene, m. p. 297°, or m-*nitrobenzylidene*, m. p. 280°, derivative is obtained (cf. Le Fèvre and Turner, A., 1926, 1131). Diazotisation and treatment with β-naphthol affords *4′-phthalimidodiphenylylazo-β-naphthol*, m. p. 273—275°. The presence of a free amino-group is thus definitely established.

III. Dibasic acid anhydrides condense with benzidine to form monosubstituted derivatives of the type $R{:}C_2O_2{:}N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$. *Naphthalylbenzidine*, m. p. above 300° (*benzylidene*, m. p. 297°, *salicylidene*, m. p. 283°, and m-*nitrobenzylidene*, m. p. 299°, derivatives), *camphorylbenzidine*, m. p. 190°, and *quinolinylbenzidine*, m. p. above 300°, are described. Tolidine and quinolinic anhydride afford *4′-aminoditolylylquinolinamic acid*, m. p. 231°, whilst benzidine and diphenic anhydride give *4′-aminodiphenylyldiphenamic acid*, m. p. 199°. *Dinaphthalylbenzidine*, m. p. above 300°, is described.

H. Burton.

Action of diazo-salts on aromatic sulphonamides. II. Mechanism of the reaction and constitution of the diazosulphonamides. A. Key and P. K. Dutt (J.C.S., 1928, 2035—2040).—The reaction $R{\cdot}SO_2{\cdot}NH_2 + R'{\cdot}N_2X \longrightarrow R{\cdot}SO_2{\cdot}NH{\cdot}N{:}NR'$ (I)$\longrightarrow R{\cdot}SO_2H + R'{\cdot}N_3$ readily takes place in presence of alkali even at low temperatures (*ibid.*, 1921, **119**, 2088). Investigation of the mechanism (where R=*p*-tolyl, R′=Ph) shows that this is not a case of true migration of the hydrogen atom from the nitrogen to the oxygen, followed by fission into the two final products, since when the pure, dry diazosulphonamide is heated alone or in a non-ionising solvent at a temperature above its decomposition point, conversion into the azoimide fails to take place. An electronic interpretation is therefore offered. It is suggested that the hydrogen in the diazosulphonamide (I) is incipiently ionised because of the strong electron attraction actuated by the neighbouring positive charges. The proton is removed as water and the complex ion $R\cdot SO_2\cdot N\cdot N{:}NR'$ (II) then undergoes further change due to the proximity of the positively-charged sulphur; the latter appropriates the two electrons between the sulphur and the nitrogen and fission into the sulphinate ion $R\cdot SO_2'$ and $R'\cdot N_3$ then takes place. The diazosulphonamide reacts with acid hydrolytic agents, forming only $R\cdot SO_2\cdot NH_2$ and R′·OH, but no $R'\cdot NH_2$. In this case, ionisation to II again takes place and the two lone pairs of electrons in the nitrogen atom then appropriate two hydrogen ions, completing the system $R\cdot SO_2\cdot NH_2$ and leaving a positive ion $R'\cdot N⋮N$ which is responsible for the formation of the phenol. When the diazosulphonamide is methylated in the cold, only one monomethyl derivative is formed. This substance yields, on reduction, $R\cdot SO_2\cdot NH_2$, ammonia, R′·NHMe, $R'\cdot NMe\cdot NH_2$, and R′·NMe·N:N·NMeR′, and must therefore have the constitution $R\cdot SO_2N{:}N\cdot NMeR'$ (III). In this case, velocity of methylation is much greater than that of the reaction yielding the azoimide, and it is accordingly the substance $R\cdot SO_2\cdot NH\cdot N{:}NR'$ and not the ion which reacts. The $R\cdot SO_2\cdot NH\cdot N{:}NMe\cdot R'X$ first formed is converted by elimination of HX into III. The isomeric methyl derivative $R\cdot SO_2\cdot NMe\cdot N{:}NR'$, prepared from $R\cdot SO_2\cdot NHMe$ and $R'\cdot N_2Cl$, yields, on reduction, $R'\cdot NH_2$ and $R'\cdot NH\cdot NH_2$. M. CLARK.

Azo dyes from acetoacetanilides. H. E. FIERZ-DAVID and E. ZIEGLER (Helv. Chim. Acta, 1928, **11**, 776—786).—Acetoacetanilides are prepared from ethyl acetoacetate and anilines in presence of xylene and a small amount of pyridine. When these are treated with diazotised sulphanilic acid or other anilines, azo dyes of the form $SO_3H\cdot C_6H_4\cdot N{:}N\cdot CHAc\cdot CO\cdot NHAr$ are obtained, which when reduced with stannous chloride and hydrochloric acid regenerate the aniline (or its reduction product) and yield 2 : 5-dimethyldihydropyrazine-3 : 6-dicarboxydianilides. The following are described : dianilide, m. p. 218° (decomp.); *di-o-toluidide*, m. p. 236—237°; *di-p-toluidide*, m. p. 227—228°; *di-m-xylidide*, m. p. 190°; *di-o-anisidide*, m. p. 231°; *di-o-chloroanilide*, m. p. 197°, and *di-2 : 5-dichloroanilide*, m. p. 215°.

Reduction of the "Hansa yellow" dyes G, GA, 3G, 5G, 10G, and R, and identification of the substituted anilines and dihydropyrazines obtained indicate that these dyes are prepared from the following diazotised anilines and acetoacetanilides: G and GA, 3-nitro-*p*-toluidine and acetoacetanilide; 3G, 4-chloro-*o*-nitroaniline and acetoacetanilide; 5G, *o*-nitroaniline and acetoacetanilide; 10G, 4-chloro-*o*-nitroaniline and acetoacet-*o*-chloroanilide; R, 2 : 5-dichloroaniline and 1-phenyl-3-methyl-5-pyrazolone. H. BURTON.

Superheating of phenyl ββ-dimethylacrylate. S. SKRAUP (Ber., 1928, **61**, [*B*], 1665—1666).—The production of *o*-ββ-dimethylacroylphenol by superheating phenyl ββ-dimethylacrylate is confirmed (cf. Skraup and Beng, A., 1927, 560). The inability of von Auwers (this vol., 407) to repeat this observation is probably due to insufficient regard to the very narrow limits of temperature within which the change occurs. H. WREN.

Additive compounds of phenols and ammonia. III. System phenol–ammonia. E. BRINER and O. AGATHON (Helv. Chim. Acta, 1928, **11**, 922—925; cf. A., 1926, 1241; 1927, 1181).—This system has now been studied by the manometric method. The results are not as conclusive as in previous systems examined by this method, since no flat portion is obtained on the curve of pressure against volume of ammonia introduced. This is attributed to a liquefaction of the phenol which occurs when brought in contact with ammonia. Support, however, is obtained for the view, advanced previously, that a compound $PhOH,NH_3$ is formed. R. N. KERR.

Additive compounds of phenols and ammonia. IV. Ammoniation of naphthols, dihydroxybenzenes, hydroxybenzoic acids, hydroxyanthraquinones, dihydroxyanthraquinones, and *o*-nitrophenol; heats of ammoniation. E. BRINER and A. MORF (Helv. Chim. Acta, 1928, **11**, 926—944; cf. preceding abstract).—The manometric method of investigation has been extended to the systems of the above compounds with ammonia. Satisfactory curves have been obtained in all cases except with salicylic acid, which, like phenol, liquefies in contact with ammonia. The dissociation pressures of the ammoniates formed have been measured and their heats of formation from the original substance and ammonia have been calculated from the dissociation pressures at two different temperatures; these are signified by Q expressed per g.-mol. Proof of the formation of the following has been obtained: *α-naphthol monoammoniate*; *β-naphthol semiammoniate*, $C_{10}H_7\cdot OH,0\cdot 5NH_3$, crystalline, $Q=5$ kg.-cal.; *β-naphthol monoammoniate*, $Q=9$ kg.-cal. The three dihydroxybenzenes form monoammoniates very readily and also diammoniates, the stabilities of which increase from *o*- to *p*-; *pyrocatechol monoammoniate*, needles, $Q=13$ kg.-cal.; *pyrocatechol diammoniate*, unstable, $Q=18$ kg.-cal.; *quinol diammoniate*, crystalline. The three hydroxybenzoic acids form *monoammoniates* very readily; the *m*- and *p*-acids form *diammoniates* at low pressures, but the *o*- requires a pressure of 2 atm. at 20°; the heats of formation of the diammoniates are *o*-, 5 kg.-cal.; *m*-, 7·5 kg.-cal.; *p*-, 8·5 kg.-cal. The mono- and di-hydroxyanthraquinones form very stable monoammoniates: *α-hydroxyanthraquinone monoammoniate*, deep red; *β-hydroxyanthraquinone monoammoniate*, yellowish-red; *alizarin monoammoniate*, violet, $Q=5$ kg.-cal.; *quinizarin monoammoniate*, violet; *hystazarin monoammoniate*, deep red. The dissociation pressures of the mono- and tri-ammoniates of *o*-nitrophenol, already described, have been determined at several temperatures; the heats of formation are respectively 17·6 and 33·6 kg.-cal.

R. N. KERR.

Chloro-*o*-xylenols. II. 3-Chloro-*o*-4-xylenol, the dichloro-*o*-4-xylenols, and 4 : 5-dichloro-*o*-3-xylenol. L. E. HINKEL, E. E. AYLING, and L. C. BEVAN (J.C.S., 1928, 2529—2533; cf. *ibid.*, 1923, **123**, 2968).—Syntheses of five of the eight remaining chloro-*o*-xylenols are described. 3-Benzeneazo-*o*-4-xylenol was reduced to 3-*amino*-o-4-*xylenol*, m. p. 126°, from which 3-*chloro*-o-4-*xylenol*, m. p. 27° (*benzoyl* derivative, m. p. 87°), was obtained. Nitration of 5-chloro-*o*-4-xylenol gave 5-*chloro*-3-*nitro*-o-4-*xylenol*, m. p. 127·5°, which was reduced to 5-*chloro*-3-*amino*-o-4-*xylenol*, m. p. 175°. Attempts to replace the amino-group by chlorine in the last compound led to a mixture of chloroxylenols from which only 3 : 5-*dichloro*-o-4-*xylenol*, m. p. 52° (*benzoyl* derivative, m. p. 89°) (also obtained from 3 : 5-dichloro-*o*-4-xylidine), was isolated. Benzenediazonium chloride coupled with 6-chloro-*o*-4-xylenol to give 6-*chloro*-5-*benzeneazo*-o-4-*xylenol*, m. p. 143°, which yielded on reduction 6-*chloro*-5-*amino*-o-4-*xylenol*, m. p. 144·5°. Attempts to displace NH_2 by Cl led to elimination of nitrogen and the regeneration of 6-chloro-*o*-4-xylenol. 3 : 5-*Dichloro*-o-3-*xylenol*, m. p. 90° (*benzoyl* derivative, m. p. 133°), 3 : 6-*dichloro*-o-4-*xylenol*, m. p. 84° (*benzoyl* derivative, m. p. 124°), and 5 : 6-dichloro-*o*-4-xylenol (cf. Hinkel, A., 1924, i, 1204) were prepared from the corresponding dichloroxylidines (this vol., 995). R. J. W. Le Fèvre.

Synthesis of 1-phenanthrol. J. B. Shoesmith and A. Guthrie (J.C.S., 1928, 2332—2334).—α-*Naphthylparaconic acid*, m. p. 169° (decomp.), prepared from α-naphthaldehyde (p-*nitrophenylhydrazone*, m. p. 233—235°), is converted by heating at 340° (metal bath temp.) into 1-*phenanthrol*, m. p. 156° (*picrate*, m. p. 182°), which on methylation yields 1-methoxyphenanthrene, m. p. 105°, identical with that obtained by Pschorr, Wolfes, and Buckow (A., 1900, i, 232). C. W. Shoppee.

Catalytic condensation of acetylene with phenols. II. Resorcinol. S. A. Flood and J. A. Nieuwland (J. Amer. Chem. Soc., 1928, **50**, 2566—2573).—2 : 4-*Dihydroxystyrene* (I) (+MeOH), decomp. above 250°, the intermediate product in the formation of 3 : 6-dihydroxy-9-methylxanthen (II) from resorcinol and acetylene in presence of a mercury catalyst (cf. A., 1924, i, 282), may be isolated from methyl-alcoholic solutions. Excess of acetylene causes resinification, and a similar resin is formed from acetal and resorcinol in presence of acid. The styrene I forms an insoluble *polymeride* when kept. It is reduced by tin and hydrochloric acid to ethylresorcinol, and its *diacetate*, m. p. 285—286°, is identical with the so-called acetalresorcinol diacetate of Causse (A., 1887, 40). With resorcinol in alcohol I gives the xanthen II. Resorcinol monomethyl ether gives amorphous products with acetylene, but the dimethyl ether gives 2 : 4-*dimethoxystyrene*, b. p. 235° (decomp.), which is oxidised by permanganate to 2 : 4-dimethoxybenzoic acid. The products I and II are also formed consecutively from acetaldehyde and resorcinol in methyl alcohol in presence of acid (cf. Möhlau and Koch, A., 1895, i, 46). H. E. F. Notton.

Reductive fission of dieugenyl ethylene ether. A. S. Pfau (Helv. Chim. Acta, 1928, **11**, 877—881).—Reduction of dieugenyl ethylene ether, m. p. 88—89° (lit. 85°; 1 part), with sodium (2 parts) and alcohol gives *m*-propylanisole (I), dihydroeugenyl β-hydroxyethyl ether, b. p. 170°/10 mm., m. p. 50·5°, *iso*eugenyl β-hydroxyethyl ether (II), m. p. 92—92·5°, and bisdihydroeugenyl ethylene ether (III), m. p. 104—104·5° (lit. 101°). When reduction is effected with 1 part of sodium the products are di-*iso*eugenyl ethylene ether, m. p. 118—119°, (I), (II), (III), and unchanged material. The first stage of the reduction is the isomerisation of the allyl to the propenyl group. H. Burton.

Naphthylene-1 : 8-disulphide. W. B. Price and S. Smiles (J.C.S., 1928, 2372—2374).—A continuation of previous work on the formation of sulphur ring systems (cf. this vol., 647, 769), which is now extended to five- and six-membered dithiorings involving the *peri*-system of naphthalene. 1-*Sulphinonaphthalene*-8-*sulphonic acid* is obtained by treatment of naphthalene-1 : 8-diazosulphonic acid with sulphurous acid and copper powder. Reduction of its *sodium* salt with sulphurous acid and dilute hydriodic acid yields 1 : 1′-*dithiodinaphthalene*-8 : 8′-*disulphonic acid*, from the di-sulphonyl chloride of which 1 : 1′-*dithiodinaphthalene*-8 : 8′-*disulphinic acid*, m. p. 144°, is obtained by reduction with sodium sulphite. Further reduction with zinc dust and alcoholic hydrochloric acid yields 1 : 8-*dithiolnaphthalene*, m. p. 113—114°, characterised by the *dimethylthiol*, m. p. 84°, and by a crystalline brownish-purple *nickel* derivative, $C_{10}H_6S_2Ni$. The dithiol is readily oxidised in air or with mild oxidising agents to *naphthylene*-1 : 8-*disulphide*, m. p. 116°, without the simultaneous formation of complex polysulphides, and condenses with benzaldehyde in the presence of hydrogen chloride to yield 2-*phenyl*-peri-*naphtha*-1 : 3-*dithian*, m. p. 116°. C. W. Shoppee.

Iodine values of some sterols by Dam's method. A. M. Copping (Biochem. J., 1928, **22**, 1142—1144).—Certain sterols and their derivatives yield abnormal values by the pyridine–sulphate–dibromide method (cf. Dam, A., 1925, ii, 444; i, 856). Ergosterol shows a high value. The presence of a ketonic group in the molecule, as in cholestenone, causes low values to be obtained. Structural differences within the molecule of the type represented by *allo*-cholesterol do not cause variations in the iodine values of sterols of the same empirical formula. Except in the case of ergosterol the duration of the reaction does not greatly affect the iodine value. S. S. Zilva.

Reduction of *p*-dimethylaminobenzaldehyde and preparation of *p*-dimethylaminobenzyl alcohol. G. R. Clemo and J. M. Smith (J.C.S., 1928, 2423—2426).—p-*Dimethylaminobenzyl alcohol* is obtained in 20% yield by reduction of the corresponding aldehyde with sodium amalgam in alcoholic solution as an oil, b. p. 123°/1 mm. [*benzoate*, m. p. 91°; m-*nitrobenzoate*, m. p. 76°; *methiodide*, m. p. 232° (decomp.); *chloroplatinate*, +2EtOH, m. p. 100° (decomp.); a picrate could not be prepared]; the substance described by Braun and Kruber (A., 1912, i, 968) as *p*-dimethylaminobenzyl alcohol picrate is probably dimethyl-*p*-toluidine picrate. Together with the alcohol is obtained a mixture of stereoisomeric s-*bis*-(p-*dimethylaminophenyl*)*ethylene glycols*, m. p. 113° [*dimethiodide* +EtOH, m. p. 97° (decomp.)] and m. p. 178° [*monomethiodide*, m. p. 232° (decomp.)], from which hydroxylic derivatives could not be prepared (cf. Rousset, A., 1895, i, 176). The alcohol could not be obtained from the aldehyde by treatment with potassium hydroxide (cf. Rousset, *loc. cit.*), and electrolytic reduction of the aldehyde yields a mixture of the alcohol, dimethyl-*p*-toluidine, 4 : 4-tetramethyldiaminodiphenylmethane, and the glycol, m. p. 178° (cf. Schepss, A., 1913, i, 1154).

C. W. Shoppee.

Dependence of rotatory power on chemical constitution. XXXII. Resolution of phenylbenzylcarbinol. W. Gerrard and J. Kenyon (J.C.S., 1928, 2564—2567).—To examine the effect of introducing two aromatic nuclei into the molecule of an aliphatic secondary alcohol the *d*- and *l*-forms of phenylbenzylcarbinol (Levene, A., 1925, i, 1375) were prepared by crystallising *quinine phenylbenzylcarbinyl phthalate* [*d*A,*l*B salt, m. p. 205° (decomp.)] and *cinchonine phenylbenzylcarbinyl phthalate* [*l*A,*d*B salt, m. p. 110°, $[\alpha]_{5461}^{25}$ $+82{\cdot}3°$ (in ethyl alcohol)], followed by acidification, giving the d- and l-*phenylbenzylcarbinyl hydrogen phthalates*, both m. p. 131°, $[\alpha]_{D}^{25}$ $+32{\cdot}75°$, $[\alpha]_{5461}^{25}$ $+38{\cdot}75°$, and $[\alpha]_{5461}^{25}$ $-38{\cdot}80°$, respectively (all in ethyl alcohol). Boiling with aqueous sodium hydroxide liberated d- and l-*phenylbenzylcarbinols*, both m. p. 67°, the specific rotatory powers of which, in both the homogeneous state at different temperatures and in various solvents together with the specific rotatory powers of l-*phenylbenzylcarbinyl acetate*, b. p. 182°/15 mm., in the homogeneous state at different temperatures and of *d*-phenylbenzylcarbinyl hydrogen phthalate in various solvents are recorded. The rotatory power of the carbinol at 20° is the highest yet recorded for a secondary alcohol. The homogeneous *d*-carbinol has $[\alpha]_{4358}$ $+16{\cdot}7°$ at 125° and $+120{\cdot}2°$ at 20°.

R. J. W. Le Fèvre.

Mobility of symmetrical triad (prototropic) systems. III. Three-carbon prototropy in an αγ-diphenylallyl ether. C. W. Shoppee (J.C.S., 1928, 2567—2571).—The assignation of one of two possible mechanisms (Burton and Ingold, this vol., 634; Ingold, Shoppee, and Thorpe, A., 1926, 939) for the change $OH{\cdot}CHR'{\cdot}CH{:}CHR'' \longrightarrow R'{\cdot}CO{\cdot}CH_2{\cdot}CH_2R''$ was attempted by examining an ether of type $\dot{O}R{\cdot}CR'{:}CH{\cdot}CH_2R''$, in which pinacolic electron displacement is precluded. αγ-Diphenylallyl alcohol (from cinnamaldehyde and magnesium phenyl bromide) gave, by treatment with hydrogen bromide in glacial acetic acid, *bis-αγ-diphenylallyl ether*, m. p. 98—99°, ozonolysis of which led to benzaldehyde and benzoic acid, whilst bromination gave *bis-βγ-dibromo-αγ-diphenylpropyl ether*. Boiling sodium ethoxide solution caused isomerisation to *bis-αγ-diphenylpropenyl ether*, the constitution of which followed from bromination in chloroform, giving *bis-β-bromo-αγ-diphenylpropenyl ether* [$(CH_2Ph{\cdot}CHBr{\cdot}CBrPh)_2O \longrightarrow (CH_2Ph{\cdot}CBr{:}CPh)_2O+2HBr$], and ozonolysis in acetic acid, yielding phenylacetaldehyde (isolated as semicarbazone) and benzoic acid. This occurrence of simple three-carbon prototropy (not involved in a pentad keto–enol complex) favours the second mechanism of Burton and Ingold (*loc. cit.*).

Phenyl β-phenylethyl ketone semicarbazone has m. p. 144°.

R. J. W. Le Fèvre.

Infra-red absorption spectra of organic compounds of sulphur. I. Aryl mercaptans and sulphides. F. K. Bell (Ber., 1928, **61**, [*B*], 1918—1923; cf. A., 1927, 1052).—The infra-red absorption spectra of benzyl mercaptan, thiophenol, thio-*p*-cresol, dibenzyl, and diphenyl sulphide have been investigated between 1·0 and 12·0 μ. The occurrence of a well-marked absorption band at 3·9 μ with the mercaptans which is not present with the sulphides allows a further extension of the author's method for the qualitative discrimination of these two classes of compounds (*loc. cit.*). The relative intensity of the 3·9 μ band is greatest for purely aryl mercaptans and least for the strictly aliphatic compounds. With arylalkyl and alkylaryl mercaptans the intensity is approximately the same and intermediate between that of the aryl and alkyl compounds.

H. Wren.

Existence of optically active carbonium salts. P. Karrer and A. Helfenstein (Helv. Chim. Acta, 1928, **11**, 842—847).—Phenyl-*o*-tolyldiphenylylmethyl chloride (I) reacts with α-methylglucoside in presence of pyridine, yielding the *phenyl*-o-*tolyldiphenylylmethyl α-methylglucoside ether*, $+0{\cdot}5H_2O$, m. p. 121°, which after one crystallisation from aqueous methyl alcohol has $[\alpha]_D$ $+49{\cdot}19°$ in methyl alcohol, and after three crystallisations $+55{\cdot}8°$. Decomposition of the ether with hydrogen chloride gives I, whilst with 0·2% alcoholic hydrochloric acid the *ethyl ether* of *phenyl*-o-*tolyldiphenylylcarbinol*, m. p. 144° after sintering at 142°, is obtained. Both these compounds are optically inactive. From *d*-camphylcarbinol and I the *phenyl*-o-*tolyldiphenylylmethyl* d-*camphylcarbinol ether* is obtained. This ether has m. p. 134°, $[\alpha]_D$ $+28{\cdot}86°$ in benzene, after one crystallisation from alcohol, and m. p. 148° (sinters at 145°), $[\alpha]_D$ $+13{\cdot}92°$, after four crystallisations. It is decomposed by hydrogen chloride, yielding I. The results indicate that in the ethers the carbinol radical exists in an optically active form, but the carbonium salts are very rapidly racemised.

H. Burton.

Oil-soluble bismuth salts; hexahydrobenzoate and camphocarbonate. M. Picon (J. Pharm. Chim., 1928, [viii], 8, 206—211; cf. this vol., 288).—Bismuth hexahydrobenzoate and camphocarbonate are prepared from bismuth oxide and the corresponding acids. *Bismuth hexahydrobenzoate*, $Bi(C_7H_{11}O_2)_3$, amorphous, pale yellow, is soluble in organic solvents not containing oxygen, but, with the exception of oils, it is decomposed by solvents containing oxygen in the molecule with the formation of the *basic hexahydrobenzoate*, $C_6H_{11}{\cdot}CO_2Bi{:}O$. The basic salt is also formed on treatment of the benzene solution of the neutral salt with water, but water alone has no action on the neutral salt, which is insoluble. *Bismuth camphocarbonate*, $Bi(C_{11}H_{15}O_3)_3$, is soluble without decomposition in all the usual organic solvents; it is insoluble in water and its solution in benzene is not attacked by water. Both salts are soluble in oils, forming solutions which yield stable emulsions with water.

E. H. Sharples.

Syntheses with diazomethane. F. Arndt, B. Eistert, and J. Amende (Ber., 1928, **61**, [*B*], 1949—1953; cf. Arndt and others, this vol., 739 and previous abstracts; Nierenstein, this vol., 739).—The amount of chloroacetophenone produced by the action of diazomethane on benzoyl chloride is determined by adding the product, after removal of ether, to a saturated solution of *o*-nitrophenylhydrazine in ether, whereby the chloro- but not the diazo-acetophenone is precipitated as the sparingly soluble *o*-nitrophenylhydrazone, m. p. 149°. From 5 g. of benzoyl chloride, 0·5 g. or 0·6 g. of chloroacetophenone is derived by the action of 2 mols. or 1 mol. of diazomethane. If ammonia is passed into the solution and the ammonium chloride removed before vaporisation of the ether, the amount of chloroacetophenone falls to 0·17 g. The bulk of the chloro-ketone is therefore produced from the diazo-ketone and free hydrogen chloride during removal of the ether. The authors accordingly share the views of Bradley and Robinson (this vol., 894) with regard to the mechanism of the action.

The authors conclude that the course of the action of diazomethane on aldehydes is governed generally by the nature of the aldehyde, although experimental conditions may have an important influence with certain definite aldehydes (cf. Mosettig, this vol., 887).

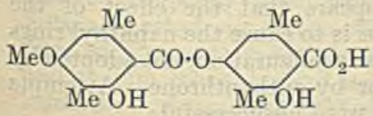
Acknowledgment is made that the isomerisation of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid is not specifically a photochemical change and that *o*-nitrophenylacetone (*o*-nitrobenzyl methyl ketone) has been obtained previously by Neber (A., 1925, i, 1073).

H. WREN.

Iminodicarboxylic and nitrilotricarboxylic acids. G. STADNIKOV and N. TITOV (Ber., 1928, **61**, [*B*], 1788—1789; cf. A., 1912, i, 116).—Nitrilodi-α-propionicphenylacetic acid, $(CO_2H\cdot CHMe)_2\!:\!N\cdot CHPh\cdot CO_2H$, m. p. 201° (decomp.), is converted by fuming hydrochloric acid at 160° into phenylglycine acid in almost quantitative yield. The same product is obtained analogously from anhydronitritodi*iso*butyricphenylacetic acid, $C_{16}H_{19}O_5N$, m. p. 187° (decomp.). Under these conditions the intermediate iminodiacetic acids are, therefore, also unstable. H. WREN.

Conversion of cyanonaphthalenesulphonic acids, and products of the conversion. I. G. FARBENIND. A.-G.—See B., 1928, 780.

Constituents of lichens. II. Constitution of barbatic acid. A. S. PFAU (Helv. Chim. Acta, 1928, **11**, 864—876; cf. Stenhouse and Groves, Annalen, 1880, **203**, 285; Hesse, A., 1903, i, 702).—Steam-distillation of the alcoholic extract from 35 kg. of the lichen *Evernia prunastri*, L. Ach., gives 2·5 g. of rhizonic acid (now shown to be 2-hydroxy-4-methoxy-3 : 6-dimethylbenzoic acid), m. p. 233—235° [*methyl* ester (I), m. p. 95°; *ethyl* ester (II), m. p. 82°], obtained also by the hydrolysis of barbatic acid (annexed formula), m. p. 191°, with barium hydroxide solution. The prolonged action of hot alcohol on barbatic acid affords II. Methylation of methyl β-orcinolcarboxylate (cf. A., 1926, 836) yields I together with *methyl* 2 : 4-*dimethoxy*-3 : 6-*dimethylbenzoate*, b. p. 161—163°/10 mm. (free *acid*, m. p. 104·5°). Treatment of a mixture of β-orcinol and formanilide with phosphorus oxychloride in absolute ether and decomposition of the resulting product with sodium hydroxide solution gives 2 : 4-*dihydroxy*-3 : 6-*dimethylbenzaldehyde*, m. p 163—164° [*oxime*, m. p. 224—225°; *semicarbazone*, m. p. 285° (decomp.)], methylated to 2-*hydroxy*-4-*methoxy*-3 : 6-*dimethylbenzaldehyde* (III), m. p. 136° (cf. Sonn, A., 1917, i, 143) (*oxime*, m. p. 188—189°).



When rhizonic acid is heated with copper powder at 200° β-orcinol monomethyl ether, b. p. 135—138°/10 mm., m. p. 67·5—68° (lit. 118—121°), is obtained. The action of formanilide and phosphorus oxychloride on this ether is to give III. Treatment of the *O*-acetyl derivative of III with zinc and ethyl bromoacetate in presence of benzene and subsequent hydrolysis of the product with alcoholic potassium hydroxide gives 5 : 8-*dimethylumbelliferone methyl ether*, m. p. 128—129°, thus demonstrating that in III the hydroxyl and aldehyde groups are in the *o*-position (cf. Sonn, *loc. cit.*).

The *iso*rhizonic acid from the lichen *Ramalina dilacerata*, Hoffm. (Nakao, J. Pharm. Soc. Japan, 1923, No. 496), and the rhizonic acids from *Evernia prunastri* and *Usnea ceratina* (Hesse, *loc. cit.*) are identical.

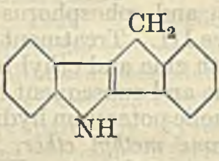
[With A. OFNER.]—β-Orcinol monomethyl ether undergoes the Gattermann reaction using zinc cyanide, yielding a mixture of 94% of III and 6% of 4-*hydroxy*-2-*methoxy*-3 : 6-*dimethylbenzaldehyde*, m. p. 150—150·5°, whilst orcinol monomethyl ether gives evernaldehyde (26%), m. p. 64°, and *iso*evernaldehyde (74%), m. p. 194—195° (lit. 188°). H. BURTON.

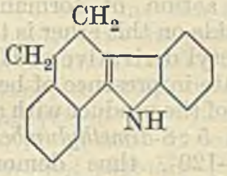
Thiophthalic acids. I. G. C. CHAKRAVARTI (J. Indian Chem. Soc., 1928, **5**, 405—410; cf. A., 1927, 970).—When phthalyl chloride is treated with alcoholic potassium hydrosulphide at −5 to 10° a mixture of 2 : 2′-*dicarboxydibenzoyl disulphide* (I), m. p. 242° (*potassium* and *lead* salts), monothiophthalic acid (II), m. p. 198° (decomp.; *sodium* and *lead* salts), *diphthalyl disulphide*, m. p. above 320°, and thiophthalic anhydride, m. p. 114°, is obtained. It is assumed that the primary product of the reaction is dithiophthalic acid, which, by loss of hydrogen sulphide, gives thiophthalic anhydride, and by atmospheric oxidation, diphthalyl disulphide. By the action of water it gives monothiophthalic acid, which oxidises with great readiness to (I). Hydrolysis of ditolyl dithiophthalate with alcoholic potassium hydrosulphide at 120° in a sealed tube gives I, also formed by oxidation of II when its ethereal solution is evaporated.

H. BURTON.

Conditions of formation of rings attached to the *o*-, *m*-, and *p*-positions of the benzene nucleus. III. A. F. TITLEY (J.C.S., 1928, 2571—2583).—Attempts are described to effect ring closure by the Dieckmann reaction between the *o*-, *m*-, and *p*-positions in esters of general formula $CO_2R\cdot C_6H_4\cdot[CH_2]_n\cdot CO_2R$ and $C_6H_4([CH_2]_n\cdot CO_2R)_2$. Thus *ethyl* β-o-*carbethoxyphenylpropionate*, b. p. 182—183°/14 mm. (from *o*-aldehydobenzoic acid and malonic acid by way of *o*-carboxycinnamic acid, by sodium amalgam reduction and esterification of the product) reacted with sodium under toluene at 100° to form successively ethyl sodio-1-hydrindone-2-carboxylate (I) and ethyl 1-hydrindone-2-carboxylate (cf. Mitchell and Thorpe, J.C.S., 1910, **97**, 2273). The phenylhydrazone of the last ester was converted by hydrochloric acid into 2 : 3-*indeno*-(1 : 2)-*indole* (II), m. p. 251° (cf. Armit and Robinson, *ibid.*, 1922, **121**, 838). Methylation (methyl iodide) of I gave ethyl 2-methyl-1-hydrindone-2-carboxylate, which did not form a phenylhydrazone or a semicarbazide. Hydrolysis gave, besides 2-methyl-1-hydrindone (Mitchell and Thorpe, *loc. cit.*), β-o-*carboxyphenyl*iso*butyric acid*, m. p. 141°.

(II.)

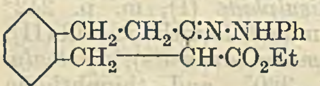




(III.)

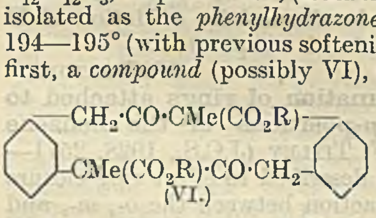
Ethyl γ-o-carbethoxyphenyl-n-*butyrate*, b. p. 188—189°/14 mm., with sodium gave ethyl 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate (IV), m. p. 33° (Hückel and Goth, A., 1924, i, 1196, give 34°), converted by treatment with phenylhydrazine hydrochloride and hydrochloric acid into 1 : 2-*indolo*-(2 : 3)-3 : 4-*dihydronaphthalene* (III), m. p. 161°. By the methyl iodide methylation of the sodio-derivative of IV, *ethyl* 1-*keto-2-methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene-2-carboxylate*, b. p. 183—184°/18 mm., was obtained, acid hydrolysis of which led to 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 143°/20 mm., whilst alkaline hydrolysis gave a mixture of this ketone with *γ-o-carboxyphenyl-α-methylbutyric acid*, m. p. 173°.

Ethyl o-*phenylenedipropionate*, b. p. 200—202°/12 mm., and sodium gave low yields of the *phenylhydrazone* of *ethyl 3-ketophenheptamethylene-2-carboxylate* (V), m. p. 198° (decomp.).



(V.)

No ring compounds were obtained by the action of sodium at 100° on *methyl* m-*phenylenediacetate*, b. p. 185—187°/15 mm., *ethyl* m-*phenylenediacetate*, b. p. 188—189°/12 mm., *methyl* p-*phenylenediacetate*, b. p. 189—190°/15 mm., or *ethyl* p-*phenylenediacetate*, m. p. 59° (all prepared by hydrolysis of corresponding nitriles by methyl- or ethyl-alcoholic hydrogen chloride), the only isolable products being: (from the second) a *compound*, $C_{12}H_{12}O_3$, m. p. 30—40°; (from the fourth) a *compound*, isolated as the *phenylhydrazone*, $C_{18}H_{18}O_2N_2$, m. p. 194—195° (with previous softening at 190°); from the first, a *compound* (possibly VI), $C_{24}H_{24}O_6$, b. p. 217—222°/1 mm., giving on alkaline hydrolysis an alkali-soluble *substance*, $C_{22}H_{18}O_5$, m. p. 345—346° (sintering at 340°), and also a fraction yielding by hydrolysis *m*-phenylenediacetic acid and *phenylene*-1-*acetic*-3-*α-propionic acid*, m. p. 132°, and from the third a *substance*, $C_{24}H_{24}O_6$, b. p. 225—228°/1 mm., together with (after hydrolysis) *p*-phenylenediacetic acid and *phenylene-1-acetic-4-α-propionic acid*, m. p. 189°.



(VI.)

The *methyl* ester, b. p. 184—185°/15 mm., of m-*carboxyphenylpropionic acid*, m. p. 177° (from *iso*phthalaldehydic acid and malonic acid through *m*-carboxycinnamic acid by sodium-amalgam reduction), by treatment with sodium etc. led only to β-m-*carboxyphenyl*iso*butyric acid*, m. p. 137—138° (corr.), synthesised by the following sequence: *m*-toluoyl chloride to *ω-chloro*-m-*toluoyl chloride*, b. p. 149—150°/20 mm. (direct chlorination), to *ethyl ω-chloro*-m-*toluate*, b. p. 168—169°/25 mm., to *ethyl* m-*carbethoxybenzylmethylmalonate*, b. p. 234°/24 mm., to the corresponding *acid*, m. p. 182—183° (decomp.), to β-*m*-carboxyphenyl*iso*butyric acid (*methyl* ester, b. p. 182°/18 mm.) identical with the compound above.

p-Carboxyphenylpropionic acid was prepared by two methods: (1) *p*-toluoyl chloride gave on bromination ω-bromo-*p*-toluoyl chloride, *ω-bromo*-p-*toluoyl bromide*, b. p. 170—171°/20 mm., m. p. 56°, and ωω-dibromo-*p*-toluoyl chloride and bromide (which gave with alcohol *ethyl ωω-dibromo*-p-*toluate*, m. p. 103°). The second of these gave *ethyl ω-bromo*-p-*toluate*, b. p. 165°/18 mm., m. p. 35—36°, which, by condensation with ethyl chloromalonate, gave *ethyl chloro*-p-*carbethoxybenzylmalonate*, b. p. 235°/20 mm., m. p. 54—55°, leading, by reduction with zinc dust and acetic acid, to *ethyl* p-*carbethoxybenzylmalonate*, b. p. 218—219°/15 mm. Hydrolysis gave p-*carboxybenzylmalonic acid*, m. p. 186—188°, which, on heating, gave *p*-carboxyphenylpropionic acid; (2) *p*-carboxycinnamic acid, m. p. 358° (decomp.) (*ethyl* ester, m. p. 52°), from terephthalaldehydic and malonic acids, gave on reduction with sodium amalgam *p*-carboxyphenylpropionic acid, m. p. 294° (lit. 280°) (*methyl* ester, m. p. 33°). *Ethyl* m-*phenylenedipropionate*, b. p. 197—198°/15 mm., and *ethyl* p-*phenylenedipropionate*, m. p. 67°, were prepared by the method of Kipping (J.C.S., 1888, **53**, 21).

R. J. W. LE FÈVRE.

Stereochemistry of aromatic compounds. VII. Inclination of rings in α-dinaphthyls. R. KUHN and O. ALBRECHT (Annalen, 1928, **465**, 282—287).—1 : 1′-Dinaphthyl-2 : 2′-dicarboxylic acid, new m. p. 268·5—270° (corr.), obtained from 1-chloro-2-naphthoyl chloride by way of methyl 1-chloro-2-naphthoate (cf. Kalb, A., 1914, i, 850), has been resolved by way of its *quinine* salt, m. p. about 202° (decomp.), $[\alpha]_D^{22}$ +230·4° (in chloroform), which is separated by crystallisation from ether into the *salt*, m. p. 197·5—198°, $[\alpha]_D^{24}$ +301·6° (in chloroform), of l-1 : 1′-*dinaphthyl-2 : 2′-dicarboxylic acid*, m. p. 177° (uncorr.) after becoming transparent at 145°, $[\alpha]_D^{22}$ −101·6°, and the impure *salt*, m. p. about 230°, $[\alpha]_D^{22\cdot5}$ +15·4°, of d-1 : 1′-*dinaphthyl-2 : 2′-dicarboxylic acid*, m. p. 239—248° (uncorr.) after sintering at about 185°, $[\alpha]_D^{22}$ +46° (in 0·1*N*-sodium hydroxide solution). The last when treated with sulphuric acid gave anthanthrone (Kalb, *loc. cit.*) with no apparent optical rotation. It thus appears that the effect of the 2 : 2′-dicarboxyl groups is to cause the naphthyl rings to assume a multiplanar configuration, not adopted by α-dinaphthyl itself, nor by anthanthrone. Attempts to racemise the *l*-acid were unsuccessful.

E. W. WIGNALL.

Addition reactions of unsaturated α-ketonic acids. II. M. REIMER and M. HOWARD (J. Amer. Chem. Soc., 1928, **50**, 2506—2512).—*o-Methoxybenzylidenepyruvic acid* (*o*-methoxystyrylglyoxylic acid) (I), orange-red, m. p. 131° (*ethyl* ester, b. p.

223°/15 mm.), has been prepared for comparison with the *p*-methoxy-derivative (A., 1926, 1139), from *o*-methoxybenzaldehyde and pyruvic acid in 10% sodium hydroxide at 0°. The acid and its *methyl* ester, m. p. 48°, are rapidly altered in sunlight. The former gives in chloroform an impure *dibromide*, m. p. 90° (decomp.), which decomposes in boiling benzene into β-*bromo*-o-*methoxystyrylglyoxylic acid*, m. p. 173°. This may also be obtained by direct bromination of the acid I or of its methyl ester; it is oxidised by alkaline hydrogen peroxide to α-bromo-*o*-methoxycinnamic acid and converted by diazomethane into its *methyl* ester, m. p. 88—89°. With 2 mols. of bromine the acid I yields impure 5-*bromo-2-methoxystyrylglyoxylic acid dibromide*, m. p. 95—100°, which decomposes in boiling 40% acetic acid into colourless β : 5-*dibromo-2-methoxystyrylglyoxylic acid*, m. p. 210° (*methyl* ester, m. p. 131°). An isomeric yellow β : 5-*dibromo-acid* (pale yellow *methyl* ester, m. p. 143°), which passes into the colourless form at 145—150°, is obtained by hydrolysing the *methyl* ester, m. p. 103—106°, of the dibromide with potassium methoxide. The series of colour changes (tabulated for 21 acids) given by the styrylglyoxylic acids with cold concentrated sulphuric acid is dependent on the presence of the ketonic group and differs sharply with the nature and position of other substituents. Thus, successive introduction of (*a*) *o*- and *p*-methoxyl, (*b*) bromine into the side-chain, and (*c*) bromine into the ring, changes the yellow to brown colour given by styrylglyoxylic acid to (*a*) *o*-, red; *p*-, orange; (*b*) orange to reddish-violet, and (*c*) green to blue. Increase in the number of substituents has, therefore, the same effect on the colour reaction as increase in the number of conjugated linkings (cf. Kuhn and Winterstein, this vol., 281). H. E. F. NOTTON.

Action of sodium benzyl cyanide with cinnamic ester. II. S. AVERY (J. Amer. Chem. Soc., 1928, **50**, 2512—2519).—γ-Cyano-βγ-diphenylbutyric acid is converted by methyl alcohol and hydrogen chloride into its *methyl* ester, m. p. 106·5° (all m. p. corr.), which is also formed from phenylacetonitrile and methyl or ethyl cinnamate in presence of sodium methoxide (cf. A., 1908, i, 343, 796). It is hydrolysed by alcoholic potassium hydroxide to γ-*carbamyl*-βγ-*diphenylbutyric acid*, m. p. 200—205° (decomp.), and by hydrochloric acid at 150° to αβ-diphenylglutaric acid, m. p. 225—228°, the methyl ester, m. p. 143·0°, of which is identical and not stereoisomeric (cf. Meerwein and Dott, A., 1919, i, 21) with that prepared by Borsche's method (A., 1910, i, 35). The product obtained by Erlenmeyer (A., 1900, i, 493) from 1 mol. of phenylacetonitrile and 2 mols. of ethyl cinnamate may also be prepared from ethyl γ-cyano-βγ-diphenylbutyrate, ethyl cinnamate, and sodium ethoxide, or from *ethyl* γ-*cyano*-βγδ-*triphenylpimelate*, m. p. 102·5°, and sodium ethoxide, and is therefore *ethyl* 5-*cyano*-2-*keto*-4 : 5 : 6-*triphenylhexahydrobenzoate*, m. p. 208—209°. The corresponding *methyl* ester, m. p. 242—244°, an impure specimen of which was previously regarded as γ-cyano-βγδ-triphenylpimelic anhydride, is prepared similarly from methyl cinnamate or from *methyl* γ-*cyano*-βγδ-*triphenylpimelate*, m. p. 108·2°. H. E. F. NOTTON.

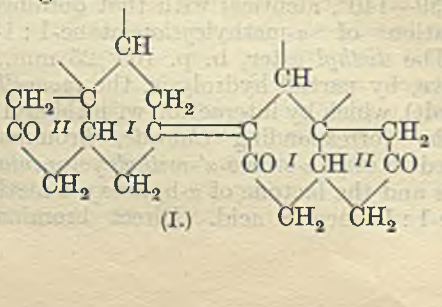
Syntheses of certain γ-ketonic acids allied to Balbiano's acid. I. Syntheses of α-methyl*cyclo*pentane-1 : 1-diacetic acid; the lactone of α-hydroxy-α-methyl*cyclo*pentane-1 : 1-diacetic acid, and 1-acetyl*cyclo*pentane-1-acetic acid. J. C. BARDHAN (J.C.S., 1928, 2591—2604).—Unsuccessful attempts to synthesise α-methyl-γ-keto*cyclo*pentane-1 : 1-diacetic acid (*cyclo*pentane analogue of Balbiano's acid) are described. The *anhydride*, b. p. 193°/24 mm., m. p. 48° [giving a β-*naphthylamic acid*, $C_{10}H_7\cdot NH\cdot CO\cdot CHMe\cdot C(:C_4H_8)\cdot CH_2\cdot CO_2H$(?), m. p. 133—134°, which when heated passed into the β-*naphthylimide*, m. p. 179°], of α-*methyl*cyclo*pentane*-1 : 1-*diacetic acid*, m. p. 90—91° (*silver* salt; *imide*, m. p. 123—124°) (prepared, along with small quantities of a *substance*, $C_{13}H_{16}O_4N_2$, m. p. 223—224°, by acid hydrolysis of the N-*methyl*-ω-*imide* of αα'-*dicyano*-α-*methyl*cyclo*pentane*-1 : 1-*diacetic acid*, m. p. 136—137°, obtained by methyl iodide–sodium ethoxide methylation of the condensation product from *cyclo*pentanone, ethyl cyanoacetate, and alcoholic ammonia), gave on bromination in a sealed tube α-*bromo*-α-*methyl*cyclo*pentane*-1 : 1-*diacetic anhydride*, m. p. 95°, which by alkaline hydrolysis yielded the *lactone* of α-*hydroxy*-α-*methyl*cyclo*pentane*-1 : 1-*diacetic acid*, m. p. 140° (*silver*, *lead*, and *barium* salts; *ethyl* ester, b. p. 197°/30 mm.). The last acid was synthesised as follows: the *anhydride*, b. p. 154°/20 mm., m. p. 30° (*anilic acid*, m. p. 167—167·5°; *anil*, m. p. 127—128°), of *cyclo*pentane-1-acetic-1-carboxylic acid (Lapworth and McRae, J.C.S., 1922, **121**, 2754) was converted successively into the corresponding *monomethyl* ester, m. p. 80—81°, and *monomethyl* ester *chloride*, b. p. 132°/16 mm. (p-*toluidide*, m. p. 111°), which, by interaction with zinc methyl iodide followed by alkaline hydrolysis of the product (I) gave 1-*acetyl*cyclo*pentane*-1-*acetic acid* (II), m. p. 83—84° (*semicarbazone*, m. p. 197°; *oxime*, m. p. 124—125°; *methyl* ester, b. p. 131°/18 mm.; *methyl* ester *semicarbazone*, m. p. 152—153°). The constitution of II was proved by its reduction by sodium and ethyl alcohol, giving the *lactone*, b. p. 132°/15 mm., $d_4^{15\cdot8}$ 1·057645, $n_D^{15\cdot8}$ 1·4742, $[R_L]_D$ 40·9, of α-hydroxy-α-methyl*cyclo*pentane-1 : 1-diacetic acid, which, when heated with potassium cyanide under pressure, yielded, after acid hydrolysis of the resulting product, α-methyl*cyclo*pentane-1 : 1-diacetic acid.

The product I on oxidation with alkaline permanganate gave α-keto*cyclo*pentane-1 : 1-diacetic acid (Lanfear and Thorpe, J.C.S., 1923, **123**, 1688), which with *o*-phenylenediamine formed the quinoxaline of α-keto*cyclo*pentane-1 : 1-diacetic acid, m. p. 221° (lit., 222°). II reacted with hydrocyanic acid, giving 1-α-*cyano*-α-*hydroxyethyl*cyclo*pentane*-1-*acetic acid*, which by acid hydrolysis gave a lactonic acid, m. p. 139—140°, identical with that obtained in the bromination of α-methyl*cyclo*pentane-1 : 1-diacetic acid. The *diethyl* ester, b. p. 165°/25 mm., of this acid gave, by partial hydrolysis, the *monoethyl* ester (*silver* salt), which by interaction with thionyl chloride gave the corresponding *chloride*, bromination of which led to *ethyl* α-*bromo*-α'-*methyl*cyclo*pentane*-1 : 1-*diacetate* and the lactone of α-hydroxy-α-methyl*cyclo*pentane-1 : 1-diacetic acid. Direct bromination of the *N*-methyl-ω-imide of αγ-dicyano-α-methyl*cyclo*pentane-1 : 1-diacetic acid readily yielded the *methylimide* of *α-bromo-αγ-dicyano-γ-methyl*cyclo*pentane-1 : 1-diacetic acid*, m. p. 180° (decomp.), which lost bromine on acid hydrolysis, giving only α-methyl*cyclo*pentane-1 : 1-diacetic acid. The Blaise reaction applied to α-methyl*cyclo*pentylideneacetic acid (from *cyclo*pentanone, ethyl α-bromopropionate, and magnesium) (*acid chloride*, b. p. 123°/30 mm.) gave *α-methyl*cyclo*pentylideneacetone* [two stereoisomeric(?) *semicarbazones*, m. p. 189° and 169°, from which were regenerated *ketones* with b. p. 108°/27 mm., 109°/25 mm., $d_4^{19\cdot2}$ 0·960808, $d_4^{20\cdot3}$ 0·958084, $n_D^{19\cdot2}$ 1·49642, $n_D^{20\cdot3}$ 1·49528, $[R_L]_D$ 41·986, 42·025, respectively].

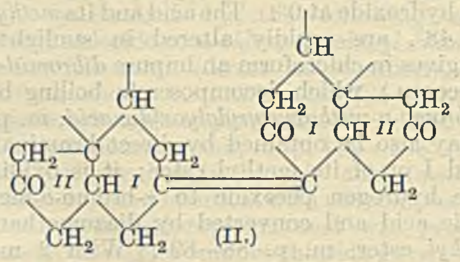
*α-Methyl-Δ¹-*cyclo*pentenylacetic acid*, b. p. 108—110°/30 mm., $d_4^{17\cdot7}$ 0·96668, $n_D^{17\cdot7}$ 1·4583, $[R_L]_D$ 47·45 (obtained by dehydration of the corresponding ester with phosphorus oxychloride), gave by hydrolysis the *acid*, b. p. 150°/28 mm., $d_4^{19\cdot7}$ 1·050988, $n_D^{18\cdot5}$ 1·4792, $[R_L]_D$ 37·79 (cf. Wallach and Martius, A., 1909, i, 383). The *acid chloride*, b. p. 86—88°/20 mm., gave with zinc methyl iodide *α-methyl-Δ¹-*cyclo*pentenylacetone*, b. p. 82°/17 mm., d_4^{20} 0·921922, n_D^{20} 1·4632, $[R_L]_D$ 41·24 (*semicarbazone*, m. p. 144°). R. J. W. Le Fèvre.

Molecular configurations of polynuclear aromatic compounds. VIII. 6 : 6′-Dimethoxydiphenic acid. J. Kenner and H. A. Turner (J.C.S., 1928, 2340—2343).—2-Nitro-*m*-cresol, prepared by the method of Gibson (*ibid.*, 1923, **123**, 1273; cf. Hodgson and Beard, A., 1925, i, 540), when methylated and oxidised yields 2-nitro-3-methoxybenzoic acid, which is converted by reduction and diazotisation into *2-iodo-3-methoxybenzoic acid*, m. p. 150—151°. The *methyl* ester, m. p. 57°, is converted by copper powder at 205—210° into *methyl 6 : 6′-dimethoxydiphenate*, m. p. 137—138°, from which *6 : 6′-dimethoxydiphenic acid*, m. p. 288—290° (decomp.), is obtained (*brucine hydrogen* salt, m. p. 268°). Resolution of the acid is accomplished through the quinine salts; *quinine l-6 : 6′-dimethoxydiphenate*, m. p. 172—173°, [α]D +126°, yields the free *l-acid*, m. p. 294—295°, [α]D −115°. *Quinine d-6 : 6′-dimethoxydiphenate* was obtained as a powder which shrank and decomposed about 60°, and had [α]D −68°. An incomplete resolution was obtained by using quinidine. C. W. Shoppee.

Bile acids. XIV. Condensation of dehydrocholic acid with itself and with aromatic aldehydes. W. Borsche and E. Feske (Z. physiol. Chem., 1928, **178**, 148—155).—When dehydrocholic acid is heated in a sealed tube at 250° for 3—4 hrs., heated in a stream of carbon dioxide at 300° for 2 hrs., or treated with hydrogen chloride in acetic acid and kept for several days, an *acid*, $C_{48}H_{66}O_9$, m. p. 309—310°, is obtained to which the constitution I or II is assigned. This is analogous to the acid $C_{48}H_{70}O_7$ described by Shimizu (A., 1923, i, 40), which may be prepared under the same conditions from dehydrodeoxycholic acid.



(I.)



(II.)

The acid $C_{48}H_{66}O_9$ yields a *dimethyl* ester, m. p. 265°, on treatment with diazomethane, and a *pentoxime*, m. p. 229° (sintering at 210°). Reduction with hydrogen and an active platinum catalyst yields a substance, considered to be *pentahydroxydicholanic acid*, of the composition $C_{48}H_{78}O_9,H_2O$ or $2C_{48}H_{78}O_9,AcOH$, m. p. 245—246° after sintering at 220°.

A mixture of benzaldehyde and dehydrocholic acid when heated in a sealed tube at 250—255° or treated with hydrogen chloride in acetic acid for a week at the ordinary temperature yielded *β-dibenzylidenedehydrocholic acid*, m. p. 219—220°, which becomes deep yellow in daylight. This would appear to have the same constitution as that assigned to (α-)dibenzylidenedehydrocholic acid, obtained by condensation in presence of sodium hydroxide (A., 1924, i, 1200), since bilianic acid, in which the ring I, containing the reactive methylene groups, is broken, does not condense with aldehydes under any conditions tried. Attempts to convert the α- into the β-form were, however, unsuccessful. *Di-*p*-chlorobenzylidenedehydrocholic acid*, m. p. 249°, was also prepared. R. K. Callow.

Isomerisation of di*cyclo*hexylacetaldehyde to a ketone. E. Venus-Danilova (Ber., 1928, **61**, [*B*], 1954—1966).—The action of magnesium *cyclo*hexyl bromide on ethyl ethoxyacetate affords a mixture of ethyl *cyclo*hexylacetate, *α-hydroxy-β-ethoxy-α-*cyclo*hexylethane*, b. p. 108°/23 mm. (oxidised to *cyclo*hexanecarboxylic acid and isomerised by sulphuric or oxalic acid to *cyclo*hexylacetaldehyde), di*cyclo*hexyl, and *α-hydroxy-β-ethoxy-αα-di*cyclo*hexylethane*, m. p. 53°. The last substance is converted by crystalline oxalic acid at 112—118° into *di*cyclo*hexylacetaldehyde*, b. p. 153—153·5°/11 mm., d_4^{20} 0·9621, which reacts only sluggishly with magenta and sulphurous acid, ammoniacal silver oxide, or sodium hydrogen sulphite, but readily yields a *semicarbazone*, m. p. 184—184·5°, and an *oxime*, m. p. 108—109°. The aldehyde is oxidised to *di*cyclo*hexylacetic acid*, m. p. 134—135° (*ammonium*, anhydrous and monohydrated *calcium* and *silver* salts), converted into the corresponding *chloride* and thence into the *anilide*, m. p. 203°, and *amide*, m. p. 188—189°.

The action of magnesium on a mixture of the iodohydrin of *cyclo*hexylcarbinol and hexahydrobenzaldehyde gives *cyclo*hexylcarbinol, *αβ-di*cyclo*hexylethane*, b. p. 136°/15 mm., and *αβ-di*cyclo*hexylethyl alcohol*, b. p. 162—164°/14 mm., m. p. 64—65°. The last-named compound is oxidised by potassium dichromate and sulphuric acid to *αβ-di*cyclo*hexyl-*

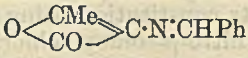
ethanone (*dodecahydrodeoxybenzoin*), b. p. 172—173°/26 mm., d_4^{20} 0·9511 (*semicarbazone*, m. p. 190—191°; *oxime*, m. p. 112—113°), which is converted by alcoholic potassium hydroxide into *cyclo*hexane and *cyclo*hexylacetic acid.

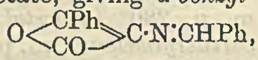
Di*cyclo*hexylacetaldehyde is isomerised to αβ-di*cyclo*hexylethanone when heated with dilute sulphuric acid or alcoholic mercuric chloride, by cold, concentrated sulphuric acid, or by decomposition of its semicarbazone with sufficiently concentrated sulphuric acid. H. WREN.

Conditions determining thermodynamic stability of cyanohydrins of carbonyl compounds. I. Effects of (*a*) substitution in aromatic aldehydes and (*b*) ring formation. A. LAPWORTH and R. H. F. MANSKE (J.C.S., 1928, 2533—2549).—The equilibrium constants ($K=C_{\mathrm{R_2CO}}\times C_{\mathrm{HCN}}/C_{\mathrm{OH\cdot CR_2\cdot CN}}$) for the dissociation of a number of aldehyde and ketone cyanohydrins have been determined in 96% alcohol at 20°±0·5°. The values of the free energy of dissociation ($\Delta F=1\cdot99\times 293\log_e K$) are relative measures of the depressant effects of substituents on the affinity of the aldehyde for hydrogen cyanide, and for nuclear-substituted benzaldehydes are as follows: *o*-substituents: $\mathrm{OH}>\mathrm{H}>\mathrm{OMe}>\mathrm{Cl}>\mathrm{NO_2}$; *m*-substituents: $\mathrm{Me}>\mathrm{OH}$, $\mathrm{H}>\mathrm{OMe}>\mathrm{NO_2}>\mathrm{Cl}$; *p*-substituents: $\mathrm{NMe_2}>\mathrm{OH}>\mathrm{OMe}>\mathrm{NO_2}>\mathrm{Me}>\mathrm{Cl}>\mathrm{H}$. The factors influencing the ionisation constants of benzoic acids (Flürscheim, J.C.S., 1909, **95**, 726) are found similarly to affect the dissociation constants of benzaldehydecyanohydrins, although the "electropolar" factor has relatively less importance in the *p*-substituted cyanohydrins and the "quantitative" factor little effect in the *meta*-series. The position of OH in the *ortho*-series is attributed to chelation between the hydroxyl and carbonyl group (Sidgwick and Callow, A., 1924, i, 506; 1925, i, 630), which would operate to reduce the stability of the cyanohydrin, and that of NO_2 in the *para*-series to the stabilising influence of a "Thiele" alternation of single and double linkings. Ring formation from a chain containing a carbonyl group leads sometimes to a large increase and sometimes to a large decrease in the dissociation constants of the derived cyanohydrins.

The bearing of the results on electronic theories is discussed and the suggestion made that the additive capacity of carbonyl and ethylenic carbon does not increase continuously with electron restraint, but reaches a maximum and then declines.

R. J. W. LE FÈVRE.

Syntheses in the amino-acid group. I. Condensation of aldoximes with esters of β-ketonic acids. G. MINUNNI and S. D'URSO (Gazzetta, 1928, **58**, 485—504; cf. A., 1925, i, 1175).—In presence of zinc chloride at 120—125° or of crystallised phosphoric acid at 110—115°, benzaldoxime and ethyl acetoacetate condense to form *α-benzylideneaminocrotono-β-lactone*,  $\mathrm{O}\!<\!\begin{smallmatrix}\mathrm{CMe}\\\mathrm{CO}\end{smallmatrix}\!>\!\mathrm{C\cdot N{:}CHPh}$, m. p. 146·5—147·5°, which, when either heated at 85—90° and then treated with potassium hydroxide or treated with hydroxylamine or its hydrochloride, yields a *compound*, m. p. 150—151°, to be studied further; when heated with phenylhydrazine in suspension in 50% alcohol, the β-lactone yields benzaldehydephenylhydrazone quantitatively and a compound which could not be obtained pure enough for analysis. The above condensation occurs in stages and yields first ethyl α-benzylideneaminoacetoacetate, $\mathrm{CO_2Et\cdot CHAc\cdot N{:}CHPh}$, this undergoing conversion into its enolic form and losing a molecule of alcohol with formation of the β-lactone.

[With G. TERRANOVA.]—Similar condensation takes place, in presence of phosphoric acid, between benzaldoxime and ethyl benzoylacetate, giving *α-benzylideneaminocinnamo-β-lactone*,  $\mathrm{O}\!<\!\begin{smallmatrix}\mathrm{CPh}\\\mathrm{CO}\end{smallmatrix}\!>\!\mathrm{C\cdot N{:}CHPh}$, m. p. 194—195°, which when heated with 1% potassium hydroxide solution yields benzaldehyde and a *compound*, m. p. 191—193°; with phenylhydrazine, the β-lactone gives the *compound* $C_{22}H_{19}O_2N_3$, decomposing at 140°. In presence of zinc chloride, however, benzaldoxime and ethyl benzoylacetate give a *compound*, C_7H_7ON, m. p. 132·5—133·5°, which, together with another *compound*, m. p. 226—227°, is formed also when zinc chloride acts on benzaldoxime alone. T. H. POPE.

Synthesis of aldehydes by means of iron pentacarbonyl. H. WOLF (Ber., 1928, **61**, [*B*], 1765—1766).—A modification of the Gattermann synthesis is described in which carbon monoxide is replaced by iron pentacarbonyl. A mixture of 17·5 g. of iron pentacarbonyl (=12 g. of carbon monoxide), 30 g. of toluene, and 45 g. of aluminium chloride saturated during 3 hrs. with hydrogen chloride at 40—45° yields 13—16 g. of *p*-tolualdehyde.

H. WREN.

By-products of the Gattermann aldehyde reaction. F. BELL and T. A. HENRY (J.C.S., 1928, 2215—2227).—When the Gattermann aldehyde reaction, as modified by Adams and Montgomery (A., 1924, i, 860), is applied to alkylphenols, two secondary reactions occur: (*a*) a reversible Friedel–Crafts reaction, whereby the alkyl group is partly transferred to the solvent used; thus, in the case of thymol, with benzene as solvent, small quantities of *iso*propylbenzene and *m*-cresolaldehyde are formed; (*b*) condensation of the cyanohydrin of the phenolaldehyde with unchanged phenol to give, for example, in the case of thymol, dithymylacetonitrile.

Investigation of the conditions of formation of such diarylacetonitriles by reaction of cyanohydrins with the corresponding phenol in presence of hydrogen cyanide shows that, under the conditions finally selected (when an alcoholic solution of equimolecular quantities of the aldehyde and phenol was treated with hydrogen cyanide and the mixture heated to the b. p. after addition of zinc chloride), the aldehydecyanohydrins may (1) be too stable to undergo condensation, (2) condense with the elimination of hydrogen cyanide to produce eventually triarylmethanes, or (3) condense with elimination of water to form diarylacetonitriles. These different types of behaviour are conditioned by the nature and orientation of the substituents in the aldehydes used. The sole example of class (1) is *o*-nitrobenzaldehyde. Class (2) includes benzaldehyde itself, *o*- or *p*-chloro-, *m*- or *p*-nitro-, and *m*-hydroxybenzaldehyde. Class (3) is represented by thymolaldehyde, carvacrolaldehyde, *o*-cresolaldehyde, salicylaldehyde, *p*-hydroxybenzaldehyde, anisaldehyde, and protocatechualdehyde. The following are described: *semicarbazones*, m. p. 198° and 226°, of 2- and 4-aldehydo-3-methyl-6-*iso*propylphenol; *semicarbazone*, m. p. 275°, of 4-hydroxy-3-aldehydo-5-methyl-2-*iso*propylphenyldicarvacryl-methane (?); *semicarbazones*, m. p. 180° and 224°, of 2- and 4-aldehydo-6-methyl-3-*iso*propylphenol; *semicarbazones*, m. p. 216° and 248° (decomp.), of 4- and 6-aldehydo-2-methylphenol; *trithymylmethane*, m. p. 280° (*triacetyl* derivative, m. p. 186°); *tricarvacrylmethane*, m. p. 275° (*triacetyl* derivative, m. p. 185°); *dithymylacetonitrile*, m. p. 205° (*diacetyl* derivative, m. p. 174°); *dithymylacetamide*, m. p. 243° (decomp.); *dicarvacrylacetonitrile*, m. p. 240° (*diacetyl* derivative, m. p. 196°); *thymylcarvacrylacetonitrile*, m. p. 227° (*diacetyl* derivative, m. p. 145°); *tolylthymylacetonitrile*, m. p. 153°; *tolylthymylacetamide*, m. p. 211°; *tolylthymylacetic acid*, m. p. 188°; *acetyltolylacetylthymylacetonitrile*, m. p. 131°; o- and p-*hydroxyphenylthymylacetonitrile*, m. p. 142° and 144°; *anisylthymylacetonitrile*, m. p. 106°; *pyrocatechylthymylacetonitrile*, m. p. 147—149°; m-*hydroxyphenyldithymylmethane*, m. p. 165°; m- and p-*nitrophenyldithymylmethane*, m. p. 171° and 145°; o- and p-*chlorophenyldithymylmethane*, m. p. 138° and 156°.

M. Clark.

Bromine substitution products of vanillin and some derivatives. L. C. Raiford and W. C. Stoesser (J. Amer. Chem. Soc., 1928, **50**, 2556—2563).—In continuation of previous work (A., 1927, 564, 768) it is shown that one *o*-substituent has no noticeable effect on the reactivity of the aldehyde group in vanillin derivatives, whilst two *o*-substituents cause less than the expected diminution in reactivity. In agreement with the results of Brady and Dunn (J.C.S., 1915, **107**, 1859), the (? *anti*-)oximes of bromovanillins could not be isomerised by means of hydrogen chloride or by Goldschmidt's method. 6-Bromovanillinoxime yields an *acetate*, m. p. 149—151°. 6-Bromo-4-acetoxy-3-methoxybenzaldehyde forms an *oxime*, m. p. 150—152°, the *acetate*, m. p. 153—154°, of which is converted by acetic anhydride into 6-*bromo*-4-*acetoxy*-3-*methoxybenzonitrile*, m. p. 148—149°. This is hydrolysed by potassium hydroxide to 6-*bromovanillic acid*, m. p. 190—191°. The nitration product of acetylvanillin contains 80% of 2-nitrovanillin (cf. Pschorr, A., 1900, i, 178) and about 5% of (?) 6-*nitrovanillin*, m. p. 212°. 5-Bromoacetylvanillin is successively converted into 5-*bromo*-2-*nitroacetylvanillin*, m. p. 128°; 5-*bromo*-2-*nitrovanillin*, m. p. 150—151°; 5-*bromo*-2-*aminovanillin*, m. p. 139—140°, and 2 : 5-*dibromovanillin*, m. p. 189°, from which an *acetate*, m. p. 68—70°; p-*nitrophenylhydrazone*, m. p. 249° (also $+C_5H_5N$); *semicarbazone*, m. p. 233—234°; *oxime*, m. p. 154—155° (*acetate*, m. p. 184—185°, and its *acetyl* derivative, m. p. 137—139°), and also 2 : 5-*dibromo*-4-*acetoxy*-3-*methoxybenzylidene diacetate*, m. p. 157—158°; *bis*-2 : 5-*dibromovanillylidenebenzidine*, m. p. above 350°; 2 : 5-*dibromo*-4-*acetoxy*-3-*methoxybenzonitrile*, m. p. 89—90°, and 2 : 5-*dibromovanillic acid*, m. p. 179—180°, have been prepared. 6-Bromoacetylvanillin is converted into 6-*bromo*-2-*nitrovanillin*, m. p. 168—170°; 6-*bromo*-2-*aminovanillin*, m. p. 217—218°, shrinking from 210°, and 2 : 6-*dibromovanillin*, m. p. 155—156° (*oxime*, m. p. 144—145°; p-*bromophenylhydrazone*, m. p. 168—170°; *semicarbazone*, m. p. 216—217°), which gives with benzidine *bis*-2 : 6-*dibromovanillylidenebenzidine*, m. p. 238—239°, and with bromine in glacial acetic acid containing sodium acetate, 2 : 5 : 6-*tribromovanillin*, m. p. 177—178° (*oxime*, m. p. 192°; p-*bromophenylhydrazone*, m. p. 169—170°; *semicarbazone*, m. p. 222—223°). *Bis*-2 : 5 : 6-*tribromovanillylidenebenzidine* has m. p. above 330°.

H. E. F. Notton.

Auto-oxidation of organic compounds. VI. Thiobenzophenone. H. Staudinger and H. Freudenberger (Ber., 1928, **61**, [*B*], 1836—1839; cf. this vol., 1010).—Auto-oxidation of thiobenzophenone gives benzophenone, a colourless *trisulphide* (probably $CPh_2<\begin{matrix}S\\S\cdot S\end{matrix}>CPh_2$), decomp. about 124°, and little sulphur dioxide. Reaction cannot occur according to the scheme $4CPh_2{:}S+2O_2=2CPh_2{:}O+SO_2+(CPh_2)_2S_3$, since it is accompanied by a slight gain in weight. It is therefore probable that the primary products are benzophenone and sulphur; the latter substance in the nascent condition causes formation of the trisulphide, is partly polymerised to amorphous sulphur, and only to a small extent oxidised. The best yields of the trisulphide are obtained when auto-oxidation of solid or dissolved thiobenzophenone occurs very slowly at a low temperature. At 120°, the trisulphide cannot be formed; under these conditions the products of auto-oxidation are benzophenone, crystalline sulphur, and a little sulphur dioxide. The auto-oxidation of thiobenzophenone is remarkable, since the oxygen reacts primarily with the carbon instead of the sulphur atom.

H. Wren.

Nitration and bromination of 4-methylbenzophenone. W. Blakey and H. A. Scarborough (J.C.S., 1928, 2489—2496).—The effect of a methyl group in the 4-position on substitution in the benzophenone series has been investigated; the methyl group is found to exert a marked directive influence. The first substituent enters the *o*-position to the methyl group (3-position) and this is unaffected by the presence of one or two nitro-groups, or by a chlorine atom. The second substituent enters the 3′-position and further substitution in this (the phenyl) nucleus is apparently inhibited by a substituent in the 3-position of the tolyl nucleus. The third entering substituent occupies the 5-position whatever the nature of the substituents previously introduced. The results are compared with those obtained for 4-methoxybenzophenone (A., 1927, 27).

Progressive nitration of 4-methylbenzophenone (Meyer, A., 1908, i, 25) yields: 3-*nitro*-4-*methylbenzophenone*, m. p. 129° (cf. Zincke and Plascuda, A., 1875, i, 69), its constitution being established by synthesis from 3-nitro-*p*-toluoyl chloride and benzene in the presence of aluminium chloride, reduced by tin and hydrochloric acid to 3-*amino*-4-*methylbenzophenone*, m. p. 109° (*hydrobromide*, m. p. 130°; *acetyl* derivative, m. p. 108°); 3 : 3′-*dinitro*-4-*methylbenzophenone*,

m. p. 135° (described by Limpricht and Lenz as the 2 : 3′-dinitro-compound, m. p. 125°); and 3 : 3′ : 5-*trinitro-4-methylbenzophenone*, m. p. 173°. The last-named compound was synthesised as follows: 3 : 5-dinitro-*p*-toluoyl chloride and benzene in the presence of aluminium chloride gave 3 : 5-*dinitro-4-methylbenzophenone*, m. p. 109° (yielding 5-*nitro-3-amino-4-methylbenzophenone*, m. p. 157°, by reduction with hydrogen sulphide and alcoholic ammonia), which on nitration yielded the 3 : 3′ : 5-trinitro-compound.

Nitration of 4′-nitro-4-methylbenzophenone yields 3 : 4′-dinitro-4-methylbenzophenone, m. p. 130° (cf. Limpricht and Lenz), reduced by hydrogen sulphide and alcoholic ammonia to 3-*nitro-4′-amino-4-methylbenzophenone*, m. p. 164°, deaminated to 3-nitro-4-methylbenzophenone (above); further nitration in concentrated sulphuric acid yields 3 : 4′ : 5-*trinitro-4-methylbenzophenone*, m. p. 160° (which does not react with piperidine, but gives an ill-defined *compound* with *p*-nitrosodimethylaniline), reduced by hydrogen sulphide and alcoholic ammonia to 3-*nitro-4′ : 5-diamino-4-methylbenzophenone*, m. p. 202°, deaminated to 3-nitro-4-methylbenzophenone (above); nitration with fuming nitric acid at 80° yields 3 : 3′ : 4′ : 5-*tetranitro-4-methylbenzophenone*, m. p. 187°, which reacts with piperidine, sodium methoxide, and alcoholic ammonia, giving indefinite brown compounds.

Bromination of 4-methylbenzophenone with excess of dry bromine in sunlight yields 3-*bromo-4-methylbenzophenone*, m. p. 107°, synthesised from 3-bromo-*p*-toluoyl chloride and benzene in the presence of aluminium chloride, and from 3-amino-4-methylbenzophenone (above) by the Sandmeyer reaction; under the same conditions 3′-nitro-4-methylbenzophenone yields 3-*bromo-3′-nitro-4-methylbenzophenone*, m. p. 124°, reduced by stannous chloride and alcoholic hydrochloric acid to 3-*bromo-3′-amino-4-methylbenzophenone*, m. p. 94°, deaminated to 3-bromo-4-methylbenzophenone (above). Bromination of 3′ : 5′-*dinitro-4-methylbenzophenone*, m. p. 134°, prepared by condensation of 3 : 5-dinitrobenzoyl chloride with toluene and aluminium chloride, yields 3-*bromo-3′ : 5′-dinitro-4-methylbenzophenone*, m. p. 173°. Similarly, 3-*bromo-4′-nitro-4-methylbenzophenone*, m. p. 119°, reduced by stannous chloride and alcoholic hydrochloric acid to 3-*bromo-4′-amino-4-methylbenzophenone*, m. p. 162°, deaminated to 3-bromo-4-methylbenzophenone, is obtained from 4′-nitro-4-methylbenzophenone.

4′-Chloro-4-methylbenzophenone, on nitration, gives an almost quantitative yield of 4′-*chloro-3-nitro-4-methylbenzophenone*, m. p. 98°, also obtained by condensing *p*-chlorobenzoyl chloride with toluene and aluminium chloride and nitrating the product (m. p. 128°), and by the Sandmeyer reaction from 3-nitro-4′-amino-4-methylbenzophenone, and from 3-nitro-*p*-toluoyl chloride with chlorobenzene and aluminium chloride; on reduction it is converted into 4′-*chloro-3-amino-4-methylbenzophenone*, m. p. 142°. Further nitration in sulphuric acid yields 4′-*chloro-3 : 3′-dinitro-4-methylbenzophenone*, m. p. 131°, also obtained by nitrating 4′-*chloro-3′-nitro-4-methylbenzophenone*, m. p. 121°, prepared by condensing 4-chloro-3-nitrobenzoyl chloride with toluene in the presence of aluminium chloride, together with 4′-*chloro-3 : 3′ : 5-trinitro-4-methylbenzophenone*, m. p. 182°, also prepared by nitration of 4′-*chloro-3 : 5-dinitro-4-methylbenzophenone*, m. p. 118°, which was synthesised from 3 : 5-dinitro-*p*-toluoyl chloride with chlorobenzene and aluminium chloride. Bromination of 4′-chloro-4-methylbenzophenone gives a quantitative yield of 4′-*chloro-3-bromo-4-methylbenzophenone*, m. p. 122°, also obtained from 4′-chloro-3-amino-4-methylbenzophenone (above) by the Sandmeyer reaction. C. W. Shoppee.

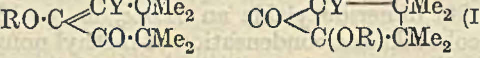
Intermolecular condensation of styryl ketones. II. Styryl nonyl ketone and the formation of dimerides. I. M. Heilbron and F. Irving (J.C.S., 1928, 2323—2326).—Methyl nonyl ketone condenses with aromatic aldehydes in the presence of cold, dilute alkali or piperidine to yield mono- and di-meric styryl nonyl ketones. The production of the latter is favoured with *p*-substituted aldehydes and by higher temperature and alkali concentration. Styryl nonyl ketone has m. p. 44° (cf. Carette, A., 1901, i, 127; Thoms, Ber. Deut. pharm. Ges., 1901, **11**, 3) and its dimeride yields an *oxime*, m. p. 125—126°. By cold alkaline condensation of methyl nonyl ketone with the appropriate aldehyde the following styryl nonyl ketones are obtained: 3 : 4-*dimethoxy*-, m. p. 61°; 4-iso*propyl*-, m. p. 40°; 2-*hydroxy*-, m. p. 79°; 4-*chloro*-, m. p. 62—63°; 3-*chloro*-, m. p. 57°; 2-*chlorostyryl nonyl ketone* was not isolated, but was characterised by its *semicarbazone*, m. p. 123—124°. With more concentrated alkali or under reflux are obtained: *bis*-(4-*methoxy*-), m. p. 120°; *bis*-(3 : 4-*dimethoxy*-), m. p. 135°; *bis*-(3 : 4-*methylenedioxy*-), m. p. 128°; *bis*-(4-*chloro*-), m. p. 126—127°; *bis*-(4-*methyl*-), m. p. 134—135°, and *bis*-(4-iso*propyl-styryl nonyl ketone*), m. p. 150°. Scholtz and Meyer (A., 1910, i, 561) erroneously describe the last two compounds as the corresponding monomerides. C. W. Shoppee.

Resolution of benzoin. I. V. Hopper and F. J. Wilson (J.C.S., 1928, 2483—2489).—l-δ-(α-*Phenylethyl*)*semicarbazide hydrochloride*, m. p. 188°, $[\alpha]_D^{12\cdot2}$ −66·06°, has been prepared in 79% yield from *l*-α-phenylethylamine and acetonesemicarbazone, and together with the *d*-isomeride (*ibid*., 1922, **121**, 869) has been used to effect a resolution of benzoin. Preliminary work with *r*-δ-(α-phenylethyl)semicarbazide hydrochloride in pyridine solution yielded three of the four possible racemic *benzoin*-δ-(α-*phenylethyl*)-*semicarbazones* (α-*modification*, m. p. 174°; β-*modification*, m. p. 154°; γ-*modification*, m. p. 137°), all yielding benzoin on hydrolysis; in alcoholic solution only the α- and β-isomerides were obtained. For comparison (see below) *d*-benzoin was prepared from *d*-mandelic acid by Wren's method (*ibid*., 1909, **95**, 1583) using quartz vessels and solvents which had been previously distilled in quartz apparatus; the product had m. p. 133—134°, $[\alpha]_D^{11}$ +118·5°, and its pyridine solution was not racemised by keeping for a week in quartz. d-*Benzoin*-d-δ-(α-*phenylethyl*)*semicarbazone* was prepared in pyridine solution and had m. p. 181—182°, $[\alpha]_D^{14}$ −140·7°.

r-Benzoin, condensed with *d*-δ-(α-phenylethyl)-semicarbazide hydrochloride, yielded as the sole crystalline product d-*benzoin*-d-δ-(α-*phenylethyl*)*semicarbazone*, m. p. 181—182°, $[\alpha]_D^{14}$ −141·5°, identical

with the synthetic product, giving on hydrolysis with oxalic acid *d*-benzoin, m. p. 133—134°, $[\alpha]_D^{11}$ +118·3°. From the non-crystalline condensation product *benzil-di*-d-δ-(α-*phenylethyl*)*semicarbazone*, m. p. 223°, $[\alpha]_D^{17}$ +178·2°, was isolated and yielded benzil on hydrolysis with concentrated hydrochloric acid. *r*-Benzoin and *l*-δ-(α-phenylethyl)semicarbazide hydrochloride similarly yielded l-*benzoin*-l-δ-(α-*phenylethyl*)*semicarbazone*, m. p. 181—182°, $[\alpha]_D^{14}$ +140·9°, as the sole crystalline product, converted by hydrolysis with oxalic acid into *l*-benzoin, m. p. 133—134°, $[\alpha]_D^{11}$ −118·5°.
C. W. SHOPPEE.

Possibility of ring–chain valency tautomerism, and of a type of mobile hydrogen tautomerism analogous to the Wagner–Meerwein rearrangement. IV. Substitution reactions of some cyclic derivatives of phorone. C. W. SHOPPEE (J.C.S., 1928, 2360—2365).—Numerous observations previously made (this vol., 414) indicate that the 5-carbon nuclei (I), (II), possess remarkable stability,

(I.)  (II.)

$$\mathrm{RO{\cdot}C}\begin{cases}\mathrm{CY{\cdot}CMe_2}\\ \mathrm{CO{\cdot}CMe_2}\end{cases}\qquad \mathrm{CO}\begin{cases}\mathrm{CY{-\!-}CMe_2}\\ \mathrm{C(OR){\cdot}CMe_2}\end{cases}$$

and exhibit a tendency to conservation of type such as is encountered in semi-aromatic and aromatic systems. The action of substituting agents has now been studied to determine the conditions under which the nuclear type is preserved. Treatment with bromine in chloroform of the acetoxy- [I, R=Ac, Y=H], methoxy- [I, R=Me, Y=H] and *p*-bromobenzyloxy- [I, $R=C_7H_6Br$, Y=H] derivatives yields bromohydroxyphorone with elimination of the substituent R; the mechanism of the reaction is discussed. Quinolinium bromide also causes elimination of the acyl group from the acetyl compound, but not of the *p*-bromobenzyloxy-group, simple nuclear substitution taking place instead. A similar result is achieved in the case of the acetyl compound by brominating with quinolinium bromide in the presence of quinoline. If the nuclear type is destroyed by reduction, bromination leads to its regeneration.

Various acyl and alkyl derivatives examined show little tendency to couple with diazonium salts, but hydroxyphorone (I and II; R=Y=H) readily does so, the position of coupling being the carbon atom bearing Y. The following are new: 2 : 5-*dibromo*-3 : 3 : 4 : 4-*tetramethyl*cyclo*pentanone*, m. p. 93°; 4-2′ : 4′ : 6′-*tribromobenzeneazo*-5-*hydroxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone*, m. p. indefinite; 4-p-*carbethoxybenzeneazo*-5-*hydroxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone*, m. p. 160° (decomp.), yielding by reduction and hydrolysis 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine. Bromination of 5-methoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone with bromine in chloroform yields bromohydroxyphorone, but in another experiment an unstable intermediate *dibromide*, $C_9H_{14}OBr_2$, m. p. 99—100°, was isolated.
C. W. SHOPPEE.

Acylation and alkylation of aromatic compounds in presence of stannic chloride. G. STADNIKOV and A. BARYSCHEVA (Ber., 1928, 61, [*B*], 1996—1999).—In contrast with its behaviour towards benzyl chloride, benzene does not react with acetyl or benzoyl chloride in the presence of stannic chloride; under similar conditions, ethyl benzoate does not react with benzyl, benzoyl, or acetyl chloride. *o*-Tolyl methyl ether and acetyl chloride in cold benzene in the presence of stannic chloride afford 4-methoxy-3-methylacetophenone, b.p. 171—172°/39 mm., d_4^{18} 1·0812, n_D^{18} 1·5538 (*semicarbazone*, m. p. 206—207°; oxime, m.p. 101—101·5°), in 84% yield; 4-methoxy-3-methylbenzophenone, m. p. 79—80°, is similarly prepared. 4-Methoxy-2-methylacetophenone, b. p. 163—164°/33 mm., d_4^{17} 1·0803, n_D^{17} 1·5527 (oxime, m. p. 80·5—81·5°; *semicarbazone*, m. p. 179—180°), and a *methoxymethylbenzophenone*, b. p. 219—221°/23 mm., m. p. 172°, are derived from *m*-tolyl methyl ether. *p*-Tolyl methyl ether gives 2-methoxy-5-methylacetophenone, b. p. 143—146°/21 mm., 260—261°/739 mm., d_4^{17} 1·0636, n_D^{17} 1·5375 (*semicarbazone*, m. p. 176—177°; oxime, m. p. 88·5—89·5°), and a *methoxymethylbenzophenone*, b. p. 210—211°/20 mm., m. p. 37—38°.

m-Tolyl methyl ether and benzyl chloride afford a *methoxymethyldiphenylmethane*, b. p. 181—187°/20 mm., d_4^{18} 1·0466, and *methoxymethyldibenzylbenzene*, m. p. 75—76°.
H. WREN.

Hydroxy-carbonyl compounds. IX. Constitution of cotoin and *iso*cotoin. *iso*Hydrocotoin. P. KARRER and N. LICHTENSTEIN (Helv. Chim. Acta, 1928, **11**, 789—795).—*p*-Toluenesulphonylation of cotoin (2 : 6-dihydroxy-4-methoxybenzophenone) gives 2-*hydroxy*-4-*methoxy*-6-p-*toluenesulphonyloxybenzophenone*, m. p. 138° (2 : 6-*di*-p-*toluenesulphonyl* derivative, m. p. 144°), which when methylated yields the p-*toluenesulphonyl* derivative, m. p. 112°, of hydrocotoin (2-hydroxy-4 : 6-dimethoxybenzophenone). *iso*Cotoin (2 : 4-dihydroxy-6-methoxybenzophenone) furnishes the 4-p-*toluenesulphonyl* derivative, m. p. 109°, together with the 2 : 4-*di*-p-*toluenesulphonyl* derivative, m. p. 137°. Partial hydrolysis of this last compound affords the 2-p-*toluenesulphonyl* derivative, m. p. 146°, of *iso*cotoin.

Phloroglucinol dimethyl ether condensed with benzonitrile in presence of zinc chloride yields a mixture of hydrocotoin and iso*hydrocotoin* (4-*hydroxy*-2 : 6-*dimethoxybenzophenone*), m. p. 177°.
H. BURTON.

Optical investigation of quinones and free radicals. S. GOLDSCHMIDT and F. GRAEF (Ber., 1928, 61, [*B*], 1858—1869).—The red form of *o*-benzoquinone can be converted into the colourless modification as often as desired if its ethereal solution is rapidly cooled to −80°. This observation, considered in conjunction with the marked differences in colour exhibited by solutions of *o*-benzoquinone and *o*-naphthaquinone in chloroform, ether, and light petroleum, suggests equilibria between polymeric or tautomeric forms of the type $C_6H_4{<}\begin{smallmatrix}O-O\\O-O\end{smallmatrix}{>}C_6H_4$, $C_6H_4{<}\begin{smallmatrix}O-\,-\\O-\,-\end{smallmatrix}$, $C_6H_4{\lll}\begin{smallmatrix}O\\O\end{smallmatrix}$, $C_6H_4{<}\begin{smallmatrix}O\\|\\O\end{smallmatrix}$. Since solutions of *o*-benzoquinone obey Beer's law, they cannot contain equilibrium mixtures of poly- and mono-meric forms. The absorption spectrum of *p*-benzoquinone differs widely from that of the *o*-compound, which resembles closely those of homo-*o*-benzoquinone and *o*-naphthaquinone. Observations of the absorption spectra of *o*-quinones in various solvents show them to have little in common with the corresponding quinols, thus differing completely in behaviour from the true aroxyls (see later). Nevertheless, the marked influence of the solvent indicates the existence of an equilibrium, aroxyl $\rightleftharpoons$ quinone and this hypothesis is supported by the conversion of *o*-benzoquinone by triphenylmethyl into a colourless, non-crystalline ether, $C_6H_4(O{\cdot}CPh_3)_2$, from which triphenylmethyl is quantitatively separated as the peroxide by exposure to air.

The ultra-violet spectra of αα-diphenyl-β-2 : 4 : 6-trinitrophenylhydrazine and αα-diphenyl-β-2 : 4 : 6-trinitrophenylhydrazyl do not show differences greater than those of *o*-benzoquinone in two different media. In the visible spectrum, the radical gives a very high, flat band, this appearing to be characteristic of the transition from ter- to bi-valent nitrogen.

The spectrum of 9-chloro-10-hydroxyphenanthrene is very closely similar to that of phenanthrene, the hydroxy-group having unexpectedly little influence. In the spectrum of the corresponding peroxide only the two bands in the far ultra-violet remain unchanged, whilst a band appears between 3300 and 3600 Å. The linkings in the *meso*-nucleus appear therefore to have suffered considerable change. Solutions containing an equilibrium mixture of peroxide and chlorophenanthroxyl do not obey Beer's law, thus affording spectroscopic evidence of radical dissociation. The curve of chlorophenanthroxyl cannot be followed far into the ultra-violet on account of the presence of pyridine (added to induce equilibrium), but its concurrence with the curve of the peroxide permits the conclusion that the change in absorption is restricted to the visible part of the spectrum in which a band appears of similar breadth and intensity as in the case of αα-diphenyl-β-2 : 4 : 6-trinitrophenylhydrazyl. On the other hand, the changes in comparison with 9-chloro-10-hydroxyphenanthrene also occur in part of the ultra-violet and are probably due to the *meso*-benzene nucleus.

The production of a *compound*, $C_{14}H_{18}O_4NCl$, m. p. 195°, from *p*-benzoquinone and 9-chloro-10-phenanthroxyl in chloroform and pyridine is recorded.

H. WREN.

Action of potassium ferricyanide on sodioformanilide in alkaline solution. Preparation of quinones and imides. E. I. ORLOV (Ukraine Chem. J., 1928, **3**, 161—169).—Sodioformanilide is oxidised by potassium ferricyanide to yield a mixture of products, amongst which 2-amino-5-hydroxy- and 2-amino-3-hydroxy-*p*-benzoquinone are identified. The tarry reaction product is partly soluble in dilute hydrochloric acid, the hydrochlorides $NH_2{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}NH_2,2HCl$ and $C_6H_4{:}NH,HCl$ being isolated from the extract. The first product of the reaction of oxidation is probably 2-amino-*p*-benzoquinone, which then reacts as follows: $2C_6H_3O_2{\cdot}NH_2+H_2O=C_6H_2O_2(OH){\cdot}NH_2+C_6H_4O_2+NH_3$.

R. TRUSZKOWSKI.

Subsidiary valency linking of nitro- and quinonoid groups. E. HERTEL and H. KURTH (Ber., 1928, **61**, [*B*], 1650—1653).—The power of 2 : 7-dinitroanthraquinone to form additive compounds with aromatic hydrocarbons has usually been ascribed to the presence of the two nitro-groups. Examination of the phase diagrams of 1 : 8-dinitronaphthalene and stilbene, 1 : 5-dinitronaphthalene and stilbene, or 3 : 3′-dinitrodiphenylmethane and naphthalene fails to disclose the production of additive compounds and attempts to isolate such products from 1 : 8- or 1 : 5-dinitronaphthalene, 3 : 3′-dinitrodiphenylmethane, and 2 : 7-dinitrofluorene and various aromatic hydrocarbons and their derivatives give only negative results. It is therefore concluded that a common residual field is not possessed by two nitro-groups present in different nuclei. The grouping, 3-nitro-carbonyl-3′-nitro-, does not induce the formation of additive compounds as evidenced by 3 : 3′-dinitrobenzophenone and naphthalene or 2 : 7-dinitrofluorenone and stilbene. The production of molecular compounds from Fritzsch's reagent is attributed to the carbonyl group strengthened by the neighbourhood of negative substituents. Thus the colour of the additive compounds of naphthalene, fluorene, acenaphthene, and anthracene with 1 : 2 : 3 : 5 : 6 : 7 : 8-heptachloro- is deeper than those with 2 : 7-dichloro-anthraquinone, but less pronounced than those with 1-nitroanthraquinone. The compounds exist only in the molten mixtures, but the introduction of two nitro-groups in different benzenoid nuclei of anthraquinone increases the quinonoid residual affinity to such an extent that additive compounds with hydrocarbons are crystalline. The behaviour of phenanthraquinone is similar to that of anthraquinone. 2 : 7-Dibromophenanthraquinone gives deeply-coloured molten mixtures with aromatic hydrocarbons but not crystalline compounds, whereas 2 : 7-dinitrophenanthraquinone affords additive *compounds* with acenaphthene (1 : 1), m. p. 255°, fluorene, (1 : 2), m. p. 270°, and anthracene (1 : 2), m. p. 250°. Additive *compounds*, m. p. 165° and 148°, respectively, are produced from 4 : 5-dinitrophenanthraquinone and acenaphthene (1 : 1) and from 2 : 6 : 7-trinitrofluorenone and stilbene (1 : 1).

H. WREN.

Production of benzanthrone derivatives [from 4-amino-3-hydroxy-1-*p*-amino-*o*-carboxyphenylnaphthalene]. I. B. ANDERSON, R. F. THOMSON, J. THOMAS, and SCOTTISH DYES LTD.—See B., 1928, 740.

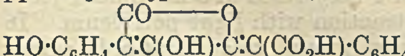
Constitution of active principle of *Chita*. I. A. C. ROY and S. DUTT (J. Indian Chem. Soc., 1928, **5**, 419—424).—*Plumbagin* (I), $C_{18}H_{15}O_5$, m. p. 77—78°, is obtained from the air-dried roots ("chita") of *Plumbago rosea* or *P. zeylanica* in a maximum yield of about 1% by extraction with light petroleum. It contains one hydroxyl group, since it affords *monoacetyl*, m. p. 138°, *monobenzoyl*, m. p. 147°, and *monocarbethoxy*-, m. p. 109°, derivatives. It is suggested that I is a *p*-quinone, since it yields a *dioxime*, m. p. 220°, but only a *monophenylhydrazone*, m. p. 198°, and a *monosemicarbazone*, m. p. above 280°. This view is supported by the formation of a colourless leuco-compound from I by reduction with zinc dust and acetic acid. When I is oxidised with cold aqueous potassium permanganate, cinnamic acid and traces of benzoic and acetic acids are obtained, whilst zinc dust distillation furnishes naphthalene and β-methylnaphthalene. *Tetranitroplumbagin*, m. p. 172°, is formed by the action of fuming nitric acid, and the action of bromine is to yield *plumbagin dibromide*, m. p. 122°. H. Burton.

Colouring matters of fungi. VI. Constitution of atromentin. F. Kögl and H. Becker [with A. Detzel and (Frl.) G. de Voss] (Annalen, 1928, **465**, 211—242).—The fungus extract, atromentin (A., 1925, i, 50, 1439), was regarded as having the formula $C_{20}H_{14}O_7$ and as being a derivative of 2 : 5-diphenylbenzoquinone containing a 3 : 2′ $OH\cdot CH_2\cdot C(OH)<$ bridge linking. The analogy between atromentin and polyporic acid, which has been shown (A., 1926, 407) to be 3 : 6-dihydroxy-2 : 5-diphenylbenzoquinone, has, however, suggested a re-investigation of the former substance, which is now found to have the formula $C_{18}H_{12}O_6$. The structure now favoured is that of 3 : 6 : 4′ : 4″-*tetrahydroxy-2 : 5-diphenylbenzoquinone* (I). The "penta-acetyl derivative," m. p. 242°, is found to be a *tetra-acetylatromentin*, and "hepta-acetyl-leucoatromentin," m. p. 236°, to be the *hexa-acetyl* compound. Reduction of tetra-acetylatromentin by zinc and acetic acid yields 3 : 6 : 4′ : 4″-*tetra-acetyl-leucoatromentin*, m. p. 248°.

Oxidation of atromentin, *e.g.*, by alkaline hydrogen peroxide, normally yields *p*-hydroxybenzoic acid. In hot acetic acid solution, however, a small quantity of hydrochloric acid, and hydrogen peroxide to furnish 4 atoms of oxygen, cause the separation of the *lactone*, m. p. 346° (decomp.), of *atromentic acid*, $C_{18}H_{12}O_7,H_2O$, m. p. 332° (decomp.). The action of acetic anhydride and sulphuric acid on either of these gives the *diacetyl* derivative, m. p. 271°, of the lactone; the last on keeping in ethyl alcohol furnishes *ethyl atromentate*, m. p. 346°.

Diazomethane converts atromentic acid into its *trimethyl ether*, m. p. 170°; the lactone dissolved in methyl alcohol and treated with diazomethane yields the fully methylated product, *methyl atromentate trimethyl ether*, m. p. 167° (depressed by admixture with the preceding compound). Chromic acid oxidises the trimethyl ether to anisic acid and *methyl* p-*methoxyphenylglyoxylate*, m. p. 54°, which is also obtained from leucoatromentin hexamethyl ether (see below), is reduced by hydriodic acid to *p*-hydroxyphenylacetic acid, and is synthesised by permanganate oxidation of *p*-methoxyacetophenone.

Hot 50% potassium hydroxide solution converts atromentic acid into *p*-hydroxyphenylacetic acid; this can be explained on the assumption that it is a pp′-*dihydroxypulvinic acid*,



$HO\cdot C_6H_4\cdot C\colon C(OH)\cdot C\colon C(CO_2H)\cdot C_6H_4\cdot OH$ (with CO—O bridge), and that the above lactone, m. p. 346°, is the corresponding dilactone. The latter reacts with alcohol to give a lactone ester (cf. Piutti and Mazza, A., 1927, 1072). Since no other aromatic degradation product is obtained, it is established that the phenyl groups of atromentin carry only *p*-hydroxy-groups; the old bridged formula is thus excluded.

It is not possible to methylate atromentin completely in one stage. Tetra-acetylatromentin dissolved in methyl-alcoholic potassium hydroxide, and acidified, yields an *atromentin monomethyl ether*, m. p. 239°, easily hydrolysed, and thus containing a 3-methoxyl group. This furnishes a *triacetyl* derivative, m. p. 202°, and, by use of sodium hyposulphite, *penta-acetyl-leucoatromentin monomethyl ether*, m. p. 196°. Atromentin dimethyl ether is easily hydrolysed, supporting the 3 : 6-structure; with acetic anhydride and sulphuric acid it gives orange pp′-*diacetylatromentin* 3 : 6-*dimethyl ether*, m. p. 212°, oxidised by chromic acid to *p*-acetoxybenzoic acid (no anisic acid). Penta-acetyl-leucoatromentin dimethyl ether is renamed 1 : 4 : 4′ : 4″-*tetra-acetyl-leucoatromentin* 3 : 6-*dimethyl ether*, m. p. 263—264°.

Complete methylation of atromentin is effected by the action of diazomethane on leucoatromentin, or by that of methyl sulphate on atromentin dimethyl ether in methyl-alcoholic potassium hydroxide; *atromentin tetramethyl ether* has m. p. 199°. If the dimethyl ether is suspended in ethyl alcohol during methylation, *atromentin trimethyl* 3-*ethyl ether*, m. p. 186°, is obtained, readily converted by methyl-alcoholic potassium hydroxide into the tetramethyl ether, which is, however, slowly decomposed itself by this reagent, giving *atromentin* 3 : 4′ : 4″-*trimethyl ether*, m. p. 167°. This last is hydrolysed by sodium hydroxide to the 4′ : 4″-*dimethyl ether*, m. p. 290°.

Leucoatromentin hexamethyl ether, m. p. 238°, is obtained by the action of methyl sulphate on leucoatromentin in presence of methyl-alcoholic potassium hydroxide, and similarly from the tetramethyl or trimethyl ethyl ethers, or from the former of these by the action of diazomethane.

All these methylated products agree with the formulation $C_{18}H_{12}O_6$ for atromentin, which cannot be considered to have been degraded in any way during methylation.

A degradation process is, on the other hand, effected by means of aqueous alkali. The action of the latter on dihydroxydialkylbenzoquinones was studied by Fichter (A., 1908, i, 658), who obtained mixtures of stereoisomeric succinic acids, $CH_2R\cdot CH(CO_2H)\cdot CHR\cdot CO_2H$, assumed to be derived from lactonic acids. Stahlschmidt (A., 1879, 382) had not obtained such results with polyporic acid, which, he stated, yielded two acids, $C_9H_9O_2$, m. p. 163°, and $C_{10}H_9O$, m. p. 156°. This work has now been repeated and both products have been found to be impure. The action of boiling 10—15% aqueous potassium hydroxide on polyporic acid actually gives rise to three products: (*a*) the known α-benzylcinnamic acid, m. p. 158°; (*b*) a new isomeric α-*benzylcinnamic acid*, m. p. 100·5°, which, like (*a*), on reduction gives dibenzylacetic acid; and (*c*), phenylbenzylsuccinic acid (Avery, A., 1908, i, 343). The results of Fichter are thus supported by analogy, oxalic acid being lost instead of carbon dioxide during the reaction, which yields a benzylcinnamic acid instead of a succinic acid.

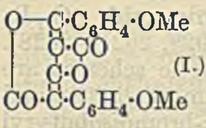
The action of alkali on atromentin (*pp*′-dihydroxypolyporic acid) follows a similar course. The product, m. p. 202°, obtained when steam is passed through a solution of atromentin in 30% alkali is now found to be $C_{18}H_4O_7,3H_2O$, and to be α-*keto*-β-p-*hydroxyphenyl*-γ-p′-*hydroxybenzylbutyrolactone*-γ-*carboxylic acid*. The acids of m. p. 183° and 164°, to which the formula $C_{11}H_{10}O_3$ was assigned, are now found to be $C_{16}H_{14}O_4$. Since the former of these is methylated by diazomethane to 4-*methoxy*-α-(p-*methoxybenzyl*)*cinnamic* *acid*, m. p. 161° (synthesised by condensation of *p*-methoxy-β-phenylpropionic acid with anisaldehyde, in presence of acetic anhydride at 160—170°), it must be 4-*hydroxy*-α-(p-*hydroxybenzyl*)*cinnamic acid*. Since the two acids yield the same acetyl derivative, the acid of m. p. 164° may be an *allo*-form.

E. W. WIGNALL.

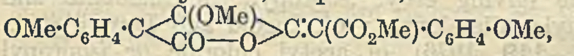
Colouring matters of fungi. VII. Synthesis of atromentin. Atromentic acid. F. KÖGL [with H. BECKER, G. DE VOSS, and E. WIRTH] (Annalen, 1928, **465**, 243—258).—Atromentin (see preceding abstract) is synthesised by condensing methyl *p*-methoxyphenylacetate with methyl oxalate by the action of sodium in ether. This yields directly 3 : 6-*dihydroxy*-2 : 5-*bis*-(p-*methoxyphenyl*)*benzoquinone* (*atromentin* 4′ : 4″-*dimethyl ether*), m. p. 285° (uncorr.), from which the tetramethyl ether is also prepared, and, by the use of hydriodic acid, atromentin itself.

A second synthesis is effected by heating 2 : 5-bis-(*p*-hydroxyphenyl)benzoquinone with methyl alcohol and zinc chloride at 160°; atromentin 3 : 6-dimethyl ether is thus obtained, and is identified as the diacetyl derivative. Free atromentin is obtained by heating with saturated sodium carbonate solution. The yield is not good, but is better than that in the first described method.

Completely methylated atromentic acid is synthesised as follows. Ethyl oxalate is condensed with *p*-methoxyphenylacetonitrile under the influence of sodium, furnishing pp′-*dimethoxydiphenylketipinodinitrile*, m. p. 260°. When heated in alcohol and sulphuric acid, pp′-*dimethoxypulvinolactone* (I), m. p. 268·5° (which has not been demethylated), is obtained. This is dissolved in methyl-alcoholic potassium hydroxide, and on acidification gives rise to the lactone ester, pp′-*dimethoxyvulpinic acid*, m. p. 174·5°, of which the *methyl ether*, m. p. 168°,

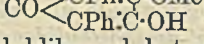


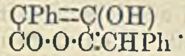
(I.)



$$\text{OMe·C}_6\text{H}_4\text{·C}\left<\begin{array}{l}\text{C(OMe)}\\ \text{CO—O}\end{array}\right>\text{C:C(CO}_2\text{Me)·C}_6\text{H}_4\text{·OMe}$$

is identical with methyl atromentate trimethyl ether (see preceding abstract).

In attempts to hydrolyse this ester to the corresponding acid by means of methyl-alcoholic potassium hydroxide with either synthetic or analytic material, the yellow solution acquired an intense violet colour, and on acidification a yellow compound, $C_{20}H_{18}O_5$, m. p. 147° (after sintering at 135°), separated. This is regarded as 3-*hydroxy*-4-*methoxy*-2 : 5-*bis*-(p-*methoxyphenyl*)cyclo*penta*-2 : 4-*dien*-1-*one*. Similarly, vulpinic acid methyl ether, prepared from silver vulpinate and methyl iodide, gives with methyl-alcoholic potassium hydroxide a violet solution from which acidification yields the corresponding diphenyl compound,  $\text{CO}\left<\begin{array}{l}\text{CPh:C·OMe}\\ \text{CPh:C·OH}\end{array}\right.$, m. p. 94—95°, identical with "oxalyldibenzyl ketone monomethyl ether" (Claisen, A., 1895, i, 373), together with a large quantity of an oily *substance* (the keto-form ?). This last also appears when the substance is prepared from the silver salt of oxalyldibenzyl ketone.

Claisen describes (*loc. cit.*) an inversion of the "oxalyldibenzyl ketone," which when heated above its m. p. is converted into "*iso*oxalyldibenzyl ketone" (pulvinone),  $\begin{array}{l}\text{CPh=C(OH)}\\ \text{CO·O·C:CHPh}\end{array}$. The new reaction can be considered as a reversal of this; in fact, pulvinone methyl ether, m. p. 104—105° (obtained by Claisen as an oil), when treated with methyl-alcoholic potassium hydroxide gives rise to the above described diphenyl compound, m. p. 94—95°.

Atromentic acid forms red crystals containing 1 mol. of water, lost at 100° to give yellow crystals which very rapidly absorb water, becoming red, loss and re-adsorption of water occurring without loss of transparency.

E. W. WIGNALL.

Gitoxin. A. WINDAUS, K. WESTPHAL, and G. STEIN (Ber., 1928, **61**, [*B*], 1847—1855).—All previously described derivatives of gitoxin have been again prepared and subjected to a series of independent analyses. To gitoxin the formula $C_{41}H_{64}O_{14}$ is ascribed and its identity with "bigitalinum crystallisatum" of Cloetta (A., 1926, 755) is established; the m. p. of the compound depends greatly on the manner of heating. Gitoxigenin has the formula $C_{23}H_{34}O_5$; analyses of its acyl derivatives are unsuitable for the deduction of composition, since they are usually mixtures, although, under definite conditions, a *diacetyl* compound, $C_{23}H_{32}O_3Ac_2$, m. p. 249—250°, is isolated. Treatment of gitoxigenin with alcoholic hydrogen chloride gives dianhydrogitoxigenin, $C_{23}H_{30}O_3$, a trebly unsaturated monohydroxylactone identical with digitaligenin from *Digitalinum verum*. Hydrogenation of gitoxigenin (cf. Cloetta, *loc. cit.*) appears to yield two isomeric dihydrogitoxigenins, $C_{23}H_{36}O_5$, m. p. 212° and 241°, $[\alpha]_D$ −48·74° in methyl alcohol, each of which is converted by hydrogen chloride in alcohol into *dianhydrodihydrogitoxigenin*, $C_{23}H_{32}O_3$, m. p. 166°. The latter compound is very readily hydrogenated in the presence of platinum-black into *tetrahydrodianhydrodihydrogitoxigenin*, a mixture of isomerides from which a product, $C_{23}H_{36}O_3$, m. p. 214°, $[\alpha]_D^{20}$ +75·7° in alcohol, is isolated. Oxidation of the product with chromic acid mixture affords *tetrahydrodianhydrogitoxigenone*, $C_{23}H_{34}O_3$, m. p. 207°, $[\alpha]_D^{20}$ +85·9° in chloroform, doubtless identical with the hexahydrodigitaligenone of Bandte (A., 1923, i, 1107). Reduction of this ketone by Clemmensen's method yields the *lactone*, $C_{23}H_{36}O_2$, m. p. 173°, $[\alpha]_D^{18}$ +71° in chloroform (Bandte, *loc. cit.*, gives formula, $C_{24}H_{38}O_2$). Oxidation of the ketone with chromic acid in excess gives a dicarboxylic *acid*, $C_{23}H_{34}O_6$, m. p. 282°, $[\alpha]_D^{20}$ +100° in glacial acetic acid (*dimethyl* ester, m. p. 163°, $[\alpha]_D^{20}$ +82·3° in chloroform); the ketone thus probably contains a cyclic $-CO·CH_2-$ group. The hexahydrodigitaligenin, m. p. 186—187°, of Bandte (*loc. cit.*) and of Windaus and Schwarte (A., 1925, i, 1295) is not homogeneous; from it the tetrahydrodianhydrodihydrogitoxigenin (see above) is isolated as the most sparingly soluble component. The acetyl derivative, m. p. 156°, and propionyl compound, m. p. 163—164°, are regarded as probably mixtures of stereoisomerides. Oxidation of "hexahydrodigitaligenin" by chromic acid affords a mixture of ketones from which tetrahydrodianhydrogitoxigenone is isolated with some difficulty. The portions of lower m. p., when oxidised with chromic acid, give an isomeric dicarboxylic acid, $C_{23}H_{34}O_6$ (see above), m. p.

278°, $[\alpha]_D^{18}$ +71° in glacial acetic acid (*dimethyl* ester, m. p. 171—172°, $[\alpha]_D^{22}$ +40° in chloroform). Distillation of the acid, $C_{23}H_{34}O_6$, in a high vacuum gives the *ketone*, $C_{22}H_{32}O_3$, m. p. 206° (*oxime*, m. p. 248°).
H. WREN.

Colouring matter of paprika. III. Catalytic hydrogenation. L. ZECHMEISTER and L. VON CHOLNOKY [with (FRL.) V. VRABÉLY] (Annalen, 1928, **465**, 288—299).—The method of isolation of capsanthin (cf. A., 1927, 669) is improved, and the new formula $C_{34}H_{48}O_3$ is obtained. The strongly unsaturated character of the substance, suspected from its ready resinification, is confirmed by catalytic hydrogenation. In alcohol or, better, acetic acid, reduction in presence of platinum introduces 9 mols. of hydrogen. A colorimetric survey of the reaction shows that 6 mols. of hydrogen are first introduced, removing all the colour, which during hydrogenation is constantly less than would be expected calculated on the assumption that there are nine conjugated ethylenic linkings present.

The product, perhydrocapsanthin, is a liquid (perhaps a mixture of stereoisomerides), with $[\alpha]_D^{20}$ −23·3° to −24·7°, possibly too low a value owing to racemisation (a preparation kept for 2 hrs. at 80° had $[\alpha]_D^{23}$ −15·3°).

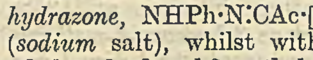
The paprika pigment must be considered to belong to the class of natural "polyene" pigments; the lævo-rotation of its hydrogenated product is compared with the similar property of perhydroxanthophyll. It is assumed that the deepening of colour of paprika during ripening is due to dehydrogenation of the parent substance; attempts to influence this by injection were unsuccessful. E. W. WIGNALL.

Xanthophyll. I. Catalytic hydrogenation. L. ZECHMEISTER and P. TUZSON (Ber., 1928, **61**, [*B*], 2003—2009).—Xanthophyll, $C_{40}H_{56}O_{21}$, m. p. 172° (corr.), is hydrogenated in ethyl or propyl alcohol, ether, chloroform, or glacial acetic acid in the presence of an unusually large amount of spongy platinum to non-crystalline *perhydroxanthophyll*, $C_{40}H_{78}O_2$, $[\alpha]_D^{20}$ −9·2° in ether, −9·8° in benzene. The hydrogenation graph of xanthophyll is very similar to that of carotin, showing a rectilinear progress until 8 mols. of hydrogen have been absorbed and the solution has become colourless. Xanthophyll therefore probably contains eight conjugated double linkings which rapidly become hydrogenated and three sluggish double linkings which are not responsible for the colour. It is possible that carotin contains two alkyl and xanthophyll two alkoxy-groups in corresponding positions in the molecule. H. WREN.

Caoutchouc. K. H. MEYER and H. MARK (Ber., 1928, **61**, [*B*], 1939—1949; cf. Katz, A., 1925, ii, 667).—Examination of the *X*-ray diagrams of stretched caoutchouc show that two superposed isoprene residues almost exactly fill the space of an identity period if the methylene groups vicinal to the double linking are in the *cis*-position to one another and the two residues are placed at an angle of 180° to one another. The screw axis and the linkings are continued through the complete crystallite along the fibre axis. The distances of the individual chains from one another coincide with those observed in crystalline fatty acids. The neighbouring main-valency chains are inclined at different angles to the α-axis in the unit substance. It is estimated that 75—150 isoprene residues are involved in the structural molecule of caoutchouc. If the tension on stretched caoutchouc is released, the interferences disappear, but are immediately observed again when the material is again placed under tension. Direct determinations of the osmotic pressure of solutions of caoutchouc in benzene and chlorobenzene indicate that the size of the micelles is much greater than has been assumed previously and that the micelles unite with considerable proportions of the solvent; in 3—5% solutions the solvent is almost completely united to the micelles.

X-Ray examination shows that vulcanisation which does not effect the reversible extension does not alter the inner arrangement of the micelles. The forces of association which the micelles exert towards one another are strengthened in some manner during vulcanisation. Analogy is drawn between the action of sulphur chloride on ethylene and caoutchouc, which leads to the union of two double linkings by a sulphur bridge. The action of the chloride occurs immediately at the surface of the micelles and leads to the formation of sulphur bridges from double linkings present in the same and in neighbouring micelles. A strong union of the micelles at various points is thus established. Vulcanisation with large amounts of sulphur or sulphur chloride destroys the extensibility probably because the many sulphur bridges on and in the micelles stabilise the whole mass. H. WREN.

Attempts to synthesise norpinic acid. G. R. CLEMO and K. N. WELCH (J.C.S., 1928, 2621—2628).—The following unsuccessful synthetic schemes are described: the condensation of dimethylketen and maleic or fumaric esters, of α-bromo*iso*butyryl bromide with ethyl sodioethanetetracarboxylate, of ethyl disodio*iso*propylidenemalonate with methylene iodide (giving ethyl *iso*propylidene malonate and methylenedimalonate; cf. Ingold and Powell, *ibid.*, 1921, **119**, 1976), of acetyl chloride or *iso*propyl bromide and ethyl sodiodicarbethoxyglutaconate, of magnesium methyl iodide and either α-acetyl-, α-bromo-α-acetyl-, or α-methyl-α-acetyl-glutaric esters.

Ethyl α-acetylglutarate gave with benzenediazonium chloride under the conditions of a Japp–Klingemann reaction *α-carboxypentane-γδ-dione-γ-phenylhydrazone*, $NHPh\cdot N{:}CAc\cdot[CH_2]_2\cdot CO_2H$, m. p. 178° (*sodium* salt), whilst with phenylhydrazine it gave *ethyl* 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-β-*propionate*,  $\begin{array}{l}CO\text{———}CH\cdot[CH_2]_2\cdot CO_2Et\\ NPh\cdot N{:}CMe\end{array}$, b. p. 215°/3 mm. *Ethyl α-bromo-α-acetylglutarate* has b. p. 162—165°/14 mm. Ethyl α-acetylglutarate reacts with boiling aniline, giving diphenylcarbamide, and with gaseous ammonia, giving *ethyl α-(α′-aminoethylidene)glutarate*, $NH_2\cdot CMe{:}C(CO_2Et)\cdot CH_2\cdot CH_2\cdot CO_2Et$, m. p. 37°. Improved methods for the preparation of acetone cyanohydrin and *iso*propylidenemalonic esters have been worked out. R. J. W. LE FÈVRE.

Ultra-violet absorption curves of terpene alcohols in relation to constitution. J. SAVARD (Compt. rend., 1928, **187**, 540—542).—The maxima at 2260—2380 Å. in the absorption curves of butylpulegol, butyl*iso*pulegol, dihydrocarvacrol, α-, β-, and γ-terpineol, and 4-terpineol are attributed to the presence of the double linking, and the regular ascension of the curve from an unlocated maximum in the extreme ultra-violet is similarly attributed to the presence of the hydroxyl group. The position of the double linking is relatively unimportant, the position of the maximum in the absorption curve of γ-terpineol being shifted about 60 Å. towards the red as compared with β-terpineol, by the side-chain displacement $⁚CH\cdot CMe⁚CH_2 \longrightarrow ⁚C⁚CMe_2$. The same change in the case of butylpulegol and butyl*iso*pulegol produces a displacement of about 80 Å. The shift of the hydroxyl group from a nuclear position (4-terpineol) to the side-chain (α-terpineol) has practically no effect on the position of the maximum (2309—2283 Å.) but produces a considerable decrease in the extinction coefficient. Substitution by the butyl group has little effect, the band being displaced from 2404 Å. (γ-terpineol) to 2325 Å. (butylpulegol), whilst β-terpineol and butyl*iso*pulegol (and also dihydrocarvacrol) show the same maximum at 2222 Å. When the position of the double linking is varied in alcohols not possessing the common menthene nucleus, the absorption intensity produced by the ethylenic linking depends on the number of carbon atoms separating the two functional groups in the molecule. The mutual induction of the two functional groups thus appears to be dependent on the nature and position of both groups.

R. Brightman.

Influence of solvents on the rotation of optically active compounds. XXV. Bornyl benzene- and naphthalene-sulphonates in various solvents. T. S. Patterson and I. M. McAlpine (J.C.S., 1928, 2472—2474).—Rotations in ethyl alcohol, benzene, pyridine, ethylene dibromide, quinoline, and nitrobenzene for mercury yellow, green, and violet light (λ=5790, 5461, and 4358) are recorded for bornyl benzenesulphonate, naphthalene-α-, and -β-sulphonate. The rotations vary considerably in the different solvents and the data lie on a characteristic diagram, the lines of which practically pass through the point of origin, in consequence of which the dispersion coefficients calculated in the ordinary way are almost constant.

M. Clark.

Decomposition of bornyl benzene- and naphthalene-sulphonates by heat. Products of hydrolysis of bornyl and menthyl benzene- and naphthalene-sulphonates. Influence of solvents on the temperature of decomposition of these bornyl and menthyl sulphonates. T. S. Patterson and I. M. McAlpine (J.C.S., 1928, 2464—2472; cf. A., 1927, 364).—Bornyl esters of benzene-, naphthalene-α- and -β-sulphonic acids, when directly distilled under reduced pressure, yield a small quantity of camphene, and a considerable quantity of dibornylene and a more complex gelatinous material which could be neither purified nor identified, as well as the corresponding sulphonic acid. When the esters are heated in sealed tubes at 80—90° for 2—3 hrs., and afterwards distilled, the products are dihydrocamphene (?), dibornylene, a gelatinous mass of high b. p., and the sulphonic acid. When the esters are heated to boiling in toluene solution, dibornylene and the sulphonic acid are obtained. The menthyl and bornyl esters of benzene- and the naphthalene-sulphonic acids do not hydrolyse to yield menthol and borneol, but decompose in somewhat the same way as when heated alone, yielding respectively menthene and camphene in small quantity. The rate at which these esters decompose in solution, investigated for toluene, nitrobenzene, ethylene dibromide, pyridine, and a series of alcohols, depends quite markedly on the nature of the solvent, and in the alcohols the velocity increases rapidly as the mol. wt. diminishes. Tables are given illustrating this behaviour. The following are described: l-*bornyl benzenesulphonate*, m. p. 52°, $[\alpha]_{5461}^{17}$ —22·40° in benzene, —22·00° in alcohol; d-*bornyl benzenesulphonate*; l-*bornyl naphthalene-β-sulphonate*, m.p. 76°, $[\alpha]_{5461}^{17}$ —16·50° in benzene, —16·00° in alcohol; d-*bornyl naphthalene-β-sulphonate*; l-*bornyl naphthalene-α-sulphonate*, m. p. 90°, $[\alpha]_{5461}^{17\cdot5}$ —23·20° in benzene, —26·4° in alcohol.

M. Clark.

Hyssop oil from the Crimea. B. Rutovski and I. Vinogradova.—See B., 1928, 768.

Constituents of Indian essential oils. XXV. *l*-α- and *l*-β-Curcumenes. B. S. Rao and J. L. Simonsen (J.C.S., 1928, 2496—2505).—Two crystalline derivatives, a nitrosate and a trihydrochloride, have been prepared from *l*-curcumene (cf. B., 1926, 1028). Fractional distillation of the oil remaining after separation of the trihydrochloride yields a sesquiterpene monohydrochloride, the parent hydrocarbon of which gives the crystalline nitrosate in a yield exceeding that obtained with the original terpene, whilst treatment with hydrochloric acid gives no trihydrochloride. *l*-Curcumene is therefore a mixture of two hydrocarbons, *l*-α-curcumene, which yields the crystalline nitrosate and liquid monohydrochloride, and *l*-β-curcumene, which yields the crystalline trihydrochloride.

Treatment of *l*-α-curcumene nitrosate, m. p. 100—101° (recrystallised after 3 weeks, m. p. 110°), with alcoholic potassium hydroxide solution yields l-*oximino-α-curcumene*, $C_{15}H_{22}⁚N\cdot OH$ (I), b. p. 182—185°/7 mm., d_{30}^{30} 0·9817, n_D^{30} 1·5134, $[\alpha]_D^{30}$ —27·2° (*benzoyl* derivative, m. p. 84—85°). Compound (I) forms a *monohydrochloride* apparently by addition of hydrogen chloride to one of the ethylenic linkings, since the product is not decomposed by alkali. Reduction of (I) with sodium in ethyl-alcoholic solution yields l-*dihydro-α-curcumenylamine*, $C_{15}H_{25}\cdot NH_2$ (II), b. p. 151—152°/17 mm., d_{30}^{30} 0·9026, n_D^{30} 1·4983, $[\alpha]_D^{30}$ —22·2° [*hydrogen oxalate* (+H_2O), m. p. 143—144°; *acetyl* derivative, m. p. 109—110°], one of the ethylenic linkings having been reduced as well as the oximino-group. This compound possesses only general toxic action. Methylation of (II) with methyl iodide in presence of alkali yields l-*dihydro-α-curcumenyltrimethylammonium iodide*, $C_{15}H_{25}\cdot NMe_3I$, m. p. 163—164°. Distillation of the corresponding hydroxide, crystalline but hygroscopic, gives a mixture of l-*dimethyldihydro-α-curcumenylamine*, $C_{15}H_{25}\cdot NMe_2$, b. p. 130—140°/15 mm., d_{30}^{30} 0·8824, n_D^{30} 1·4913, $[\alpha]_D^{30}$ —23·0°, and pure l-*α-curcumene*, b. p. 128—130°/7 mm., d_{30}^{30} 0·8633, n_D^{30} 1·4944, $[\alpha]_D^{30}$ —22·9° (*monohydro-*

chloride, b. p. 150—155°/8 mm.). *l*-α-Curcumene is very stable. It is not reduced by sodium in ethyl or amyl alcohol, is unattacked by dilute sulphuric acid, and only slowly oxidised by alkaline permanganate. It is not isomerised by heating at 380° in an inert atmosphere. It is not dehydrogenated with formation of a naphthalene derivative when heated at 270° with sulphur or selenium. When dissolved in chloroform it absorbs 1 mol. of bromine. The presence of three ethylenic linkings in the molecule is established by oxidation with perbenzoic acid (cf. Nametkin, A., 1926, 420). Catalytic reduction of *l*-α-curcumene in presence of platinum oxide yields *hexahydro-α-curcumene*, $C_{15}H_{30}$, b. p. about 128°/7 mm., d_{30}^{30} 0·8283, n_D^{30} 1·4592, $[\alpha]_D^{30}$ +0°. l-α-*Curcumene-nitrolbenzylamine* has m. p. 102—104°.

Treatment of *l*-β-curcumene trihydrochloride with anhydrous sodium acetate in acetic acid solution yields pure l-β-*curcumene*, b. p. 128—130°/6 mm., d_{30}^{30} 0·8810, n_D^{30} 1·4940, $[\alpha]_D^{30}$ −27·9°, a monocyclic terpene containing three ethylenic linkings, indicated by titration with bromine as well as by formation of the trihydrochloride. Catalytic reduction gives l-*hexahydro*-β-*curcumene*, b. p. about 128°/7 mm., d_{30}^{30} 0·8283, n_D^{30} 1·4552, $[\alpha]_D^{30}$ +6·3°. *l*-β-Curcumene is very unstable and is readily isomerised. It is converted by treatment with 10% sulphuric acid into a dicyclic *terpene* (?), b. p. 115—117°/7 mm., d_{30}^{30} 0·8932, n_D^{30} 1·4936, $[\alpha]_D^{30}$ −11·9. It is not reduced by sodium in amyl alcohol, but undergoes isomerisation and no longer yields the trihydrochloride. It is also isomerised by heating in an inert atmosphere at 380° under pressure. Dehydrogenation with either sulphur or selenium yielded no recognisable products.

M. Clark.

Aromadendrene. I. L. H. Briggs and W. F. Short (J.C.S., 1928, 2524—2529).—Careful fractionation of the sesquiterpene fraction from the oil of *Eucalyptus nova-angelica* (Baker and Smith, "A Research on the Eucalypts," Sydney, 1920, pp. 46, 417) yields only aromadendrene, $C_{15}H_{24}$, a single tricyclic sesquiterpene (cf. Smith ,*op. cit.*, p. 417; Semmler, "Die Ätherischen Oele," 1906, II, 530) which exhibits an exaltation of approximately one unit in its molecular refractive power. Exhaustive hydrogenation of aromadendrene, either by the method of Skita or by that of Paal, gives *dihydroaromadendrene*, $C_{15}H_{26}$, b. p. 121—122°/10 mm., d_4^{17} 0·9014, n_D^{17} 1·4871, which also shows an exaltation of one unit in molecular refractive power. The exaltation exhibited by the sesquiterpene is therefore due to structural peculiarity and not to contamination with dicyclic sesquiterpenes. From its likeness in this respect to α-gurjunene and copaene (Semmler, A., 1914, i, 704; 1915, i, 427) it is probable that aromadendrene may contain either a *cyclo*propane ring conjugated with a double linking together with a *cyclo*butane ring, or, less probably, two *cyclo*propane rings. Dehydrogenation of aromadendrene with sulphur yields a deep blue oil, b. p. 122—165°/12 mm., from which no naphthalene hydrocarbon could be obtained, although a small quantity of a black picrate (azulene picrate ?), m. p. 114—116°, was isolated. The presence of the group $C\cdot C(:CH_2)\cdot C$ in aromadendrene is clearly indicated by ozonisation in acetic acid solution, which gives *aromadendrone*, $C_{14}H_{22}O$, m. p. 80—81° [*oxime*, m. p. 103°, yielding no nitrile when digested with acetic anhydride; *semicarbazone*, m. p. 189·5—190·5° (decomp.)]. Aromadendrone did not yield an enol-acetate when boiled with acetic anhydride and sodium acetate. The carbonyl group is therefore either in the side-chain or attached to two quaternary carbon atoms in the nucleus.

M. Clark.

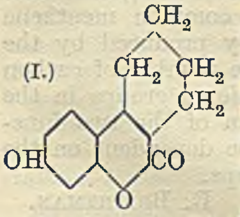
Essential oil of "Hiba" wood. Essential oil of Hiba leaves. S. Uchida.—See B., 1928, 768.

Essential oil of leaves of "Hinoki." S. Uchida.—See B., 1928, 768.

Essential oil of leaves of "Sawara." S. Uchida.—See B., 1928, 768.

Heterocyclic compounds. III. Interaction of *cyclo*hexanone-2-carboxylates with phenols. H. K. Sen and U. Basu (J. Indian Chem. Soc., 1928, 5, 467—476).—Ethyl *cyclo*hexanone-2-carboxylate condenses with resorcinol in presence of concentrated sulphuric acid (cf. Dieckmann, A., 1901, i, 539), forming 8-hydroxy-1 : 2 : 3 : 4-tetrahydrobenzcoumarin (I), m. p. 201—202° (*acetyl* derivative, m. p. 186—187°; *benzoyl* derivative, m. p. 157°; *methyl ether*, m. p. 121—122°). Condensation with phosphorus pentoxide gave tarry products. Similarly, 2-cyano-*cyclo*hexanone and resorcinol give a *compound*, m. p. 290°, which when hydrolysed with potassium hydroxide solution affords I. Boiling potassium hydroxide solution has little effect on I, whilst potassium hydroxide fusion gives benzoic acid and a *compound*, $C_{13}H_8O_3$, m. p. 230° (*benzoyl* derivative, m. p. 195°), probably a dehydrogenated coumarin. Similarly, the above ester and *m*-cresol and α-naphthol give 8-*methyl*-1 : 2 : 3 : 4-*tetrahydrobenzcoumarin*, m. p. 119°, and 1 : 2 : 3 : 4-*tetrahydrobenznaphthacoumarin*, m. p. 190° (*nitro*-derivative, m. p. 244°), respectively.

(I.)



Ethyl 5-methyl*cyclo*hexanone-2-carboxylate condenses with phloroglucinol, orcinol, and pyrogallol, yielding 8 : 10-*dihydroxy*-, m. p. 264—266°, 8-*hydroxy*-10-*methyl*-, m. p. 249°, and 7 : 8-*dihydroxy*-, m. p. 231°, -1 : 2 : 3 : 4-*tetrahydro-2-methylbenzcoumarin*, respectively.

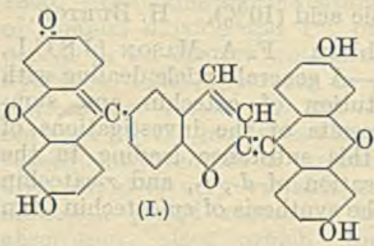
H. Burton.

Derivatives of 2-phenyl-6-methyl-4-pyrone. Non-resolution of 2-phenyl-6-methyl-4-pyrone *d*-α-bromocamphor-π-sulphonate. C. S. Gibson and J. L. Simonsen (J.C.S., 1928, 2307—2312).—Attempts to resolve into its diastereoisomerides the *d*-α-bromocamphor-π-sulphonate of 2-phenyl-6-methyl-4-pyrone were unsuccessful (cf. Levy, Holmyard, and Ruhemann, Proc. C.S., 1913, 29, 159). This non-resolution provides negative evidence in support of Hantzsch's co-ordination formulation of the salts of the 4-pyrones (A., 1920, i, 72). The following are described: 2-phenyl-6-methyl-4-pyrone (*hydrochloride*, m. p. 165°; *perchlorate*, m. p. 145—147°; *sulphate*, m. p. 168—169°; *methylmethosulphate*, m. p. 140—143°; *methiodide*, decomp. 105°, unstable); silver *d*-α-bromocamphor-π-sulphonate (+H_2O). 2-*Phenyl*-6-*piperonylidenemethyl*-4-*pyrone* (I) (*per-*

chlorate, decomp. 143°) has m. p. 194°. The intense orange colour of the d-α-*bromocamphor*-π-*sulphonate*, m. p. 205—206°, makes stereochemical investigation of this salt impossible. Treatment of I with bromine in chloroform solution gives a *compound* (*dibromo*-derivative?), m. p. 155—157°, decomposing on recrystallisation from acetone with loss of hydrobromic acid and formation of the *monobromo*-derivative, decomp. 222°. M. Clark.

Alkali sulphonates of coumarin and nitrocoumarin. R. N. Sen and D. Chakravarti (J. Indian Chem. Soc., 1928, 5, 433—437).—Sulphonation of coumarin with fuming sulphuric acid at water-bath temperature (cf. Perkin, J.C.S., 1873, **24**, 37) gives coumarin-6-sulphonic acid (*sodium* salt; *acid chloride*, m. p. 115°; *acid amide*, m. p. 186°; *anilide*, m. p. 132°), oxidised by alkaline potassium permanganate to 5-sulphosalicylic acid. When sulphonation is carried out at 150° coumarin-3 : 6-disulphonic acid (*sodium* salt; *dichloride*, m. p. 170—173°; *diamide*, m. p. above 240°; *dianilide*) is obtained, which is oxidised to 5-sulphosalicylic acid also. 6-Nitrocoumarin affords 6-*nitrocoumarin*-3-*sulphonic acid* (*sodium* salt; *chloride*, m. p. 205°; *amide*, m. p. above 260°; *anilide*, m. p. 130°), oxidised to 5-nitrosalicylic acid. H. Burton.

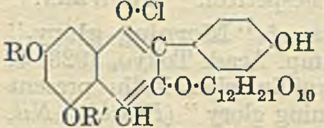
6-Aldehydocoumarin and derived dyes. R. Sen and D. Chakravarti (J. Amer. Chem. Soc., 1928, **50**, 2428—2436).—6-Aldehydocoumarin (*phenylhydrazone*, m. p. 205—207°) (Stoermer and Oetker, A., 1904, i, 244) is conveniently obtained in approximately 20% yield, together with a resinous product which contains a *substance*, m. p. 174—175° (decomp.), from coumarin by the Reimer–Tiemann method. It undergoes the benzoin reaction, giving *coumaroin*, $C_{20}H_{12}O_6$, m. p. 178—180°, and condenses with acetone and acetophenone in presence of alkali to *dicoumarylideneacetone* (αε-di-6-coumaryl-$\Delta^{\alpha\delta}$-pentadien-γ-one), m. p. 159°, and *coumarylideneacetophenone* (γ-phenyl-α-6-coumaryl-Δ^{α}-propen-γ-one), m. p. above 250°. The following azomethine dyes, $(C_9H_5O_2{\cdot}CH{:}N)_nR$, are formed by condensing the aldehyde with the appropriate amine in alcoholic hydrochloric or acetic acid: 6-*coumarylidene*-p-*toluidine*, yellow, m. p. 145—147°; *coumarylidene*-β-*naphthylamine*, pale yellow, m. p. 173°; *coumarylidene*-p-*nitroaniline*, yellow, m. p. above 250°; *coumarylideneaminoazobenzene*, reddish-yellow, m. p. 169°; *dicoumarylidene*-p-*phenylenediamine*, brown, m. p. above 250°; *dicoumarylidene*-m-*phenylenediamine*, brown, m. p. above 250°; *dicoumarylidene*-o-*phenylenediamine*, yellow, m. p. above 250°; *coumarylidenebenzidine*, yellow, m. p. above 250°; *tricoumarylidenerosaniline*, reddish-violet, m. p. 142°; *dicoumarylidenesafranine*, reddish-violet, and *coumarylidenechrysoidine*, orange, m. p. 210—212°. The aldehyde condenses with dimethylaniline in presence of hydrochloric acid at 100° to *tetramethyldiaminodiphenylcoumarylmethane*, m. p. 220°, which is oxidised by lead dioxide to the bluish-green *tetramethyldiaminodiphenylcoumarylcarbinol* (*hydrochloride*). Dyes containing two xanthen nuclei are formed from the aldehyde and 4 mols. of a phenol in presence of sulphuric acid at 120—130°, both the 6-aldehydo- and the 2-keto-groups being attacked (cf. Krishna, J.C.S., 1921, **119**, 1420; Sen and Sarkar, A., 1925, i, 812). Thus, resorcinol yields the red *product* (I) (*tripotassium* salt; *hexabromo*-derivative), quinol a reddish-violet *isomeride* (*tetrapotassium* salt; *tetrabromo*-derivative), β-naphthol a colourless *product*, $C_{50}H_{30}O_4$, α-naphthol an isomeric *product*, and gallic acid a polygenetic *dye*, $C_{38}H_{20}O_{19}$. Under similar conditions, however, the aldehyde combines with only 2 mols. of *m*-diethylaminophenol, forming bluish-violet 3 : 6-*bisdiethylamino*-9-*hydroxy*-9 : 6′-*coumarylxanthen*. The colours produced by these dyes on silk and wool are tabulated and it is shown that the coumaryl dyes are more bluish than the corresponding phenyl derivatives. H. E. F. Notton.



(I.)

Constitution of delphinin. K. Kondu (Helv. Chim. Acta, 1928, **11**, 919—921).—Methylation of delphinin chloride obtained from the flowers of *Delphinium consolida*, L. (Willstätter and Mieg, A., 1915, i, 284), with methyl sulphate and sodium hydroxide solution and subsequent treatment with 2% methyl-alcoholic hydrogen chloride gives a light red *chloride*, $C_{41}H_{34}O_{16}Cl(OMe)_5$, which when hydrolysed with aqueous-alcoholic sodium hydroxide affords anisic acid and a methylated *delphinidin chloride*, $C_{15}H_8O_4Cl(OMe)_3$. H. Burton.

Plant colouring matters. VIII. Constitution of monardæin. P. Karrer and R. Widmer (Helv. Chim. Acta, 1928, **11**, 837—842).—Methylation of monardæin chloride (A., 1927, 252) with methyl sulphate and sodium hydroxide, followed by hydrolysis of the product with alcoholic potassium hydroxide solution, and subsequent acidification with hydrochloric acid gives *p*-methoxycinnamic acid and *monardin dimethyl ether chloride*, red needles. Hydrolysis of this with 20% hydrochloric acid affords *pelargonidin dimethyl ether*. The annexed structure is assigned to monardæin chloride (R and R′=either H or $OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO$). H. Burton.



Plant colouring matters. IX. Yellow colouring matter from red rose. Organic acids from several flowers. P. Karrer and K. Schwarz (Helv. Chim. Acta, 1928, **11**, 916—919).—The petals of *Rosæ rubræ* are digested with sulphuric acid to hydrolyse the colouring matter glucoside, and after removal of water with anhydrous sodium sulphate the mixture is extracted with ether. There are obtained a colourless hydrocarbon and quercetin. When penta-acetylquercetin is treated with ozone, protocatechuic and diacetylprotocatechuic acids are obtained.

The flowers of the red peony, red pink, red rose, dark mallow, blue larkspur, violet poppy, and salmon-coloured dahlia (Tsingtau) all contain acetic (1—2%) and formic acids (0·1—0·2%). Several of the flowers contain varying quantities of citric acid (0·7—7%); the poppy contains caffeic acid (2%), the dahlia a tannin, and the peony a tannic acid (10%). H. Burton.

The catechin problem. F. A. Mason (J.S.C.I., 1928, **47**, 269—276T).—A general article dealing with the chemical constitution of catechin and summarising the chief results of the investigations of K. Freudenberg on this substance leading to the isolation and identification of *d*-, *l*-, and *r*-catechin and *epi*catechin and the synthesis of *epi*catechin from cyanidin.

The catechin problem. M. Nierenstein (Chem. Age, 1928, **19**, 291).—A criticism of Mason's article on the subject (preceding abstract). The constitution of cyanidin is regarded as being *sub judice*.

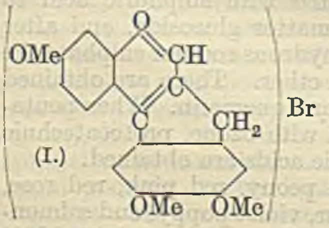
E. E. Turner.

The catechin problem. R. Robinson (Chem. Age, 1928, **19**, 337).—A reply to Nierenstein (preceding abstract). It is pointed out that in view of the two recorded syntheses (Willstätter; Robinson) of cyanidin, the constitution of the latter substance is satisfactorily established. E. E. Turner.

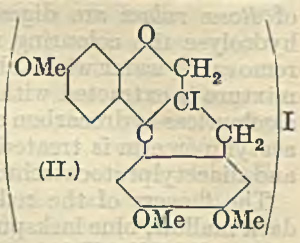
Flavanone glucosides. III. Reduction of flavone and flavanone derivatives. T. Asahina and M. Inubuse (Ber., 1928, **61**, [*B*], 1646—1650; cf. this vol., 1020).—Apigenin, suspended in water, is converted by reduction with sodium amalgam followed by treatment of the filtered solution with hydrochloric acid into apigenidin chloride, $C_{15}H_{11}O_4Cl$, m. p. not below 300°, which does not appear completely identical with the synthetic product of Pratt and Robinson (A., 1925, i, 825). The chloride is analytically and spectroscopically identical with the compound derived similarly from naringenin. Sakuranetin is reduced to the *chloride*, $C_{15}H_{10}O_3Cl\cdot OMe$, m. p. 236—237° (decomp.) (also *monohydrate*), whilst the analogous *substance*, $C_{15}H_{10}O_4Cl\cdot OMe$, m. p. 231—232° (decomp.) (also *dihydrate*), is derived from hesperitin. H. Wren.

Anthocyanin pigments of "Morning glory." II. T. Kataoka (Proc. Imp. Acad. Tokyo, 1928, **4**, 389—392).—The anthocyanidin pharbitidin present in the red flower of "Morning glory" (*Pharbitis Nil*, Chois.) (A., 1926, 1150) is identical with pelargonidin. Fission of the anthocyanidin into *p*-hydroxybenzoic acid is effected by a much lower concentration of alkali if hydrogen peroxide is also added. J. W. Baker.

Brazilin and hæmatoxylin. VIII. Reduction of trimethylbrazilone and tetramethylhæmatoxylone. P. Pfeiffer, O. Angern, E. Haack, and J. Willems (Ber., 1928, **61**, [*B*], 1923—1932; cf. this vol., 426, 647).—The action of bromine in benzene on trimethylanhydrobrazilin leads through a non-isolable, red intermediate phase to the *pyrylium bromide* (I), gradual decomp. above 170°, whereas iodine affords the *di-iodide* (II), m. p. 175° (decomp.), converted by aqueous silver nitrate into the *iodonitrate* which rapidly loses hydrogen iodide and passes into a pyrylium salt.

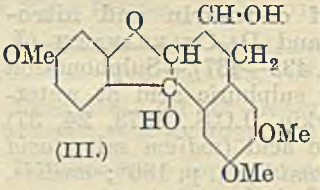


(I.)



(II.)

Reduction of trimethylbrazilone in glacial acetic acid by hydrogen in the presence of spongy platinum at the atmospheric temperature yields a dihydroxy-*compound* (probably III), m. p. 151—152° (also *monohydrate*; mono-*p*-nitrobenzoyl derivative, m. p. 103—105°), regarded as identical (in spite of recorded difference in m. p.) with the product obtained by Perkin, Rây, and Robinson (this vol., 895) by reduction of trimethylbrazilone with aluminium amalgam in acetic acid. The compound is also obtained in good yield by treatment of trimethylbrazilone with magnesium in a mixture of benzene and glacial acetic acid; two *by-products*, m. p. 267° and 285°, respectively, are isolated. The compound cannot be re-converted by oxidation into trimethylbrazilone, a carboxylic acid, m. p. 225°, being obtained. Reduction of trimethylbrazilone by sodium amalgam in presence of alcohol and glacial acetic acid gives a monohydroxy-*compound*, $C_{16}H_{10}O(OMe)_3\cdot OH$, m. p. 133—134° (*acetyl* derivative, m. p. 123—124°), isomeric with trimethylbrazilin. Tetramethylhæmatoxylone is converted by catalytic reduction in presence of spongy platinum into a dihydroxy-*compound*, $C_{16}H_8O(OMe)_4(OH)_2$, m. p. 185—188°, which is completely analogous to the corresponding compound of the brazilin series; the *monoacetyl* derivative, m. p. 150—152°, and *mono*-p-*nitrobenzoyl* compound, m. p. 177—178°, are described. Tetramethylhæmatoxylone is not obtained from it by oxidation. The dihydroxy-compound is also obtained by reduction of tetramethylhæmatoxylone by magnesium in glacial acetic acid and benzene; two *by-products*, $C_{20}H_{22}O_7$, m. p. 283° (decomp.), and an *isomeride*, $C_{16}H_9O(OMe)_4\cdot OH$, of tetramethylhæmatoxylin, m. p. 188—192°, are characterised.



(III.)

H. Wren.

Pyrrolidine derivatives. F. B. LaForge (J. Amer. Chem. Soc., 1928, **50**, 2471—2477).—Ethyl sodioacetoacetate and β-*p*-tolyloxyethyl bromide (Weddige, A., 1881, 1136) yield *ethyl* β-p-*tolyloxyethylacetoacetate*, b. p. 202—204°/16 mm. This is hydrolysed by alcoholic sodium hydroxide to *methyl* γ-p-*tolyloxypropyl ketone*, b. p. 165—175°/16 mm. (*semicarbazone*, m. p. 158°), and a little γ-p-*tolyloxybutyric acid*, m. p. 84—85°. *Methyl* γ-p-*tolyloxypropyl ketoxime*, m. p. 54°, is reduced by sodium amalgam and acetic acid in alcohol to δ-*amino*-α-p-*tolyloxypentane*, b. p. 280—283°/760 mm. (*carbonate*), the *hydrochloride* of which is converted by 45% hydrochloric acid at 100° into 2-methylpyrrolidine (Fenner and Tafel, A., 1898, i, 446). α-Phenyl-*n*-butyl bromide, from phenylpropylcarbinol and hydrogen bromide, yields with methylamine α-*methylamino*-α-*phenylbutane*, b. p. 117—118°/33 mm., which could not be converted into a pyrrolidine derivative by bromination and removal of hydrogen bromide. The product (? αδ-dibromo-α-phenylbutane) obtained by saturating phenylallylcarbinol with hydrogen bromide in sunlight gives with alcoholic methylamine an unsaturated *amine*, $C_{11}H_{15}N$, b. p. 209—216°/770 mm., instead of the expected pyrrolidine. γ-Benzoylpropyl bromide and methylamine yield benzoyl*cyclo*propane (cf. Perkin, J.C.S., 1885, 47, 836) and 2-*phenyl*-1-*methylpyrroline*, b. p. 136—139°/34 mm., which could not be reduced to a pyrrolidine derivative. Ethyl sodiobenzoylacetate and β-*p*-tolyloxyethyl bromide yield *ethyl* β-p-*tolyloxyethylbenzoylacetate*, b. p. 240—250°/8 mm., from which *phenyl* γ-p-*tolyloxypropyl ketone*, b. p. 250—260°/8 mm., m. p. 63°; its *ketoxime*, m. p. 75°; δ-*amino*-α-p-*tolyloxy*-δ-*phenylbutane hydrochloride* and *nitrate*; δ-*chloro*-α-*amino*-α-*phenylbutane hydrochloride*, m. p. 200—205° (decomp.), and 2-*phenylpyrrolidine*, b. p. 236—238°/757 mm., are successively prepared.

2-Phenylpyrrolidine and methyl iodide in methyl alcohol yield 2-*phenyl*-1-*methylpyrrolidine*, b. p. 225—227°/760 mm. In spite of their structural relationship to nicotine, the above pyrrolidines and 2 : 5-dimethylpyrrolidine have only a slight insecticidal action.

H. E. F. Notton.

Products of the hydrogenation of quinoline under pressure in the presence of osmium and cerium. V. S. Sadikov and A. K. Michailov (Ber., 1928, 61, [*B*], 1801—1806).—The presence of 1% of osmium dioxide in the cerium oxide–asbestos catalyst causes a more intense hydrogenation of quinoline beyond the tetrahydro-stage which is reached with cerium dioxide alone, thus causing a diminution in the amount of substances of high b. p. On the other hand, the use of the combined catalyst (20 or 1% of cerium dioxide with 1 or 20% of osmium dioxide) induces the production of compounds of low b. p. by further change from decahydroquinoline. From the products of high b. p. a base, b. p. 275—290°/15 mm. (*dihydrochloride*; *ferrocyanide*), is isolated which, on the basis of analyses and ability to give an additive product with methyl iodide, is regarded as 7-*methyldi*-1 : 2 : 3 : 4 : 7 : 8-*hexahydro*-1 : 1′-*quinolyl*. The substance, 1 : 2′-*methyl*-3′-*ethylpiperidino*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroquinoline* (*dihydrochloride*, m. p. 276°), is derived from the fractions of lower b. p.

From the products of the interrupted hydrogenation of quinoline the following compounds are isolated: from the fraction of b. p. 150—175°, the *hydrochlorides*, $C_{10}H_{20}N_2,HCl$, m. p. 226°, and $C_9H_{17}N,HCl$, m. p. 156°, probably derived respectively from 2-amino-3-methyldecahydroquinoline and 2-methyl-3-ethylpiperidine; from the fraction of b. p. 175—190°, a *hydrochloride*, $C_{19}H_{35}N_3,2HCl$, m. p. 172° probably derived from 2-amino-3-methyldidecahydro-1 : 1′-quinolyl, a base, $C_{14}H_{26}N_2$, possibly 1-piperidinodecahydroquinoline, and a *ferrocyanide*, $C_{14}H_{27}N,H_4FeC_6N_6$, probably a salt of 1-methyl-2 : 3-diethyldecahydroquinoline. Treatment of the fractions of b. p. 175—190° and 190—200° in alcohol with carbon dioxide or distillation in a current of carbon dioxide yields the *compounds* $C_{18}H_{36}O_2N_2$ and $C_{27}H_{55}O_2N_3$, respectively.

H. Wren.

Catalytic hydrogenation. Interrupted hydrogenation of quinoline under pressure in the presence of osmium and cerium. V. S. Sadikov and A. K. Michailov (Ber., 1928, 61, [*B*], 1797—1800).—Quinoline and the catalyst (asbestos with 20% of osmium dioxide and 1% of cerium dioxide) are placed in an Ipatiev autoclave under 100 atm. of hydrogen. The apparatus is placed in an electric furnace pre-heated to 320—340° and the times required for the incidence of maximum pressure and subsequently the fall in pressure are observed. The first period is very variable and is followed by an induction period succeeded by one of oscillatory absorption, after which the catalyst becomes exhausted. If, however, the apparatus is cooled to the atmospheric pressure, hydrogenation of the quinoline again proceeds. It appears therefore that the permanent maintenance of high optimal temperatures is not necessary for the hydrogenation of the majority of cyclic compounds and that the high temperature only excites a process which subsequently occurs independently of temperature. Prolonged exposure to a high temperature tends to impair the activity of the catalyst.

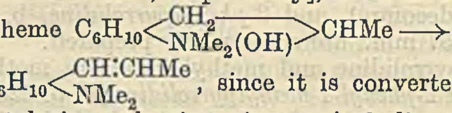
H. Wren.

Fission of hydrocarbostyril and its derivatives to *o*-aminophenyl-propionic and -butyric acids. F. Mayer, H. Philipps, F. W. Ruppert, and A. T. Schmitt (Ber., 1928, 61, [*B*], 1966—1975).—2-Keto-1 : 2 : 3 : 4-tetrahydroquinoline suffers fission of the ring when heated with aqueous barium hydroxide at about 150°, giving the barium salts of *o*-aminophenylpropionic and -butyric acids. Excess of barium hydroxide is exactly removed by carbon dioxide and the barium salts are transformed into the corresponding sodium salts. As exemplified by β-*o*-aminophenylpropionic acid, the free acids readily pass into the cyclic forms. The *sodium* salts of the following acids have been isolated: β-*o*-aminophenyl- (benzoyl derivative, m. p. 155—158°); β-3-chloro-2-aminophenyl-; β-5-chloro-2-aminophenyl- (*benzoyl* derivative, m. p. 189—192°); β-3 : 5-dichloro-2-aminophenyl-; β-3-methyl-2-aminophenyl-; β-5-methyl-2-aminophenyl- (*benzoyl* derivative, m. p. 170—172°); 3 : 6-diaminophenyl-1 : 2-ββ′-di- (*benzoyl* derivative, m. p. 274°); β-5-methoxy-2-aminophenyl- (*benzoyl* derivative, m. p. 183—184°) -propionic acid: β-2-aminophenyl-; β-5-chloro-2-aminophenyl-; β-3-chloro-2-aminophenyl-; β-3 : 5-dichloro-2-aminophenyl-*n*-butyric acid. *Sodium* β-o-*methylaminophenylpropionate* from 2-keto-1-methyl-1 : 2 : 3 : 4-tetrahydroquinoline is converted by methyl sulphate into *methyl* β-o-*dimethylaminophenylpropionate*, b. p. 140°/20 mm., transformed by hydrochloric acid into β-o-*dimethylaminophenylpropionic acid hydrochloride*, m. p. 183—184°, from which *N*-methylhydrocarbostyryl is obtained by sodium acetate. *Methyl* β-o-*methylethylaminophenylpropionate*, b. p. 145°/20 mm., is converted by hydrochloric acid into β-o-*methylethylaminophenylpropionic acid hydrochloride*, m. p. 130—133°, from which the free *acid*, b. p. 190°/20 mm., is obtained in almost homogeneous form. *Methyl* β-o-*phenylmethylaminophenylpropionate*, b. p. 200°/15 mm., is hydrolysed to *N*-phenylhydrocarbostyril.

The sodium salts of the aminophenyl-propionic or -butyric acids are mixed with sodium nitrite and water and added to dilute hydrochloric acid. The diazo-solution is added to aqueous copper sulphate and sodium chloride. The free acids are converted by thionyl chloride into their chlorides and thence into indanones. The following substances are thus obtained: β-2-chlorophenylpropionic acid, m. p. 97°, its *chloride*, b. p. 155—158°/20 mm., and 4-*chloro*-1-*keto*-2 : 3-*dihydroindene*, m. p. 92°; β-2-*bromophenylpropionic acid*, m. p. 98°, its *chloride*, b. p. 160—165°/18 mm., and 4-bromo-1-keto-2 : 3-dihydroindene, m. p. 98—99°; β-2 : 3-*dichlorophenylpropionic acid*, m. p. 114°, its *chloride*, b. p. 178—182°/28 mm., and 4 : 5-*dichloro*-1-*keto*-2 : 3-*dihydroindene*, m. p. 88°; β-2 : 5-*dichlorophenylpropionic acid*, m. p. 118°, its *chloride*, b. p. 154—158°/18 mm., and 4 : 7-*dichloro*-1-*keto*-2 : 3-*dihydroindene*, m. p. 124°; β-2 : 3 : 5-*trichlorophenylpropionic acid*, m. p. 113°, its *chloride*, b. p. 201—203°/12 mm., and 4 : 5 : 7-*trichloro*-1-*keto*-2 : 3-*dihydroindene*, m. p. 114°; β-2-*chloro*-3-*methylphenylpropionic acid*, m. p. 118°, its *chloride*, b. p. 140—146°/18 mm., and 4-*chloro*-1-*keto*-5-*methyl*-2 : 3-*dihydroindene*, m. p. 82°; β-2-*chloro*-5-*methylphenylpropionic acid*, m. p. 93°, its *chloride*, b. p. 160—168°/18 mm., and 4-*chloro*-1-*keto*-7-*methyl*-2 : 3-*dihydroindene*, b. p. 168—173°/18 mm.; β-2-*chloro*-5-*methoxyphenylpropionic acid*, b. p. 200°/15 mm., m. p. 72—73°, its *chloride*, and 4-*chloro*-7-*hydroxy*-1-*keto*-2 : 3-*dihydroindene*, m. p. 122°; β-2-*chlorophenyl*-n-*butyric acid*, b. p. 150°/13 mm., m. p. 60°, its *chloride*, b. p. 140°/20 mm., and 4-*chloro*-1-*keto*-3-*methyl*-2 : 3-*dihydroindene*, m. p. 55°; β-2 : 5-*dichlorophenyl*-n-*butyric acid*, b. p. 180°/15 mm., m. p. 71°, its *chloride*, b. p. 160°/15 mm., and 4 : 7-*dichloro*-1-*keto*-3-*methyl*-2 : 3-*dihydroindene*, m. p. 103°; β-5-*chloro*-2-*bromophenyl*-n-*butyric acid*, b. p. 200°/15 mm., m. p. 87°; β-2 : 3-*dichlorophenyl*-n-*butyric acid*, m. p. 115°, its *chloride*, b. p. 180°/15 mm., and 4 : 5-*dichloro*-1-*keto*-3-*methyl*-2 : 3-*dihydroindene*, b. p. 170°/15 mm., m. p. 44°; β-2 : 3 : 5-*trichlorophenyl*-n-*butyric acid*, b. p. 190°/15 mm., m. p. 115—116°, its *chloride*, b. p. 160°/15 mm., and 4 : 5 : 7-*trichloro*-1-*keto*-3-*methyl*-2 : 3-*dihydroindene*, m. p. 88—89°.

β-2-*Cyanophenylpropionic acid*, m. p. 136°, is hydrolysed to β-2-carboxyphenylpropionic acid, m. p. 165—166°. Similarly, β-5-*chloro*-2-*cyanophenyl*-n-*butyric acid*, b. p. 160°/15 mm., m. p. 120°, yields β-5-*chloro*-2-*carboxyphenyl*-n-*butyric acid*, m. p. 185°. Sodium β-2-aminophenylpropionate is converted into 1-chromanone, m. p. 25°, and sodium β-5-chloro-2-aminophenyl-*n*-butyrate into 6-*chloro*-4-*methyl*-1-*chromanone*, b. p. 145—150°/15 mm., m. p. 66°; the latter compound is transformed by bromine at 250° into 6-chloro-4-methylcoumarin, m. p. 186°. Suitable treatment of sodium β-2-aminophenylpropionate yields β-phenylpropionic acid, m. p. 49°, β-*phenylpropionic*-2-*sulphinic acid* (as *sodium* salt), and β-2-*thiolphenylpropionic acid*, m. p. 118°. 6-*Chloro*-4-*methylthiohydrocoumarin*, m. p. 56°, and β-5-*chloro*-2-*thiolphenyl*-n-*butyric acid*, m. p. 81—82°, are described.

H. Wren.

Decahydroquinoline derivatives. IV. Hofmann degradation of 2-methyloctahydroindole. S. Fujise (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 9, 91—98).—Reduction of 2-methylindole in glacial acetic acid at 40—45° with hydrogen and platinum-black yields cis-2-*methyloctahydroindole*, b. p. 187·5—188°, d_4^{25} 0·9103, n_D^{25} 1·47432 [*hydrobromide*, m. p. 148—149°; *chloroaurate*, m. p. 118°; methiodide, m. p. 233—234° (decomp.); picrate, m. p. 178—179° (decomp.); benzenesulphonyl derivative, m. p. 125°; von Braun and Bayer, A., 1925, i, 428, give 296°, 192—193°, and 120—121°, respectively, for the last three derivatives, their specimen probably being contaminated with *o*-propyl*cyclo*hexylamine or with the *trans*-compound]. This by exhaustive methylation yields o-*dimethylaminopropenyl*cyclo*hexane*, b. p. 211—213°, d_4^{25} 0·8670, n_D^{25} 1·47196 [methiodide, m. p. 212° (decomp.); picrate, m. p. 146° (decomp.); von Braun, Bayer, and Blessing, A., 1924, i, 545, give, for the unidentified base, 187—188° and 129—130°, respectively], in accordance with the scheme  $C_6H_{10}{<}^{CH_2—————}_{NMe_2(OH)}{>}CHMe \longrightarrow C_6H_{10}{<}^{CH:CHMe}_{NMe_2}$, since it is converted by further catalytic reduction into *cis*-2-dimethylamino-*n*-propyl*cyclo*hexane, b. p. 214°, d_4^{20} 0·8602, n_D^{20} 1·46386, identical with the product obtained by the exhaustive methylation of *cis*-decahydroquinoline (this vol., 1022).

J. W. Baker.

Stereoisomerism in polycyclic systems. V. W. H. Perkin, jun., and S. G. P. Plant (J.C.S., 1928, 2583—2590; cf. this vol., 72, 527).—The simultaneous formation of relatively large quantities of both *cis*- and *trans*-modifications of 2 : 3 : 4 : 5 : 11 : 12-hexahydroheptindole and 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline during reduction of 2 : 3 : 4 : 5-tetrahydroheptindole and 7 : 8 : 9 : 10-tetrahydroheptaquinoline respectively might be anticipated from consideration of the strains existing in the multiplanar configurations of these reduction products. The results are not in accordance with expectation. 2 : 3 : 4 : 5-*Tetrahydroheptindole*, m. p. 144° (*picrate*, m. p. 142°), is obtained by Fischer's indole synthesis from suberonephenylhydrazone. When this compound is reduced with tin and hydrochloric acid in aqueous alcohol, the product consists almost entirely of a single form (presumably the *cis*, which is likely to be the less strained) of 2 : 3 : 4 : 5 : 11 : 12-*hexahydroheptindole* (I), m. p. 77° [*picrate*, m. p. 176° (decomp.); *hydrochloride*; 10-*acetyl* derivative, m. p. 87°; 10-*benzoyl* derivative, m. p. 116°]. Not more than 5% of any stereoisomeride is present. When 7-*bromo*-2 : 3 : 4 : 5-*tetrahydroheptindole*, m. p. 129—130°, prepared from *suberone*-p-*bromophenylhydrazone*, m. p. 57°, is similarly reduced, it undergoes partial debromination. Reduction of 7 : 8 : 9 : 10-tetrahydroheptaquinoline with tin and hydrochloric acid in aqueous-alcoholic solution yields a product consisting almost entirely of one of the possible forms of 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-*octahydroheptaquinoline* (II), b. p. 203°/24 mm. (*picrate*, m. p. 96°; 5-*benzoyl* derivative, m. p. 145°). The same substance is obtained as sole product when 11-*keto*-5 : 7 : 8 : 9 : 10 : 11-*hexahydroheptaquinoline*, m. p. 344—345°, obtained by condensation of anthranilic acid and suberone, is reduced with sodium amalgam.

The relative amounts of octahydroacridine-*A* and octahydroacridine-*B* formed by reducing tetrahydroacridine with tin and aqueous-alcoholic hydrochloric acid (Perkin and Sedgwick, A., 1925, i, 63) are now found to be in the ratio of approximately 1 to 4. The reduction of tetrahydroacridone with tin and aqueous-alcoholic hydrochloric acid yields a small quantity of one of the two possible forms of *hexahydroacridone*, m. p. 180° (*oxime*, m. p. 215—216°).

M. Clark.

Derivatives of tetrahydrocarbazole. VII. Reactions of 3-methyltetrahydrocarbazole, 6-chlorotetrahydrocarbazole, and their acyl derivatives. S. G. P. Plant and R. J. Rosser (J.C.S., 1928, 2454—2464).—Like 9-benzoyltetrahydrocarbazole (*ibid.*, 1923, **123**, 676), the 9-benzoyl derivatives of 3-methyl- and 6-chloro-tetrahydrocarbazole react with nitric acid producing, in each case, the direct nitration product, together with a substance formed by addition of OH and NO_2 at the double linking; 9-carbethoxy-6-chlorotetrahydrocarbazole behaves in like fashion. Like 9-acetyltetrahydrocarbazole, the 9-acetyl derivatives undergo addition of OH and OH at the double linking; 9-carbethoxy-3-methyltetrahydrocarbazole behaves similarly. The *phenylhydrazone*, o- and p-*nitrophenylhydrazones*, m. p. 59° and 128·5°, of 4-methyl*cyclo*hexanone are converted by the Fischer indole synthesis into 3-*methyltetrahydrocarbazole*, m. p. 109—110°, and its 8- and 6-*nitro*-derivatives, m. p. 188° and 165—166°, respectively. The m-*nitrophenylhydrazone*, m. p. 80—81°, yields a mixture of 5(or 7)- and 7(or 5)-*nitro*-3-*methyltetrahydrocarbazoles*, m. p. 188° and 175°. Nitration of the 3-methyl-carbazole in sulphuric acid solution yields the 6-nitro-derivative as sole product. Nitration of the 9-*acetyl* derivative, m. p. 108·5°, in acetic acid solution, yields a mixture of 5(or 7)-*nitro*-9-*acetyl*-3-*methyltetrahydrocarbazole*, m. p. 134°, and 10 : 11-*dihydroxy*-9-*acetyl*-3-*methylhexahydrocarbazole*, m. p. 189—190°. Treatment of the last-named compound with acetic anhydride yields 6-*acetyl*-3-*methyl*-ψ-*indoxyl*spirocyclo*pentane*, m. p. 93·5°. 3-*Methyl*-ψ-*indoxyl*spirocyclo*pentane*, has m. p. 114·5°. Nitration of 9-*benzoyl*-3-*methyltetrahydrocarbazole*, m. p. 99° (prepared by successive treatment with magnesium methyl iodide and benzoyl chloride), in acetic acid solution yields a mixture of the 5(or 7)-*nitro*-9-*benzoyl* derivative, m. p. 142·5°, and 11-*nitro*-10-*hydroxy*-9-*benzoyl*-3-*methylhexahydrocarbazole*, m. p. 123° (decomp.). Nitration of 9-*carbethoxy*-3-*methyltetrahydrocarbazole*, m. p. 66—67°, under similar conditions yields a mixture of the 5(or 7)-*nitro*-9-*carbethoxy*-derivative, m. p. 104°, and *ethyl* 10 : 11-*dihydroxy*-3-*methylhexahydrocarbazole*-9-*carboxylate*, m. p. 135°.

Nitration of 6-chlorotetrahydrocarbazole in concentrated sulphuric acid solution yields the 5(or 7)-*nitro*-derivative (I), m. p. 183·5°. 4-*Chloro*-3-*nitrophenylhydrazine*, m. p. 109°, from 4-chloro-3-nitroaniline, reacts with *cyclo*hexanone, giving cyclo*hexanone* 4-*chloro*-3-*nitrophenylhydrazone*, m. p. 106—107°. The last-named compound is converted by the Fischer indole synthesis into a mixture of I and 6-*chloro*-7(or 5)-*nitro*-6-*tetrahydrocarbazole*, m. p. 162°. Similar reactions, starting with 4-chloro-o-nitroaniline, yield 4-*chloro*-2-*nitrophenylhydrazine*, m. p. 134°, cyclo*hexanone*-4-*chloro*-2-*nitrophenylhydrazone*, m. p. 101°, and 6-*chloro*-8-*nitrotetrahydrocarbazole*, m. p. 213°. Nitration of 6-*chloro*-9-*acetyltetrahydrocarbazole*, m. p. 136°, in hot acetic acid solution yields the 5(or 7)-*nitro*-derivative, m. p. 184·5—185·5°, and 6-*chloro*-10 : 11-*dihydroxy*-9-*acetylhexahydrocarbazole*, m. p. 222°. Similar nitration of 6-*chloro*-9-*benzoyltetrahydrocarbazole*, m. p. 122—123°, yields the 5(or 7)-*nitro*-derivative, m. p. 148°, and 6-*chloro*-11-*nitro*-10-*hydroxy*-9-*benzoylhexahydrocarbazole*, m. p. 147° (decomp.). Nitration of 6-*chloro*-9-*carbethoxytetrahydrocarbazole*, m. p. 111—112°, in hot acetic acid solution yields the 5(or 7)-*nitro*-derivative, m. p. 126°; when fuming nitric acid is used, the product is *ethyl* 6-*chloro*-11-*nitro*-10-*hydroxyhexahydrocarbazole*-9-*carboxylate*, m. p. 136—137°. When an alcoholic solution of the last-named compound is boiled for 1 hr., conversion into *ethyl* 6-*chloro*-10 : 11-*dihydroxyhexahydrocarbazole*-9-*carboxylate*, m. p. 132°, takes place.

When 3-methyltetrahydrocarbazole is reduced with tin and hydrochloric acid in aqueous alcohol, two stereoisomeric modifications of 3-*methylhexahydrocarbazole* (A), m. p. 58·5°, and (B), m. p. 128°, are obtained. The (A) modification (9-*acetyl* derivative, m. p. 101°; 9-*benzoyl* derivative, m. p. 81·5°; *picrate*, m. p. 115—116°) is the sole product of electrolytic reduction.

M. Clark.

***ms*-Acridine derivatives.** K. Lehmstedt and E. Wirth (Ber., 1928, **61**, [*B*], 2044—2049).—Acridine is converted by a boiling aqueous solution of sodium sulphite and hydrogen sulphite into colourless *sodium* 9 : 10-*dihydroacridine*-9-*sulphonate*, slowly oxidised by air when moist or when its solution is evaporated to the sparingly soluble red sulphite, converted by alkali hydroxide into the colourless salt and acridine. The colourless salt is converted into acridine by alkali hydroxide, thus permitting a ready separation of acridine from other bases. It is transformed by potassium cyanide in boiling alcoholic suspension into 9-*cyano*-9 : 10-*dihydroacridine*, m. p. 146° (*hydrochloride*; *picrate*, m. p. 222°), in which the cyano-group is replaced by the hydroxy-group by hydrolysing agents. Protracted boiling of an alcoholic solution of 9-cyano-9 : 10-dihydroacridine leads to the production of 9 : 10 : 9′ : 10′-*tetrahydro*-9 : 9′-*diacridyl*, m. p. 214° with decomposition into acridine and 9 : 10-dihydroacridine. Dehydrogenation of 9-cyano-9 : 10-dihydroacridine affords 9-*cyanoacridine*, m. p. 186° (*hydrochloride*; *picrate*, m. p. 229°), converted by 90% sulphuric acid at 100° into acridine-9-carboxylamide, m. p. 263—264°, and by the successive action of sulphuric acid and sodium nitrite into *acridine*-9-*carboxylic acid*, decomp. 289—290°. 9-Cyanoacridine and alcoholic ammonium sulphide yield *acridine*-9-*thiocarboxylamide*, m. p. 240°.

H. Wren.

Chloroform-soluble metal pyridine cyanates. T. L. Davis and A. V. Logan (J. Amer. Chem. Soc., 1928, **50**, 2493—2499).—Blue *hexapyridinecupric*, blue *hexapyridinenickelous*, pink *hexapyridinecobaltous*, and *hexapyridinecadmium cyanates* are extracted by chloroform from aqueous solutions of their components. They are stable in presence of pyridine vapour, but decompose on exposure to the air into dipyridinecupric (cf. Werner, J.C.S., 1923, **123**, 2577), pale blue *tetrapyridinenickelous*, blue *dipyridinecobaltous*, and *dipyridinecadmium cyanates*, respectively. *Dipyridine-*

zinc cyanate is stable in air, but *monopyridinesilver cyanate* loses pyridine. Both absorb pyridine vapour with deliquescence. Chloroform solutions of hexapyridinecobaltous and hexapyridinecupric cyanates show approximately 6·5 times the b. p. elevation calculated for the undissociated compounds. The colour of the former solution is that of the dipyridine derivative, but it changes towards that of the hexapyridine salt when pyridine is added or the temperature is lowered. H. E. F. Notton.

2-Acetamidopyridine. E. Plažek and E. Sucharda (Ber., 1928, 61, [*B*], 1813—1816).—The action of nitric acid (*d* 1·5) on 2-acetamidopyridine in glacial acetic acid and acetic anhydride yields 2-*acetamidopyridine nitrate*, m. p. 190°. Acetylation of the amino-group of 2-aminopyridine destroys completely its ability to facilitate the entry of the nitro-group. The nitrate is unaffected by boiling, fuming nitric acid or by a boiling mixture of nitric acid and acetic anhydride. It is converted by concentrated sulphuric acid into a mixture of 3- and 5-nitro-2-aminopyridines; since 2-nitroaminopyridine is an intermediate product of the reaction, it follows that nitration is preceded by hydrolysis of the acetamido-group. 2-Acetamidopyridine is converted by bromine into 5-*bromo*-2-*acetamidopyridine*, m. p. 175°, identified by hydrolysis to 5-bromo-2-aminopyridine, m. p. 137°. H. Wren.

Derivatives of pyridine. F. B. LaForge (J. Amer. Chem. Soc., 1928, 50, 2477—2483).—Cyanopyridine (cf. Camps, A., 1902, i, 823) and magnesium methyl iodide followed by sulphuric acid yield 3-pyridyl methyl ketone (Engler, A., 1891, 1505), the oxime of which is reduced by zinc dust and acetic acid to α-3-*pyridylethylamine*, b. p. 219—221°/765 mm. (*picrate*, m. p. 186—187°). This gives with ethyl iodide α-3-*pyridyldiethylamine*, b. p. 223—226°/773 mm. 3-*Pyridyl propyl ketone*, b. p. 240—248° (*semicarbazone*, m. p. 169—170°), yields a hydrazone, m. p. 129—130° (cf. Engler, *loc. cit.*), which is converted by concentrated hydrochloric acid into 2-β-*pyridyl*-3-*ethylindole*, m. p. 158° (yellow *hydrochloride*), and by zinc dust and acetic acid into α-3-*pyridylbutylamine*, b. p. 247—251°. *Methyl*-α-3-*pyridylbutylamine* has b. p. 244—247°. The new pyridylalkylamines have only a slight insecticidal action, but nicotyrin, dihydro*metanicotine*, and especially *meta*nicotine have a toxicity approaching that of nicotine.

H. E. F. Notton.

2-, 3-, and 4-Benzylpyridines. F. B. LaForge (J. Amer. Chem. Soc., 1928, 50, 2484—2487).—2- and 4-Benzylpyridines are conveniently isolated from the mixture obtained by Tschitschibabin's method (A., 1901, i, 484) by oxidation with permanganate to the benzoylpyridines, which are easily separated by crystallisation of the picrates, and reduced by Clemmensen's method. 3-Benzoylpyridine, from 3-cyanopyridine and magnesium phenyl bromide, is converted by reduction of the oxime into α-3-*pyridylbenzylamine*, b. p. 329—331°/760 mm. This yields, with nitrous acid, α-3-*pyridylbenzyl alcohol*, which is reduced by hydriodic acid to 3-benzylpyridine (*picrate*, m. p. 119°) (cf. A., 1903, i, 853). H. E. F. Notton.

Diphenylpyridylmethane dyes. E. Plažek and E. Sucharda (Ber., 1928, 61, [*B*], 1811—1813; cf. A., 1924, i, 881).—*Tetramethyltriaminodiphenylpyridylmethane*, m. p. 163—165° (also $+0\cdot5C_6H_6$), is obtained by the action of aqueous sulphuric acid on Michler's hydrol and 2-aminopyridine. It is not oxidised by manganese dioxide or lead peroxide to the corresponding dye below 100°. H. Wren.

Modification of the Skraup synthesis of quinoline. B. E. Cohn and R. G. Gustavson (J. Amer. Chem. Soc., 1928, 50, 2709—2711).—Addition of acetic acid causes the reaction to proceed smoothly, without diminishing the yield. Thus, 38 g. of aniline, 24 g. of nitrobenzene, 100 g. of glycerol, 60 c.c. of acetic acid (80%), and 54 c.c. of sulphuric acid, gently refluxed for 16 hrs., yield 33 g. of quinoline

H. E. F. Notton.

Complex salts of amphoteric hydroxyquinoline derivatives. E. Hertel and H. Kleu (Ber., 1928, 61, [*B*], 1653—1654).—Addition of copper sulphate to a solution of 5 : 7-dibromo-8-hydroxyquinoline gives an amorphous precipitate which becomes crystalline when heated. This *copper* salt and that derived similarly from 5 : 7-dichloro-8-hydroxyquinoline dissolve in halogen acids, giving intensely coloured *salts*, $(CuCl_4):(H\cdot\cdot NC_9H_4Cl_2\cdot OH)_2,2H_2O$;
$(CuCl_4):(H\cdot\cdot NC_9H_4Br_2\cdot OH),2H_2O$;
$(CuBr_4):(H\cdot\cdot NC_9H_4Cl_2\cdot OH)_2,2H_2O$;
$(CuBr_4):(H\cdot\cdot NC_9H_4Br_2\cdot OH)_2,2H_2O$;
$(CuI_4):(H\cdot\cdot NC_9H_4Br_2\cdot OH)_2,2H_2O$. The chlorides and iodides at 90° lose 2 mols. of water and 4 mols. of halogen acid, giving the copper salts, $Cu(O\cdot C_9H_4NX_2)_2$, whereas the bromides exhibit greater thermostability. H. Wren.

Preparation of 2-phenylquinoline-4-carboxylic acid [atophan]. F. Chemnitius.—See B., 1928, 767.

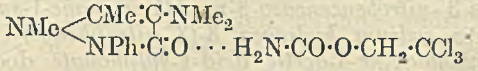
Pyrazolones. Action of thiosemicarbazide and semicarbazide on ketonic esters. II. S. C. De and N. C. Dutt (J. Indian Chem. Soc., 1928, 5, 459—465).—Ethyl benzoylacetate reacts with thiosemicarbazide, yielding 3-*phenylpyrazolone*-1-*thiocarbamide*, m. p. 161° (4 : 4-*dibromo*-derivative, loses bromine at 130°; 4-iso*nitroso*-derivative, m. p. 174°), and with 4-phenyl-, 4-*p*-tolyl-, and 4-ethyl-thiosemicarbazides, forming 3-*phenylpyrazolone*-1-*thiocarbophenylamide*, m. p. 127°, -p-*tolylamide*, m. p. 106°, and -*ethylamide*, m. p. 136°, respectively. 3-*Phenylpyrazolone*-1-*carbamide*, m. p. 179° (4 : 4-*dibromo*-derivative, m. p. 144°; 4-iso*nitroso*-derivative, m. p. 204°), is obtained similarly from semicarbazide.

Ethyl diacetosuccinate and semicarbazide give 4 : 4′-*bis*-3-*methylpyrazolone*-1-*carbamide*, m. p. 128° (-1-*thiocarbamide*, m. p. 197°; -1-*thiocarbophenylamide*, m. p. 191°; -1-*thiocarbo*-p-*tolylamide*, m. p. 201—202°; -1-*thiocarboethylamide*, m. p. 191°), which when heated above its m. p. decomposes into 4 : 4′-bis-3-methylpyrazolone, m. p. 290° after darkening at 250°.

Ethyl acetoacetate and 4-phenylthiosemicarbazide give 3-methylpyrazolone-1-thiocarbophenylamide, m. p. 117°. The corresponding *p*-tolylamide and ethylamide have m. p. 121° and 84°, respectively.

H. Burton.

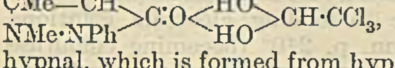
Constitution of "compral." P. Pfeiffer and R. Seydel (Z. physiol. Chem., 1928, 178, 81—96). Compral is an additive compound of pyramidone and voluntal, $CCl_3{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}NH_2$ (1 : 1, m. p. about 76°). Investigation of the m.-p. curves of related compounds led to the conclusion that the acid amide group, and not the dimethylamino-group of pyramidone was the cause of the formation of additive compounds, whilst the hydrogen atoms of the amino-group in voluntal were indispensable, and the replacement of the chlorine by hydrogen greatly weakened the tendency to form additive compounds. Compral is assigned the constitution :



$$\mathrm{NMe}<\begin{matrix}\mathrm{CMe{:}C{\cdot}NMe_2}\\ \mathrm{NPh{\cdot}C{:}O}\end{matrix}\cdots\mathrm{H_2N{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CCl_3}$$

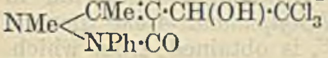
The m.-p. curves of the following pairs of substances were examined : acetamidoantipyrine–voluntal (*compound*, 1 : 1); antipyrine–voluntal (*compound*, 1 : 1); sarcosine anhydride–voluntal (*compound*, 1 : 2, m. p. 73°); pyramidone–*N*-phenylvoluntal; acetamidoantipyrine–*N*-phenylvoluntal; antipyrine–*N*-phenylvoluntal (*compound*, 1 : 1, m. p. 70°); sarcosine anhydride–*N*-phenylvoluntal (*compound*, 1 : 2, m. p. 121°); antipyrine–*N*-phenyl-*N*-methylvoluntal; pyramidone–*N*-phenyl-*N*-methylvoluntal; sarcosine anhydride–*N*-phenyl-*N*-methylvoluntal; antipyrine–urethane; sarcosine anhydride–urethane (*compound*, 1 : 2, m. p. 70°); and sarcosine anhydride–*N*-phenylurethane (*compound*, 1 : 2, m. p. 95—97°). R. K. Callow.

Constitution of hypnal and trigemin. P. Pfeiffer and R. Seydel (Z. physiol. Chem., 1928, **178**, 97—108).—Hypnal and bihypnal were shown by Tsakalotos (A., 1913, i, 521) to be additive compounds of antipyrine and chloral hydrate in the proportions 1 : 1 and 1 : 2, respectively. This was confirmed by examination of the m.-p. curves, and the existence of additive *compounds* of pyramidone and butylchloral hydrate (1 : 1, m. p. 84°) (trigemin, cf. G.P. 150799) and of antipyrine and butylchloral hydrate (1 : 1, m. p. 72°) was also shown. The investigation of the m.-p. curves of related compounds showed that additive *compounds* were formed by sarcosine anhydride and chloral hydrate (1 : 1, m. p. 92—95°; 1 : 2, m. p. 83—86·5°). On the other hand, antipyrine, pyramidone, or sarcosine anhydride formed no additive compounds with cholesterol or mannitol, suggesting that the existence of two hydroxyl groups on the same carbon atom is the cause of formation of additive compounds by chloral hydrate. The loose combination of the components in hypnal is shown by the ease with which each reacts separately with appropriate reagents. To it is assigned the constitution :



$$\begin{matrix}\mathrm{CMe{=}CH}\\ \mathrm{NMe{\cdot}NPh}\end{matrix}>\mathrm{C{:}O}<\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}>\mathrm{CH{\cdot}CCl_3},$$

whilst anhydrohypnal, which is formed from hypnal by loss of water, is a " normal valency compound " :



$$\mathrm{NMe}<\begin{matrix}\mathrm{CMe{:}C{\cdot}CH(OH){\cdot}CCl_3}\\ \mathrm{NPh{\cdot}CO}\end{matrix}$$

(cf. Krey, Diss., Jena, 1892). R. K. Callow.

Hydrogenation of glyoxaline ring. E. Waser and A. Gratsos (Helv. Chim. Acta, 1928, **11**, 944—964).—Hydrogenation of lophine (2 : 4 : 5-triphenylglyoxaline) with hydrogen in presence of acetic acid and platinum-black gives 2 : 4 : 5-*tri*cyclo*hexyl*-4 : 5-*dihydroglyoxaline* (I), m. p. 211—213° (corr.) [*acetate* (II), m. p. 162—163° (corr.); *hydrochloride*, $+0{\cdot}5H_2O$, m. p. 268—270°; *hydrobromide* (III), m. p. 290—292°; *chloroplatinate*, $+6H_2O$, m. p. 251—252°; *styphnate*, m. p. 201—202°; *nitroso*-derivative, m. p. 175° (decomp.)], which on oxidation with chromic and acetic acids furnishes a small amount of *cyclo*hexanecarboxylamide. The action of hot nitric acid (*d* 1·4) on II is to give adipic acid, a *dinitro*-derivative, m. p. 249·5—251°, of I, and a red oil, whilst the action of ozone has afforded in one experiment a *substance*, $C_{12}H_{19}O_2N$ or $C_{12}H_{21}O_2N$, m. p. 192·5—193·5°, and in another case a *compound*, $C_{21}H_{31}ON_2$, m. p. 266·5—267°, together with oily products. Bromine (1 mol.) is decolorised by I in cold carbon tetrachloride solution, but after removal of the solvent the product is III. With 3 mols. of bromine a *dibromide hydrobromide*, $C_{21}H_{37}N_2Br_3$, m. p. 162°, is obtained, which is decomposed by treatment with petrol, or by heating at 220° into III. Excess of bromine converts amarine (2 : 4 : 5-triphenyl-4 : 5-dihydroglyoxaline) into a *dibromide hydrobromide*, m. p. 122° (decomp.), which when decomposed with petrol gives amarine hydrobromide, but when heated at 220° or treated with alcoholic potassium hydroxide it eliminates 2 mols. of hydrogen bromide, yielding lophine hydrobromide and lophine, respectively. When lophine is treated with a 4% solution of bromine in chloroform the product, m. p. about 78°, is a substitution derivative; with a 2% solution lophine hydrobromide is obtained.

Hydrogenation of amarine gives a mixture of I and 2 : 4 : 5-*tri*cyclo*hexyltetrahydroglyoxaline*, m. p. 171—172° (corr.) [*hydrochloride*, decomp. 302° after sintering at 292°; *hydrobromide*, m. p. 296° (decomp.); *acetate*, m. p. 152—153°; *chloroplatinate*, $+4H_2O$, m. p. 216·5—217°; *styphnate*, m. p. 168·5—169·5°; *nitroso*-derivative].

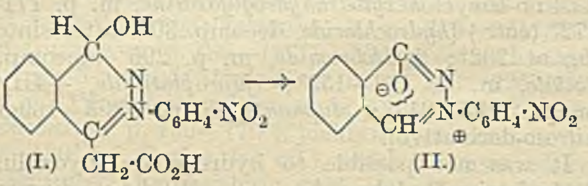
It was not possible to hydrogenate glyoxaline, 2 : 4 : 5-trimethylglyoxaline, 2-methyl-4 : 5-dihydroglyoxaline, histidine, or benziminazole. H. Burton.

Absorption of ultra-violet light by α-amino-acids, polypeptides, 2 : 5-diketopiperazines, and betaines. E. Abderhalden and E. Rossner (Z. physiol. Chem., 1928, **178**, 156—163).—The absorption spectra in the ultra-violet were measured of most carefully purified samples of glycylglycine, glycine anhydride, *dl*-leucylglycine, *dl*-leucylglycine anhydride, glycyl-*dl*-leucine, *dl*-leucylglycylglycine, betaine, betaine hydrochloride, hordenine, and hordenine hydrochloride. The spectrographic method was applied to determine whether perfectly pure cysteine was spontaneously transformed into cystine. The purest specimen of cysteine obtained, either free or as hydrochloride, still gave evidence of this transformation on keeping the solutions. R. K. Callow.

Diketones. I. Reaction between 4-phenylsemicarbazide and acetylacetone. A. S. Wheeler and R. D. Norton (J. Amer. Chem. Soc., 1928, **50**, 2488—2490).—In aqueous alcohol a *product*, m. p. 255—257°, and 1-*phenylcarbamyl*-3 : 5-*dimethylpyrazole*, m. p. 69° to an opaque liquid which clears at 200°, are formed in proportions varying with the conditions. The latter is identified by its conversion by boiling alcohol into 3 : 5-dimethylpyrazole and phenylurethane, by boiling water into carbon dioxide, carbanilide, and dimethylpyrazole, and by bromine into 4-*bromo*-1-*phenylcarbamyl*-3 : 5-*dimethylpyrazole*, m. p. 100—101°, which with boiling water yields 4-bromo-3 : 5-dimethylpyrazole, m. p. 123° (cf. Morgan and Ackerman, J.C.S., 1923, **123**, 1316). H. E. F. NOTTON.

Preparation of 2 : 2′-dipyridyl. F. HEIN and W. RETTER (Ber., 1928, **61**, [*B*], 1790—1791).—2 : 2′-Dipyridyl is obtained in 52% yield by heating pyridine with sublimed ferric chloride in a sealed tube for about 35 hrs. at 300°. The product is dissolved in water and the solution is successively extracted with ether and distilled with steam after neutralisation with sodium hydrogen carbonate, whereby pyridine is removed. The residual solution is rendered strongly alkaline and again distilled with steam, thus giving 2 : 2′-dipyridyl, which is decolorised with charcoal and crystallised from aqueous alcohol. H. WREN.

New reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. II. Constitution of nitro- and amino-phenylphthalazones. F. M. ROWE and E. LEVIN (J.C.S., 1928, 2550—2555).—The soluble product obtained by boiling an aqueous-sulphuric acid solution of 1-hydroxy-3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid (I) is shown to be 4′-*nitro*-3-*phenylphthalaz*-1-*one* (II), m. p. 333°, reduction of which gave 4′-*amino*-3-*phenylphthalaz*-1-*one*, m. p. 259° (previously described as 4′-amino-3-phenylphthalaz-4-one, A., 1926, 625). Attempts to deaminate the last compound were unsuccessful. The compound described by Seekles (A., 1924, i, 642) as a nitrophenylphthalazone is found to be the *lactone*, m. p. 254° (previous darkening at 228°), of o-*carboxybenzaldehyde*-p-*nitrophenylhydrazone*, decomp. 21·8° (resolidifying at 249°), but when boiled in nitrobenzene solution this passed into 4′-*nitro*-3-*phenylphthalaz*-4-*one*, m. p. 258°, not identical with II. Reduction with sodium sulphide gave 4′-*amino*-3-*phenylphthalaz*-4-*one*, m. p. 184° (*hydrochloride*; *acetyl* derivative, m. p. 233°), whilst zinc dust and hydrochloric acid gave 4′-amino-*N*-phenylphthalimidine. The amphoteric nature of 4′-nitro-3-phenylphthalaz-1-one is best explained by II; thus it forms well-crystallised *salts*, and a *picrate*, m. p. 218°. Treatment with methyl sulphate in nitrobenzene solution led to an aqueous solution of the *methosulphate*, which was isolated (by addition of sodium carbonate) as a *substance*, m. p. 138—141° and 173—175° after crystallisation from ethyl and methyl alcohols respectively (*hydrochloride*). These when heated formed 4-*keto*-1-*methoxy*-3-(4′-*nitrophenyl*)-3 : 4-*dihydrophthalazine* (neutral), m. p. 199°, demethylation of which gave 1 : 4-*diketo*-3-(4′-*nitrophenyl*)*tetrahydrophthalazine*, m. p. 307°. R. J. W. LE FÈVRE.



(I.) (II.)

Reaction of diazosulphonates derived from β-naphthol-1-sulphonic acid. III. Preparation of phthalazine, phthalazone, and phthalimidine derivatives from *m*-nitroaniline. F. M. ROWE, M. A. HIMMAT, and E. LEVIN (J.C.S., 1928, 2556—2563; cf. preceding abstract).—Conversion of 3′-nitrobenzene-2-naphthol-1-diazosulphonate through *sodium* 3′-*nitrobenzeneazo*-β-*naphthaquinone*-1-*sulphonate* into *sodium hydrogen* 3-(3′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid*-1-*sulphonate* does not proceed so readily as in the case of the 4′-nitro-isomeride. On boiling the product with concentrated hydrochloric acid 1-*hydroxy*-3-(3′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid*, m. p. 234° (*methyl* ester, m. p. 184°; *ethyl* ester, m. p. 195°; *anilide*, m. p. 239°), is obtained. Reduction with stannous chloride and hydrochloric acid (alkaline reduction gives an indefinite product: compounds in the 3′-nitro-series are more sensitive to alkalis than their 4′-nitro-isomerides) gives 1-*hydroxy*-3-(3′-*aminophenyl*)*tetrahydrophthalazine*-4-*acetic acid*, m. p. 252° (*acetyl* derivative, m. p. 167°), which when boiled with aqueous sulphuric acid gives 3′-*amino*-3-*phenylphthalaz*-1-*one*, m. p. 210° (*hydrochloride*; *acetyl* derivative, m. p. 204°), from which ammonia can be eliminated by treatment with zinc dust and hydrochloric acid, giving 3′-*amino*-N-*phenylphthalimidine*, m. p. 175° (*acetyl* derivative, m. p. 204°; *zinc double chloride*), which, in turn, readily (relatively to the corresponding 4′-amine) gives 3-*hydroxy*-N-*phenylphthalimidine*, m. p. 268° (*methyl ether*, m. p. 122°; *ethyl ether*, m. p. 115°), by diazotisation. By boiling 1-hydroxy-3-(3′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid with sulphuric acid, 3′-*nitro*-3-*phenylphthalaz*-1-*one*, m. p. 324° (well-crystallised *salts*; *picrate*, m. p. 234°), is obtained, reduction of which by sodium sulphide or zinc dust and hydrochloric acid gives 3′-amino-3-phenylphthalaz-1-one or 3′-amino-*N*-phenylphthalimidine, respectively. Treatment with methyl sulphate in boiling nitrobenzene (cf. 4′-nitro-analogue, preceding abstract) gives a *substance*, m. p. 114—117° or 116—120° after crystallisation from methyl or ethyl alcohol, respectively, which, when heated, gives 4-*keto*-1-*methoxy*-3-(3′-*nitrophenyl*)-3 : 4-*dihydrophthalazine*, m. p. 182°, accompanied (especially if heating be rapid) by a complex *substance*, m. p. 289°. Hydrobromic acid reacts with the above methoxy-compound, giving 1 : 4-*diketo*-3-(3′-*nitrophenyl*)*tetrahydrophthalazine*, m. p. 280°. Phthalaldehydic acid and *m*-nitrophenylhydrazine condense in boiling alcoholic solutions, giving the *lactone*, m. p. 240° (becoming colourless at 200°), of *o*-carboxybenzaldehyde-*m*-nitrophenylhydrazone; from this, by boiling its solution in nitrobenzene, 3′-*nitro*-3-*phenylphthalaz*-4-*one* (neutral and inactive), m. p. 240°, is obtained, from which, by alkaline hyposulphite reduction, 3′-*amino*-3-*phenylphthalaz*-4-*one*, m. p. 156° (*hydrochloride*), can be obtained. R. J. W. LE FÈVRE.

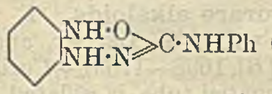
Dihydroxy- and dichloro-ketohexahydrotriazines. J. B. EKELEY and A. A. O'KELLY (J. Amer.

Chem. Soc., 1928, **50**, 2731—2733).—The additive products of αβ-diketones with 2 mols. of sodium hydrogen sulphite yield with semicarbazide hydrochloride in hot water 5 : 6-dihydroxy-3-keto-5 : 6-dialkylhexahydro-1 : 2 : 4-triazines, the lower homologues of which are converted by phosphorus trichloride into 5 : 6-dichloro-3-keto-5 : 6-dialkylhexahydro-1 : 2 : 4-triazines. γδ-Diketo-β-methylpentane does not yield a triazine derivative by this method. The decomposition temperatures of the following are: (*a*) sodium hydrogen sulphite additive *compounds* of: β*γ-diketobutane*, 145—155°; β*γ-diketopentane*, 135—150°; β*γ-diketohexane*, 130—140°; β*γ-diketoheptane*, 100—110°, and β*γ-diketo-octane*, 95—100°; (*b*) derivatives of 5 : 6-*dihydroxy*-3-*keto-hexahydro*-1 : 2 : 4-*triazine*, 265—270°: 5- or 6-*methyl*-, 250—255°; 5 : 6-*dimethyl*-, 240—245°; 5 : 6-(or 6 : 5)-*methylethyl*-, 230—235°; 5 : 6-*methylpropyl*-, 240—245°; 5 : 6-*methylbutyl*-, 230—235°, and 5 : 6-*methylamyl*-, 100—105°; (*c*) derivatives of 5 : 6-*dichloro*-3-*ketohexahydro*-1 : 2 : 4-*triazine*, 265—270°: 5- or 6-*methyl*-, 260—270°; 5 : 6-*dimethyl*-, 250—260°; 5 : 6-*methylethyl*-, 240—245°; 5 : 6-*methylpropyl*-, 230—235°.

H. E. F. NOTTON.

o-Aminophenylhydrazine and heterocyclic compounds derived from it. IV. Lengthened o-di-derivatives of benzene and their ring-closure. P. C. GUHA and T. N. GHOSH (J. Indian Chem. Soc., 1928, **5**, 439—451).—Reduction of 1-o-*nitrophenyl*-4-*phenylsemicarbazide*, m. p. 202°, with tin and concentrated hydrochloric acid gives a mixture of 1-o-*aminophenyl*-4-*phenylsemicarbazide* (I), m. p. 145° (*hydrochloride*, decomp. 250—251° after darkening; o-*nitrobenzylidene* derivative, m. p. 245—246°), and 3-*keto*-4-*phenyl*-1 : 2 : 3 : 4-*tetrahydrobenz*-1 : 2 : 4-*triazine* (II; R=Ph), m. p. 170—171°, also formed by the action of boiling acetic anhydride on I. 1-*Carbamido*-, m. p. above 290°, 1-*phenylcarbamido*-, m. p. above 290°, and 1-*phenylthiocarbamido*-, not melted at 290°, -2-*phenylsemicarbazidobenzenes* are described. Oxidation of I with ferric chloride gives the *compound* (III), not melted at 290°, whilst the action of hydrazine hydrate is to give the *compound* (IV), m. p. 90—91°. Reduction of 1-o-*nitrophenylsemicarbazide*, m. p. 225° (decomp.), gives 3-*imino*-1 : 2 : 3 : 4-*tetrahydrobenz*-1 : 2 : 4-*triazine* (II; R=H, O=:NH), m. p. 85° [*hydrochloride*, m. p. 248—249° (decomp.); *acetyl* derivative, m. p. 182—183°], also formed during the reduction of 1-o-*nitrophenylthiosemicarbazide*, m. p. 200° (decomp.). o-*Chlorobenzaldehyde*-o-*nitrophenylhydrazone*, m. p. 171°, is reduced to the *compound* (V), m. p. 217—218°; *glyoxal*-o-*nitrophenylosazone*, m. p. 279—280° (decomp.), to *bisbenziminazole*, not melted at 300° [*hydrochloride*, m. p. 253° (decomp.); *diacetyl* derivative, m. p. 183—184°]; *methyl* o-*nitrophenyldithiocarbazinate*, m. p. 113—114°, to the *compound* (VI), m. p. 199—200°; *di*-o-*nitrophenylcarbohydrazide*, m. p. 260—261°, to the *compound* (VII), isolated only as the *hydrochloride*, m. p. 251—252° (decomp.). *Ethyl* o-*nitrophenylcarbazinate* has m. p. 185°.

(II.)



(III.)

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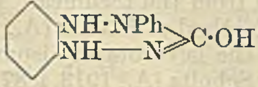

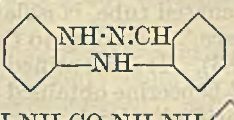

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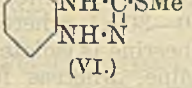

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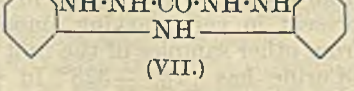


(VII.)

H. BURTON.

Transformation of uric acid into carbamide by oxidation with chromic and sulphuric acids. (MLLE.) J. SCHWANDER and H. CORDEBARD (Bull. Soc. Chim. biol., 1928, **10**, 920—931).—The rate of hydrolysis of carbamide by aqueous sulphuric acid increases with rise of temperature, is greatest when the concentration of the acid is 0·5—0·1*N* (depending on the temperature), and increases with the duration of the operation and with the concentration of the carbamide. Addition of potassium dichromate to the mixture has no other effect than the formation of small amounts of nitric acid. By the use of these results to select favourable conditions, carbamide may be obtained from uric acid in more than 96% yield.

G. A. C. GOUGH.

Modifications of hydroxyhæmin. A. HAMSÍK (Z. physiol. Chem., 1928, **178**, 67—74; cf A., 1925, i, 1476; this vol., 1148).—The β- and ψ-hydroxyhæmins, formed by the action of acids and alkalis on the α-hydroxyhæmin derived directly from blood, are distinguished chiefly by increased solubility, weak attachment of chlorine in the corresponding chlorohæmins, and low yield of protoporphyrin on removal of iron, the ψ-modification showing these properties more strongly. Details are given of the preparation of β-hydroxyhæmin (i) by the action of alkalis (the prolonged action of methyl-alcoholic potassium hydroxide on blood coagulum, or the action of aqueous potassium hydroxide on defibrinated blood followed by extraction of the precipitate with alcohol containing oxalic acid), and (ii) by the action of acids (the prolonged action of sulphuric, hydrochloric, acetic, and oxalic acids on defibrinated blood, or the action of these acids on α-hydroxyhæmin).

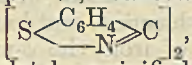
R. K. CALLOW.

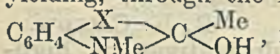
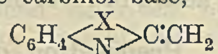
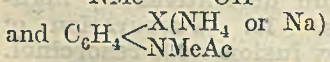
Preparation of hæmin derivatives by high-temperature reactions. II. Preparation of pyratin from hæmin by fusion with resorcinol. Preparation and properties of pyroporphyrin. Introduction of iron into porphyrins in the "iron–phenol fusion," and transformation of iron porphyratins by phenols and phenol–sulphuric acid mixtures. O. SCHUMM (Z. physiol. Chem., 1928, **178**, 1—18; cf. this vol., 1148). When hæmin is fused with a large excess of resorcinol at 180—190°, the process being followed by spectroscopic observations, and the mixture is poured into water, pyratin is precipitated. It may be purified by reprecipitating it from very dilute alkali by the addition of acetic acid, and may be converted into pyratin chloride by Küster's method (A., 1904, i, 356). It is reduced to pyroporphyrin by hydrazine and acetic acid (cf. Papendieck and Donath, A., 1925, i, 711) and also when heated with pyruvic acid, hydriodic and acetic acids, phenol and oxalic acid, oxalic acid, 10% sulphuric acid, or 25% hydrochloric acid. The spectroscopic comparison of pyroporphyrin and copratoporphyrin suggests complete identity, in concordance with the close similarity of composition and solubility and the apparent identity of pyratin and copratin. Treatment of pyroporphyrin with hydrogen chloride in methyl alcohol yields pyroporphyrin methyl ester, m. p. of different specimens 218°, 221°, and 223°, of the same composition as copratoporphyrin methyl ester, m. p. 221°.

Fusion of pyroporphyrin, copratoporphyrin, Nencki's hæmatoporphyrin, mesoporphyrin, or hæmateric acid with 100—200 parts of phenol and iron powder or ferrous oxide yields the corresponding iron compounds.

An account is given of preliminary investigations of the behaviour of hæmin when heated with various phenols and a little sulphuric acid. Spectroscopic observations show that under various conditions derivatives either with or without combined iron, or mixtures of these, are obtained.

R. K. CALLOW.

Benz*iso*thiazolone. A. REISSERT [with H. DÜSTERDIEK] (Ber., 1928, **61**, [*B*], 1680—1682).—In his recent publication (this vol., 883), the author has overlooked the priority of McClelland (J.C.S., 1922, **121**, 86, and subsequent papers) in the description of certain compounds. Attempts to convert benz*iso*thiazolone into the corresponding thiazole were unsuccessful. Thus, when distilled with zinc dust it yields benzonitrile. With phosphorus pentachloride it affords 3-*chlorobenz*iso*thiazole*, m. p. 40°, reduced by zinc dust to 3 : 3-*dibenz*iso*thiazolyl*,  $\left[S<\begin{smallmatrix}C_6H_4\\—N\end{smallmatrix}>C\right]_2$, m. p. 100°. The thiazolone is completely resinified by fuming hydriodic acid at 230°. H. WREN.

Methylene bases from 1-methylbenzthiazole and 1-methylbenzselenazole methiodides ; preparation of 1-substituted benzthiazoles. L. M. CLARK (J.C.S., 1928, 2313—2320).—1-Methylbenzthiazole and 1-methylbenzselenazole methiodides react with ammonia and with sodium hydroxide solution, yielding, through the intermediate carbinol base,  $C_6H_4<\begin{smallmatrix}X—\\NMe\end{smallmatrix}>C<\begin{smallmatrix}Me\\OH\end{smallmatrix}$, mixtures of  $C_6H_4<\begin{smallmatrix}X\\N\end{smallmatrix}>C{:}CH_2$ and  $C_6H_4<\begin{smallmatrix}X(NH_4 \text{ or } Na)\\NMeAc\end{smallmatrix}$, where X is sulphur or selenium (cf. Clark, A., 1925, i, 841 ; König and Meier, *ibid.*, 705). A much higher proportion of the methylene base is formed from 1-methylbenzselenazole methiodide than from the analogous sulphur compound. 2-Methyl-1-methylenebenzthiazoline condenses with *p*-dimethylaminobenzaldehyde, giving a highly-coloured product (cf. Mills and Raper, A., 1926, 77) which could not be isolated. *p*-Dimethylaminostyrylbenzthiazole methiodide is formed, however, when hydriodic acid is added to the reaction mixture. Selenocarbocyanines which, like the thiocarbocyanines, are powerful sensitisers of the photographic plate, are obtained in good yield by condensation of 1-methylbenzselenazole alkiodides with orthoformic ester in pyridine solutions (Hamer, this vol., 76).

An attempt to isolate the carbinol base from 1-phenylbenzthiazole methiodide by treatment with silver hydroxide resulted only in the formation of an insoluble compound containing silver (silver salt of *o*-benzoylmethylaminothiophenol ?).

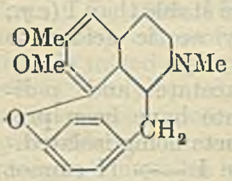
Acylation of 2 : 2′-diaminodiphenyl disulphide with the appropriate acid or acid chloride, followed by reduction of the product with sodium hyposulphite, gives rise to *o*-acylaminothiophenols, which suffer internal condensation to form the corresponding 1-substituted benzthiazoles. The following are described : 2-methyl-1-methylenebenzthiazoline, m. p. 170° (lit. 164°) (a dark red crystalline *substance* and a colourless *compound*, m. p. 164°, were obtained as by-products) ; *benzoyl* derivative, m. p. 87°, of *o*-acetmethylamidothiophenol ; 1-methylbenzthiazole [*methopicrate*, m. p. 94° ; *hydrogen sulphate*, m. p. 177—178° ; *methochloroplatinate*, m. p. 224° (decomp.) ; *perchlorate*, m. p. 149°] ; *benzoyl* derivative, m. p. 130—131°, of *o*-benzoylmethylaminothiophenol ; 1-phenylbenzthiazole [*methochloroplatinate*, m. p. 243° (decomp.) ; *methopicrate*, m. p. 125—126° ; *methoperchlorate*, m. p. 220°] ; 1-*methylbenzselenazole*, b. p. 140°/51 mm., obtained by the action of acetyl chloride on the zinc salt of *o*-aminoselenophenol [*chloroplatinate* ; *methiodide*, m. p. 221° (decomp.) ; *ethiodide*, m. p. 212° (decomp.) ; *methochloroplatinate*, m. p. 214° (decomp.)] ; 2-*methyl*-1-*methylenebenzselenazoline*, m. p. 157—158° ; 2 : 2′-*diacetmethylamidodiphenyl diselenide*, m. p. 141° ; 2 : 2′-*dimethylselenocarbocyanine iodide*, m. p. 267—268° (decomp.) ; 2 : 2′-*diethylselenocarbocyanine iodide*, m. p. 270—271° (decomp.) ; 2 : 2′-*diacetamidodiphenyl disulphide*, m. p. 165—166° ; 2 : 2′-*dipropionamidodiphenyl disulphide*, m. p. 138° ; 1-*ethylbenzthiazole picrate*, m. p. 138° ; 2 : 2′-*dibenzamidodiphenyl disulphide*, m. p. 143—144·5°.

M. CLARK.

Reaction of eserine (physostigmine). M. MOKRAGNATZ (Bull. Soc. Chim. biol., 1928, **10**, 905—908).—Solutions containing eserine (more than 0·002 mg.) yield a fairly permanent, intense violet coloration on treatment with a 2% solution of benzidine in 20% aqueous acetic acid (1—2 drops) followed by the addition of hydrogen peroxide (30% ; 1 drop). Under these conditions 20 of the better-known alkaloids (in the free state) give a slight yellow colour and chlorides and bromides give a blue or bluish-green colour. Eserine may be detected in mixtures of alkaloids or in viscera by this method. Ptomaines give an evanescent green colour. G. A. C. GOUGH.

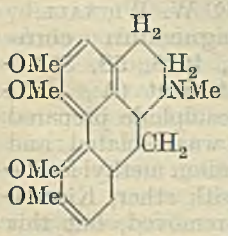
Curare alkaloids. I. Constitution of curine. E. SPÄTH, W. LEITHE, and F. LADECK (Ber., 1928, **61**, [*B*], 1698—1709).—Curine, m. p. 221—221·5° in an evacuated tube, is isolated from the technical "tubocurare" according to the method of Boehm (A., 1898, i, 283). It is identified as the lævorotatory isomeride of *d*-bebeerine obtained by Scholtz (A., 1913, i, 87, 385) from *Radix Parieræ bravæ*, in which it is shown to be present in very varying amount (0—30%), whereas from other samples of the root *l*-bebeerine is isolated. *l*-Curine has $[\alpha]_D^{20}$ −328° in pyridine, whereas for *d*-bebeerine the values, m. p. 221—221·5°, $[\alpha]_D^{20}$ +332° in pyridine, are now recorded. The latter alkaloid separates from ether, benzene (m. p. 161°), and methyl alcohol with solvent of crystallisation which is more or less firmly retained. Admixture of equal amounts of *l*-curine and *d*-bebeerine affords *r*-bebeerine, m. p.

299—300° (cf. Scholtz, *loc. cit.*). Analyses and determinations of mol. wt. by Rast's method support the formula $C_{18}H_{19}O_3N$ for the base. It contains one hydroxyl and one methoxyl group. *d*-Bebeerine is transformed by diazomethane into the amorphous *methyl ether*, which is converted by methyl iodide in benzene at 100° into the corresponding methiodide (cf. Scholtz, *loc. cit.*). The latter compound is transformed by successive treatment with silver chloride and sodium amalgam into the optically inactive methine base (*hydrochloride*, $C_{20}H_{26}O_3NCl$, m. p. 238—241° (decomp.) in an evacuated tube, which, by repetition of the treatments with methyl iodide, silver chloride, and sodium amalgam, is converted into trimethylamine and a *substance*, $C_{18}H_{20}O_3$, m. p. 186—187°; since this compound does not absorb hydrogen in the presence of palladised charcoal, an aliphatic double linking is probably not present. The Emde degradation of *l*-curine affords identical products. Distillation of demethylated *l*-curine or *d*-bebeerine with zinc dust affords 1-methyl*iso*quinoline instead of 1-methoxy*iso*quinoline described by Scholtz. Curine or the products of its degradation do not appear to be oxidised by nitric acid to benzene-1 : 2 : 3 : 4-tetracarboxylic acid so that a phenanthrene complex is probably not present in the alkaloid. Fusion of *d*-bebeerine or its demethylated derivative with potassium hydroxide, followed by methylation of the mixture of acids thus obtained, yields mainly veratric and anisic acids. If bebeerine is methylated and then oxidised with permanganate, neither veratric nor anisic acid is obtained, so that the 4-hydroxybenzyl or 3 : 4-dihydroxybenzyl complex as such or methylated does not appear pre-formed in bebeerine or its methyl ether. If, however, the oxidation is carried out under extremely mild conditions, *p*-hydroxybenzoic acid is produced, indicating the presence of a *p*-hydroxybenzyl complex in which the hydroxylic oxygen is linked to a benzene nucleus. The constitution I is provisionally suggested for bebeerine methyl ether in which the position of the methoxy-groups and the point of attachment of the oxygen bridge remain undecided.



H. WREN.

Alkaloids of *Corydalis cava*. XIII. Synthesis of *d*-corytuberine dimethyl ether. E. SPÄTH and O. HROMATKA (Ber., 1928, 61, [*B*], 1692—1698).—The structure, I, ascribed to corytuberine dimethyl ether by Gadamer (A., 1912, i, 46), is confirmed by synthesis.



2-Nitrohomoveratric acid is converted by thionyl chloride into 2-nitrohomoveratroyl chloride, m. p. 56°, which, with homoveratrylamine, gives the *amide*, $NO_2\cdot C_6H_2(OMe)_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot C_6H_3(OMe)_2$, m. p. 72° after softening at 69° in an evacuated tube. The latter compound is converted by phosphoric oxide in the presence of boiling toluene into 6 : 7-*dimethoxy*-1-2′-*nitro*-3′ : 4′-*dimethoxybenzyl*-3 : 4-*dihydro*iso*quinoline*, m. p. 165—166°, transformed successively into the corresponding *methiodide*, m. p. 179—182° (decomp.) [also *sesquihydrate*, m. p. 102—104°], and *methochloride trihydrate*, m. p. 101—103°. Reduction of the chloride with tin and hydrochloric acid in presence of alcohol affords 6 : 7-*dimethoxy*-2-*methyl*-1-2′-*amino*-3′ : 4′-*dimethoxybenzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, converted by diazotisation and subsequent treatment with copper powder into *dl*-corytuberine dimethyl ether. The product is purified by fractional distillation in a high vacuum and from it by means of *l*-tartaric acid, *d*-corytuberine dimethyl ether hydrogen *l*-tartrate, m. p. 213—215°, $[\alpha]_D^{25}$ +147° in water, is derived, identical with that obtained from natural sources. The synthetic product is also transformed into its methiodide, identical with that derived from corytuberine dimethyl ether from corydine.

H. WREN.

Composition of strychnine phosphomolybdate. C. ANTONIANI (Giorn. Chim. Ind. Appl., 1928, 10, 408—410).—When washed with 10% nitric acid (this vol., 979), strychnine phosphomolybdate has a composition corresponding with the formula $11MoO_3,H_3PO_4,(Str.)_3,2HNO_3$, which is in agreement with the value 0·0257 for the ratio P_2O_5 : precipitate. The most favourable proportions for the precipitation are 350 parts of MoO_3, 2500 parts of HNO_3, and 10 parts of strychnine to 1 part of P_2O_5.

T. H. POPE.

Alkaloids of Kurchi bark (*Holarrhena antidysenterica*). I. Two new alkaloids in Indian Holarrhena. S. GHOSH and N. N. GHOSH (J. Indian Chem. Soc., 1928, 5, 477—482).—Details are given for the extraction of conessine, and the new alkaloids *kurchicine*, m. p. 175°, and *kurchine*, m. p. 75°, from Kurchi bark (total alkaloids 1·2%). H. BURTON.

Microchemistry of the alkaloids. H. BECKMANN (Pharm.-Ztg., 1928, 73, 1165—1166).—Two simple types of micro-sublimation apparatus and a scheme for the micro-chemical detection of alkaloids by colour reactions are described. E. H. SHARPLES.

Aryl arsenoxides and the corresponding dichloro- and di-iodo-arsines. G. NEWBERY and M. A. PHILLIPS (J.C.S., 1928, 2375—2381).—Certain phenyl-dichloro- and -di-iodoarsine derivatives have been prepared for therapeutic investigation. The aminophenyldichloroarsines were obtained by sulphurous acid reduction of the corresponding arsinic acid in hydrochloric acid at the ordinary temperature, a trace of potassium iodide being present; some acetamido-derivatives were prepared by a modification of this method. The aminophenyldi-iodoarsine hydriodides were prepared from the corresponding chloro-derivatives by addition of hydriodic acid or potassium iodide in aqueous solution. In general, the attachment of the iodine atom to the arsenic atom appears to be firmer than that of the chlorine atom in the corresponding chloro-compound; this stability extends to concentrated nitric acid and in the case of 3 : 5-diamino-4-hydroxyphenyldi-iodoarsine dihydriodide, even to 5*N*-sodium hydroxide solution. The arsenoxides were obtained by aqueous hydrolysis of the halogen compounds. The following are described: 3-*nitro*-5-*acetamido*-2- (obtained by nitration of 5-acetamido-2-hydroxyphenylarsinic acid), 3-*amino*-5-*acetamido*-4- and 2-, and 3 : 5-*diacetamido*-2-*hydroxy*-

phenylarsinic acids; 3-*amino*-5-*acetamido*-4-*hydroxyphenyl-dichloroarsine hydrochloride*, -*arsenoxide hydrochloride* and *hydriodide*, and -*di-iodoarsine hydriodide*; 3 : 5-*diamino*-4-*hydroxyphenyl-dichloroarsine dihydrochloride* and -*di-iodoarsine dihydriodide*; 3-*amino*-5-*acetamido*-2-*hydroxyphenyl-di-iodoarsine hydriodide* and -*arsenoxide hydriodide*; 3 : 5-*diacetamido*-2- and -4-*hydroxyphenyldichloroarsines*; 3 : 5-*diacetamido*-4-*hydroxyphenylarsinous acid* (the arsenoxide apparently exists only in this form); 3 : 5-*diacetamido*-2-*hydroxyphenylarsenoxide*; 3-*amino*-4-*hydroxyphenyl-di-iodoarsine hydriodide*; 3-*acetamido*-4-*hydroxyphenylarsenoxide*; 5-*amino*-2-*hydroxyphenyl-dichloroarsine hydrochloride*, -*di-iodoarsine hydriodide*, and -*arsenoxide hydrochloride* and *hydriodide*; 5-*acetamido*-2-*hydroxyphenylarsenoxide*; 3-*acetamido*-4-*hydroxy*- and 5-*acetamido*-2-*hydroxy-phenyldichloroarsines*; 3-*nitro*-4-*hydroxy*-5-*aminophenyldi-iodoarsine hydriodide*; 3-*nitro*-4-*hydroxy*-5-*acetamidophenylarsenoxide*; 3-*acetamido*-4-*hydroxy*- and 5-*acetamido*-2-*hydroxyphenylmethoxychloroarsines*, obtained by the action of methyl-alcoholic hydrogen chloride on the corresponding arsenoxides, which are regenerated by treatment with water; 3-*acetamido*-4-*hydroxyphenylarsine* and 5-*acetamido*-2-*hydroxyphenylarsine*.

The four compounds 3-amino-5-acetamido-2- and -4-hydroxyphenylarsenoxide hydrochlorides and hydriodides dissolve in water only after keeping for a few seconds; the formulation $NH_2\cdot C_6H_2(OH)(NHAc)\cdot AsCl\cdot OH$, hydrolysed by water to $HCl,NH_2\cdot C_6H_2(OH)(NHAc)\cdot AsO$, is suggested.

M. CLARK.

Organic compounds of arsenic. XIII. *cyclo*-Penta-*n*-propylpenta-arsine and the thermal decomposition of arseno-derivatives. W. STEINKOPF and H. DUDEK (Ber., 1928, **61**, [*B*], 1906—1911; cf. this vol., 654).—Magnesium *n*-propylarsinate is reduced by sodium hypophosphite and sulphuric acid to cyclo*penta*-n-*propylpenta-arsine*, $[C_3H_7As]_5$, b. p. 177—179°/1 mm. (slight decomp.), which contains about 5% of propylcacodyl. In freezing nitrobenzene the product has the expected mol. wt., thus affording indirect evidence in favour of the cyclic constitution assigned to the pentamethylpenta-arsine (*loc. cit.*). The compound is decomposed when distilled under 13 mm. pressure into arsenic and *propylcacodyl*, b. p. 165—167°/13 mm., converted by exhaustive methylation into *dimethyldi*-n-*propylarsonium tri-iodide*; this change explains the unavoidable presence of propylcacodyl in distilled *cyclo*penta-*n*-propylpenta-arsine. Similarly, *cyclo*pentamethylpenta-arsine is decomposed at 270°/atm. into arsenic and cacodyl. Arsenobenzene at 255° analogously yields arsenic and phenylcacodyl. H. WREN.

Mercuration of aromatic amines and the problem of substitution. I. A. F. ALBERT and W. SCHNEIDER (Annalen, 1928, **465**, 257—272).—On the basis of Wieland's addition theory of substitution, Kharasch and Jacobsohn (A., 1922, i, 189) postulated the production of complex salts in the mercuration of aromatic amines. Such salts have now been isolated. The action of mercuric acetate on an aromatic amine may be represented by the typical scheme: $NH_2Ph \rightarrow$ (I) $[NH_2Ph\cdot Hg\cdot OAc]OAc \longrightarrow$ (II*a*) $NHPh\cdot Hg\cdot OAc +$ (II*b*) $NHPh\cdot Hg\cdot OH \longrightarrow$ (III) $NH_2\cdot C_6H_4\cdot Hg\cdot OAc$. With aniline, a methyl-alcoholic solution of the amine is treated with a methyl-alcoholic suspension of mercuric acetate; after addition of a little acetic acid the mixture becomes clear and on cooling deposits *aniline acetate* N-*mercuriacetate* (I), m. p. 87°. Similarly are obtained: p-*toluidine*, m. p. 155°, o-*toluidine*, m. p. 76°, m-*aminoacetophenone*, m. p. 104°, p-*anisidine*, m. p. 125°, and *bis*-o-*toluidine*, m. p. 96°, *acetate* N-*mercuriacetates*. These compounds are very unstable, changing slowly on keeping, or at once on melting, or heating in aqueous or alcoholic solution, into the mono- and di-nuclear-substituted products. (When aniline acetate *N*-mercuriacetate was kept in a vacuum, no change of composition occurred, but the m. p. changed.) In the cold, ammonium sulphide, sodium hydroxide, or sodium iodide solutions all give with I the corresponding mercuric compound. Sodium iodide may be employed to distinguish between the different stages of the reaction, since with I sodium acetate is formed in solution, but with II, sodium hydroxide also. At stage III alkalinity is developed only in so far as mercury is being removed from the nucleus.

The stage II compound is obtained, in the case of aniline, by shaking I with ether; *aniline* N-*mercuriacetate* is obtained impure, m. p. about 154°. Stage II is the first result of the action of mercuric acetate on ethyl *p*-aminobenzoate, which gives a *product*, m. p. 117°, estimated, from the analytical results, to contain 80% of II*a*, 12% of II*b*, and 8% of mercuric acetate. Stage II compounds have a great surface-activity, *e.g.*, in adsorbing impurities; the above product when prepared in ether yields a solid mass, which contains adsorbed ether, and becomes gelatinous in water. *p*-Aminoacetophenone and *m*-nitroaniline also give stage II products. These are more stable than I (*e.g.*, in water), but are converted by acetic acid into nuclear-substituted compounds.

p-Ethylaminophenylmercuric acetate and *p*-dimethylaminophenylmercuric acetate have been prepared, without intermediate products being isolated.

It is suggested that if the stage I $\longrightarrow$ II cannot take place at the ordinary temperature, mercuration will not occur (cf. mercuric chloride).

Attention is directed to the danger that, since impurities may be introduced by adsorption, pharmacological mercury compounds may be impure.

E. W. WIGNALL.

Constitution of organo-magnesium compounds. Q. MINGOIA (Gazzetta, 1928, **58**, 532—541).—Contrary to Kierzek's statement (A., 1927, 1176), the magnesium bromohydrosulphide prepared by the author (A., 1926, 388) was isolated and analysed. By decomposing magnesium methyl iodide with water and then extracting with ether, Kierzek found that magnesium iodide is removed, but this author's conclusion that the organo-magnesium compound and water react with formation of magnesium hydroxide and iodide in equimolecular proportions is fallacious, since by prolonged extraction with ether he was able to extract only 72·63% of the iodide, the residual compound still containing 25·25% of iodine, in spite of the appreciable solubility of magnesium iodide in anhydrous ether. The change of colour from white to brown during the treatment with ether is explainable more readily by assuming gradual decomposition of the magnesium iodohydroxide into magnesium iodide and hydroxide. Further, treatment with pyridine of the organo-magnesium solution decomposed by water fails to yield $[Mg(C_5H_5N)_6]I_2$ or $[Mg(C_5H_5N)_4(Et_2O)_2]I_2$ (cf. Spacu, A., 1922, i, 859), this behaviour being in agreement with the predominant basic properties of magnesium iodohydroxide. On the other hand, if the decomposition is effected by means of hydrogen sulphide, treatment with pyridine yields the additive compound of pyridine and magnesium bromohydrosulphide, in accord with the distinctly saline properties of the latter compound. The asymmetric formula for the organo-magnesium compounds is upheld in preference to the doubled symmetrical formula. T. H. Pope.

Method of preparing selenophen. H. V. A. Briscoe, J. B. Peel, and P. L. Robinson (J.C.S., 1928, 2628—2629).—Selenium, in portions of 5 g., is heated in an inclined Pyrex tube, closed at the lower end, and provided with an axial inlet tube delivering acetylene some inches above the selenium and well below a side tube leading to a condenser. The middle of the tube is heated to redness, and the selenium is slowly vaporised by heating it from the surface downwards. Flashing of the acetylene, accompanied by deposition of carbon, takes place and a liquid condensate is formed thereafter at the rate of 3—4 c.c. in 4 hrs. Fractionation of the crude oil yields a high percentage of selenophen (cf. this vol., 1021). M. Clark.

Attempted preparation of optically active derivatives of quadrivalent tin. F. B. Kipping (J.C.S., 1928, 2365—2372; cf. Pope and Peachey, Proc. C.S., 1900, **16**, 42, 116).—The relative ease of removal by iodine of aromatic groups attached to a tin atom in mixed arylstannanes decreases in the following order: *o*-tolyl, *p*-tolyl, phenyl, benzyl. The tin aryls are also decomposed by boiling with concentrated hydrochloric acid, which frequently removes two aryl groups. The order in which this removal occurs is the same as that with iodine, except that whereas iodine removes one of the benzyl groups from tribenzylethylstannane, hydrochloric acid removes the ethyl group. Three compounds containing an asymmetric tin atom are described: phenyl-*p*-tolylbenzylstannic hydroxide, phenylbenzyl-*n*-butylstannic hydroxide, and benzylethyl-*n*-butylstannic iodide. Their salts with *d*-camphorsulphonic, *d*-α-bromo-π-camphorsulphonic, and tartaric acids have been prepared, but in no case could crystalline salts or any evidence of optical activity of the tin atom be obtained. The following are described: *phenyltribenzylstannane*, b. p. 290°/5 mm.; *tribenzylstannic iodide*, m. p. 102—103°; *triphenylbenzylstannane*, m. p. 90°, b. p. 250°/3 mm.; *phenylbenzylstannic chloride*, m. p. 83—84°; p-*tolyltribenzylstannane*; *triphenyl*-o-*tolylstannane*, m. p. 165°; *tri*-p-*tolyl*-o-*tolylstannane*, m. p. 168°; *tri*-m-*tolylstannic chloride*, m. p. 108—109°; *tri*-m-*tolyl*-p-*tolylstannane*, m. p. 103°; *phenyldi*-p-*tolylbenzylstannane*, b. p. 265—270°/2—3 mm.; *phenyl*-p-*tolylbenzylstannic hydroxide*, m. p. 136—137° (oily *iodide*, d-*camphorsulphonate*, d-α-*bromo*-π-*camphorsulphonate*; d-*tartrate*); *triphenyl*-n-*butylstannane*, m. p. 61—62°, b. p. 222°/3 mm.; *phenyl*-n-*butylstannic chloride*, m. p. 50°; *diphenylbenzyl*-n-*butylstannane*, b. p. 215°/2—3 mm.; *phenylbenzyl*-n-*butylstannic hydroxide*, m. p. 135—137° (*fluoride*, m. p. 218°, oily *chloride*, *bromide*, *iodide*, d-*camphorsulphonate*, d-α-*bromo*-π-*camphorsulphonate* and d-*camphorate*; d-*tartrate*); *dibenzylethyl*-n-*butylstannane*, b. p. 195—200°/3—5 mm.; *benzylethyl*-n-*butylstannic iodide*. M. Clark.

Apparatus for chromic anhydride oxidations. W. F. Short (J.C.S., 1928, 2630).—A slight modification of Walker's apparatus (*ibid.*, 1892, **61**, 717) for the preparation of alkyl iodides is described, the adaptor and side-tube being sealed together as in a Soxhlet apparatus. A. I. Vogel.

Partial decomposition of alkali chlorides in the incineration of organic matter (particularly nitrogenous organic matter). P. Fleury and P. Ambert (Bull. Soc. Chim. biol., 1928, **10**, 869—878).—Incineration of mixtures of sodium chloride and various organic substances (especially those of the purine group) results in the loss of chlorine (46—80%) and the formation of sodium hydroxide and carbonate. The presence of salts of nitrous, hydrocyanic, cyanic, or oxalic acids could not be detected.

G. A. C. Gough.

Micro-determination of sulphur in an organic compound. S. Hanai (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 915—919).—The substance is weighed into a platinum boat which is introduced into a Pregl micro-combustion tube containing freshly reduced, pure nickel (from the oxalate). After displacement of air by hydrogen the substance is gently heated to 200° and allowed to volatilise on to the nickel catalyst, which retains all the sulphur as sulphide. The contents of the tube are dissolved in hydrochloric acid in an atmosphere of hydrogen and the hydrogen sulphide is passed into an ammoniacal solution of cadmium chloride; the cadmium sulphide is oxidised by iodine (liberated from permanganate and potassium iodide), and the excess of iodine is titrated with thiosulphate. J. W. Baker.

Jaffe's picric acid reaction. W. Weise and C. Tropp (Z. physiol. Chem., 1928, **178**, 125—138).—The picric acid reaction (red coloration in alkaline solution) first given for creatinine by Jaffe (A., 1886, 1056) is a particular case of a general reaction of compounds with active methylene or methine groups. It is distinct from Braun's reaction (1865) for dextrose and other reducing substances, in which the partial reduction of picric acid to red picramic acid takes place. Generally this reaction takes place only on warming. Jaffe's reaction, according to Reissert (A., 1904, i, 389), is probably a condensation process. In tests of a large number of compounds the following order was found for the power of groups in activating methylene or methine groups so that the compound gave Jaffe's reaction: NO_2, diazo-$>$:CO$>$·CN, CH_2:CH·$>$·CO·NH_2, ·CO_2Et.

R. K. Callow.

Creatine-phosphoric acid and methods of determination. D. Ferdmann [with O. Feinschmidt] (Z. physiol. Chem., 1928, **178**, 52—61).—The creatine-phosphoric acid (phosphagen, cf. Eggleton and Eggleton, A., 1927, 271, 274; Fiske and Subbarow, *ibid.*, 990) of muscle is rapidly destroyed at the ordinary temperature by grinding the muscle, but this fermentative change can be inhibited by grinding with quartz sand and sodium borate, thus enabling a quantitative determination of the creatine-phosphoric acid to be made, using a modification of Eggleton's method. The formation of lactacidogen, as shown by the decrease in inorganic phosphate, still takes place when the creatine-phosphoric acid has been destroyed, and the presence of the latter is, therefore, not essential for this process. R. K. Callow.

Determination of pyruvic acid. B. H. R. Krishna and M. Sreenivasaya.—See this vol., 1292.

Determination of carnosine. W. M. Clifford and V. H. Mottram.—See this vol., 1292.

Determination of tryptophan and tyrosine in proteins. J. Tillmans, P. Hirsch, and F. Stoppel. —See this vol., 1278.

Biochemistry.

Gas and electrolyte equilibria in blood. XII. Value of *pK'* in the Henderson–Hasselbalch equation for blood-serum. A. B. Hastings, J. Sendroy, jun., and D. D. Van Slyke (J. Biol. Chem., 1928, **79**, 183—192).—Taking the solubility coefficient of carbon dioxide in blood-serum to be 0·510, as recently determined by Van Slyke and others (this vol., 1150), the value of *pK'* in the Henderson–Hasselbalch equation for blood-serum at 38° is 6·10; taking Bohr's value of 0·541 as the solubility coefficient, *pK'* becomes 6·13.
C. R. Harington.

Gas and electrolyte equilibria in blood. XIII. Distribution of chloride and hydrogen carbonate in blood of normal and pathological human subjects. A. B. Hastings, J. Sendroy, jun., J. F. McIntosh, and D. D. Van Slyke (J. Biol. Chem., 1928, **79**, 193—209).—In normal human blood the ratios $[Cl]_{cells}:[Cl]_{serum}$ and $[BHCO_3]_{cells}:[BHCO_3]_{serum}$ are higher than those previously determined (A., 1923, i, 1249) for horse blood; this is ascribed to the higher base-binding capacity of the proteins of the latter. In a variety of pathological conditions, the distribution of the electrolytes in human blood was found to obey the same laws as in the normal. C. R. Harington.

Determination of p_H [of blood] by hydrogen electrode and by colorimetric methods. C. G. Johnston (J. Biol. Chem., 1928, **79**, 297—307).—Comparison of the p_H of blood as determined by the hydrogen electrode and by the colorimetric methods of Cullen (A., 1922, ii, 672), Hastings and Sendroy (A., 1924, ii, 869), and of Dale and Evans (A., 1921, i, 142) indicates that the results of the colorimetric determinations differ from those of the electrometric method by inconstant amounts, the range of variation being greater than that observed by previous workers; particularly inconstant values were obtained in dog's blood after hæmorrhage. It is therefore suggested that no colorimetric method is at present trustworthy for the determination of the p_H of blood with accuracy. C. R. Harington.

Electrometric titration of hæmin and hæmatin. J. B. Conant, G. A. Alles, and C. O. Tongberg (J. Biol. Chem., 1928, **79**, 89—93).—The conclusions of Hill and Holden and of Haurowitz (A., 1927, 686, 689) that the reduction of hæmatin involves one equivalent are confirmed by the electrometric titration of hæmin with titanous chloride in presence of tartrate. C. R. Harington.

Blood-corpuscles of cows and fœtuses in hypertonic salt solutions. D. von Deseö (Biochem. Z., 1928, **199**, 41—47).—Fœtal blood-corpuscles shrink more in hypertonic salt solutions, contain more free water, have a greater volume, and contain more colloidal material than those of the mother.
J. H. Birkinshaw.

Blood-cell metabolism. II. Effect of methylene-blue and other dyes on glycolysis and lactic acid formation of erythrocytes. E. S. G. Barron and G. A. Harrop, jun. (J. Biol. Chem., 1928, **79**, 65—87).—The glycolysis brought about by mammalian erythrocytes is essentially anaërobic in character, the proportion of lactic acid produced to dextrose destroyed being high; with avian erythrocytes a larger proportion of the dextrose is oxidised. In both cases the addition of small amounts of methylene-blue or of other dyes with similar oxidation–reduction potentials favours the oxidative part of the process. The effect of the dye is exercised over a considerable range of concentration and is probably catalytic in character. The rate of glycolysis is increased by rise of temperature up to 37°. The catalytic effect of methylene-blue is not affected by the presence of cyanides, but is increased by addition of phosphates and requires the presence of molecular oxygen, whence it is probable that the dye catalyses the oxidation of hexosephosphate. Damage or destruction of the surface of the erythrocytes inhibits partly or entirely their glycolytic activity.
C. R. Harington.

Blood glycolysis. I. General consideration of glycolysis in relation to the blood-cells, and the production of lactic acid and carbon dioxide. I. Katayama (J. Lab. Clin. Med., 1926, **12**, 239—254).—The sugar content of shed blood decreases on keeping, most rapidly at 38° and least rapidly at 0°; that of plasma, serum, or hæmolysed blood is unaltered. Saturation of whole blood with carbon monoxide does not inhibit glycolysis. Glycolysis takes place when washed blood-cells are added to Ringer or physiological saline solution containing dextrose, lævulose, or galactose (order of decreasing effect). The rate of glycolysis is the

same for diabetic and non-diabetic blood. Insulin has no effect on the rate. Lactic and evidently other acids, but not carbon dioxide, are produced.
CHEMICAL ABSTRACTS.

Carbohydrate degradation and phosphoric acid in blood. W. A. ENGELHARDT and A. E. BRAUNSTEIN (Klin. Woch., 1928, 7, 215).—Of the two processes contributing to the phosphoric acid balance in blood observed *in vitro*, the separation of inorganic phosphate is independent of glycolysis, whilst the union of phosphoric acid as an organic stabilisation product is directly connected with the disappearance of sugar. Conditions diminishing or inhibiting glycolysis cause a corresponding diminution of phosphoric acid stabilisation. Addition of dextrose to erythrocyte suspensions reduces the speed of liberation of phosphoric acid, but such addition is without influence in systems where glycolysis cannot occur. Addition of arsenate prevents phosphoric acid stabilisation when disappearance of sugar is proceeding.
A. A. ELDRIDGE.

Catalytic decomposition of hydrogen peroxide by blood. I. Chemical dynamics of blood-catalase. II. Effect of temperature on blood-catalase. III. Catalytic activity of the red cells. IV. So-called heat-activation and influence of some organic substances on the red blood-cell catalysis. K. NOSAKA (J. Biochem. Japan, 1928, 8, 275—299, 301—309, 311—330, 331—340).—I. The catalytic decomposition of hydrogen peroxide (0·009—0·036N) by blood solutions is not unimolecular, but corresponds with Yamazaki's formulation, $-dc/dt=kEC$; $-dE/dt=k'EC$, where E is the concentration of catalase and C that of hydrogen peroxide. Variation of values of k with variable quantities of enzyme is corrected by $k_1/k_2=(E_1/E_2)^m$, where m is constant (1·07) for different temperatures. Blood-serum has no catalytic effect, but is protective. The optimal p_H for blood-catalase is 7; the p_H has practically no influence on the destruction of catalase by the hydrogen peroxide.

II. The temperature curve for blood-catalase shows a wide optimum range at about 40°; between 0° and 20° the coefficient is 1·49 per 10°. The temperature curve for the destruction of the catalase by hydrogen peroxide is very steep and has no optimum; between 0° and 35° the coefficient is 2·22 per 10°. Inactivation by heat is not a unimolecular reaction. Blood-catalase is inactivated by heating for 30 min. at 65° or 15 min. at 70°.

III. A suspension of red blood-cells in physiological sodium chloride solution decomposes hydrogen peroxide unimolecularly provided there is no hæmolysis; serum and plasma have a stimulating effect. The reaction is regarded as a special case of hydrogen peroxide catalysis without the intervention of catalase.

IV. The catalytic effect of the red-cell suspension on hydrogen peroxide is considerably increased, owing to hæmolysis, by heating at 45°. Activation by various protoplasmic poisons is similarly occasioned.
CHEMICAL ABSTRACTS.

Effect of carbon monoxide on the metabolism of leucocytes. A. FUJITA (Biochem. Z., 1928, 197, 189—192).—When the ratio $CO/O_2=18$ the respiration of leucocytes and of white bone-marrow cells as well as that of blood-platelets is checked, the effect being very strong in the case of the last two. Illumination with a metal-filament lamp diminished the effect, especially in the case of the marrow cells and platelets.
W. McCARTNEY.

Peroxidase properties of leucocytes. K. NICOLAJEV (Zhur. exp. biol. Med., 1928, 8, 33—41).—Leucocytic extracts have peroxidase properties which disappear on boiling. The intensity of the oxidation process has no relation to the iron content.
CHEMICAL ABSTRACTS.

Decomposition of uric acid in blood. M. GOMOLIŃSKA (Biochem. J., 1928, 22, 1307—1311).—Uric acid is quantitatively oxidised by blood to allantoin, urea, and ammonia within 48 hrs. at 37°. Stromata and blood-plasma are inactive in this respect. Hæmoglobin is most probably the uricolytic agent present in blood. The reaction of uricolysis is inhibited by propyl and butyl alcohols but not by cyanides.
S. S. ZILVA.

Precipitation of blood-calcium by lead. F. BISCHOFF and L. C. MAXWELL (J. Biol. Chem., 1928, 79, 5—17).—Addition of lead acetate to blood-serum at p_H 6·9—8·3 causes precipitation of an equivalent amount of calcium and of phosphoric acid sufficient to form the phosphates of both the lead and the calcium. The reaction is independent of the concentration of calcium, carbonate, and phosphate, and is a specific effect of lead.
C. R. HARINGTON.

Electrical transference of calcium in blood-serum protein solutions. D. M. GREENBERG (J. Biol. Chem., 1928, 79, 177—182).—Blood-serum was freed from electrolytes by electrodialysis, and the resulting solution was treated with varying amounts of calcium hydroxide alone or together with sodium hydroxide. Measurement of the electrical transport numbers of such solutions affords evidence of the formation of complex calcium–protein ions, although this complex ion formation is not so marked as with caseinogen (this vol., 241).
C. R. HARINGTON.

Calcium and inorganic phosphorus in the blood of rabbits. III. Periodic and progressive variations in normal rabbits. W. H. BROWN and M. HOWARD (J. Exp. Med., 1928, 47, 637—662).—Periodic variations of calcium and the calcium/inorganic phosphorus ratio, and progressive variations of inorganic phosphorus and the same ratio, were observed.
CHEMICAL ABSTRACTS.

Determination of chloride in blood and serum. D. W. WILSON and E. G. BALL (J. Biol. Chem., 1928, 79, 221—227).—The method of Van Slyke (A., 1924, ii, 271) for the determination of chloride yields better results if the material be treated first with silver nitrate in aqueous solution and then with concentrated nitric acid.
C. R. HARINGTON.

Iron content of blood-serum. G. BARKAN (Z. physiol. Chem., 1928, 177, 205—207).—A comment on the work of Abderhalden and Möller (this vol., 913).
J. H. BIRKINSHAW.

[Iron content of blood-serum.] E. Abderhalden (Z. physiol. Chem., 1928, **177**, 207—210).—A reply to Barkan (cf. preceding abstract).

J. H. Birkinshaw.

Determination of sulphur in blood and organic products. A. Lesure and A. Dunez (Bull. Soc. Chim. biol., 1928, **10**, 879—890).—After removal of the protein with acetic acid, the residue is oxidised with boiling, fuming nitric acid and the product decolorised with hydrogen peroxide. A 4% solution of benzidine in 4% hydrochloric acid is then added and the benzidine sulphate washed with pure acetone. The sulphate is finally determined by titration with sodium hydroxide solution. G. A. C. Gough.

Irradiated proteins. IV. Effect of short-wave radiation on the ultra-violet absorption of serum and of serum-protein. M. Spiegel-Adolf (Biochem. Z., 1928, **197**, 197—209).—The absorptive power of irradiated serum-albumin is independent of the presence of oxygen. Serum-albumin kept in an atmosphere of nitrogen exhibits quantitatively and qualitatively the same changes, and serum-albumin free from electrolytes, under the same conditions, also remains insoluble after treatment with alkali (cf. A., 1927, 893; this vol., 190, 659). Serum diluted with physiological salt solution and also pseudoglobulin irradiated in presence of alkali show an increase in absorbing power after irradiation. Euglobulin, under the same conditions, exhibits no such change. As regards the extent of change in absorbing power undergone, the substances form the descending series: serum-albumin, serum, pseudoglobulin, euglobulin. The permeability of irradiated and unirradiated solutions of these substances by light of short wave-length provides confirmation of the results determined spectrographically.

W. McCartney.

Presence of polypeptides in blood-plasma and -serum. Application of erepsin and trypsin-kinase for their detection. E. Abderhalden and E. Rossner (Fermentforsch., 1928, **10**, 102—110).—Serum dialysates contain at most only very small amounts of compounds giving rise to free amino-groups when subjected to the action of purified erepsin or trypsin-kinase. W. O. Kermack.

Composition of the compounds containing residual carbon and nitrogen; oxyproteic acids in blood. O. Deutschberger (Biochem. Z., 1928, **198**, 268—295).—The residual carbon of blood (horse) filtrates is 182·5 mg./100 c.c. The sum of the carbon contents of known constituents is 165·6 mg. of carbon per 100 c.c. of blood, made up of sugar 38·4, lactic acid 6·5, amino-acids 47·0, carbamide 4·7, creatine and creatinine 3·2, oxyproteic acids 65·8 mg. The residual nitrogen is 44 mg./100 c.c. of blood, made up of oxyproteic acids 19, amino-nitrogen 11, carbamide 11, and creatine and creatinine 3 mg. The whole of the nitrogen and most of the carbon of the filtrates are therefore accounted for in terms of known substances. The mean values for the oxyproteic acid fractions of the filtrate were residual carbon 66, hydrogen 8, and nitrogen 19 mg. per 100 c.c. of blood.

P. W. Clutterbuck.

Micro-method for determination of fats and lipins of blood. J. A. Milroy (Biochem. J., 1928, **22**, 1206—1211).—The extracted compounds of the blood are hydrolysed and the amount of fatty acids is determined colorimetrically, using Nile-blue hydrochloride as the stain. In the case of the total fatty acids the blood (0·1 c.c.) is extracted with alcohol and ether, and in that of the fatty acids from neutral fats with alcohol and light petroleum.

S. S. Zilva.

[Non-]effect of splenectomy on the blood-sugar. A. M. Blinov (Zhur. exp. biol. Med., 1928, 8, 467—470). Chemical Abstracts.

Conversion of blood- into bile-pigments. E. Pollak (Biochem. Z., 1928, **198**, 311—316).—The pigment previously obtained by Brugsch and Pollak (A., 1924, i, 1127) by the action of pyrocatechol on hæmin and claimed to be bilirubin has now been obtained in quantity; it has mol. wt. 300—330, empirical formula $C_{16}H_{16}N_2O_4$, and gives a blue hydrochloride showing an absorption band in the orange. The substance is not bilirubin, since it cannot be extracted from chloroform solution with sodium hydroxide or ammonia, the mol. wt. is not reconcilable, and the substance does not appear to be a pyrrole derivative. P. W. Clutterbuck.

Keeping properties of specific anti-sera for the precipitin test. F. Bamford (Analyst, 1928, **53**, 531—532).—Anti-sera prepared by the Lister Institute and kept in Cairo in an ice-chest for nearly 5 years showed a very definite reaction with fowl blood-serum diluted to 1 in 2000. Another set of anti-sera, with the utmost precautions against temperature changes, was quite unsatisfactory from the first, but a third set had good specificity although kept for about 12 days at 30—35°. Temperature variations alone are regarded as insufficient causes of instability in anti-sera. D. G. Hewer.

Hæmolysis of chicken blood. G. E. Shattuck (J. Gen. Physiol., 1928, **12**, 17—28).—The hæmolytic action of saponin, sodium taurocholate, and sodium oleate on nucleated erythrocytes from chicken blood has been studied and comparison is made between the action of these lipins on nucleated and on non-nucleated blood-cells. E. A. Lunt.

Hæmolysis by saponin and sodium taurocholate with special reference to the series of Ryvosh. J. F. Yeager (J. Gen. Physiol., 1928, **11**, 779—787).—The resistances of the red blood-corpuscles of various animals to hæmolysis by sodium taurocholate do not follow the order found by Ryvosh (Arch. ges. Physiol., 1907, **116**) and confirmed by Ponder (Brit. J. Exp. Path., 1927, 8, 267) for resistance to hæmolysis by saponin.

W. O. Kermack.

Hæmolytic action of inorganic acids. Lipoid solubility, permeability, and hæmolytic action of saturated fatty acids. M. Bodansky (J. Biol. Chem., 1928, **79**, 229—239, 241—255).—Red blood-corpuscles are very readily permeable to mineral acids; the hæmolytic powers of phosphoric, sulphuric, hydrochloric, and nitric acids are in descending order of magnitude. The effect of these acids is one of destruction of the cell membrane rather than of osmosis. Human erythrocytes are less resistant to hæmolysis than those of the dog, but erythrocytes from normal and anæmic individuals are equally resistant.

Curves are given showing the relationship between p_H and hæmolytic action for a number of fatty acids; since increase in the osmotic concentration of the outer fluid diminishes the hæmolytic action, the latter must be, in part at least, an osmotic effect. The power of the fatty acids to penetrate the erythrocyte increases approximately with the mol. wt., and the effectiveness as a hæmolytic agent runs parallel to the lipoid solubility as determined from the partition coefficient between olive oil and water. C. R. Harington.

Second protein (livetin) of egg-yolk. H. D. Kay and P. G. Marshall (Biochem. J., 1928, **22**, 1264—1296; cf. Plimmer, J.C.S., 1908, **93**, 1500).—After removing the vitellin from the yolk the protein is precipitated and reprecipitated several times by half saturation with ammonium sulphate. The lipins are removed by extraction with alcohol and ether at —15° and the ammonium sulphate is eliminated by dialysis at 3° and p_H 5·0. The protein contains 5·2% of tyrosine, 2·1% of tryptophan, 3·9% of cystine, 0·067% of phosphorus, and 1·8% of sulphur. It has its isoelectric point at about p_H 4·8—5·0 and $[\alpha]^{20}_{5461}$ —55·5°. In the fresh yolk the ratio vitellin/livetin is fairly constant from one egg to another. Between one quarter and one fifth of the yolk-proteins of the hen's or duck's egg is livetin. A method based on the above technique is described for determining the amount of this protein in a single egg-yolk. S. S. Zilva.

Reaction of tissues. A. B. Carlström, R. Ege, and V. Henriques (Biochem. Z., 1928, **198**, 442—462).—A colorimetric method is elaborated for determining the reaction of tissues and a correction employed for a systematic protein error. The glass electrode is also used with satisfactory results. The formation of lactic acid takes place in the cellular tissue and not in the tissue extract. Formation of the acid is detectable in finely minced muscle at 0°. The buffer curve of cross-striated rabbit's muscle and the *post mortem* changes in reaction are determined. The p_H of muscle is displaced from 7 to 6 by 0·055*M*-acid, corresponding with the presence of 525 mg. of lactic acid per 100 g. of muscle. The temperature correction for the reaction of tissue is determined, an increase of 1° causing the p_H to be decreased by 0·007. The p_H of resting muscle at 37° is 6·8—6·95, that of muscle when the production of lactic acid is prevented is 7·0, that of muscle free from lactic acid is calculated as 7·1 and that of muscle in rigor is 5·9. P. W. Clutterbuck.

Relative reactions within living mammalian tissues. X. Litmus constituents as vital stains. R. Elman, D. R. Drury, and P. D. McMaster (J. Exp. Med., 1928, **47**, 777—796).—Erythrolitmin is advantageous as a vital stain, but erythrolein is useless and azolitmin is toxic. Methods for the separation of these substances from litmus are described. Chemical Abstracts.

Coloration of animal membranes with copper sulphate solutions. M. Chanoz (Compt. rend. Soc. Biol., 1927, **97**, 1539—1541; Chem. Zentr., 1928, i, 1972).—Animal membranes are coloured by copper sulphate solutions less acid than $10^{-5}N$. It is considered that in acid solutions a colourless protein–sulphate salt is formed, whilst in more alkaline solutions a green copper–protein compound is produced. A. A. Eldridge.

Cystine content of keratins. T. Takeda (Bul. Sci. Fak. Terkultura Kjusu, 1926, **2**, 262—272).—A comparison of human and monkey hair, wool, and feathers. Chemical Abstracts.

Occurrence of gold in food and organs. R. Berg (Biochem. Z., 1928, **198**, 424—427).—A method for determining traces of gold is outlined and the following values are obtained: oat flakes, 0·2 mg.; commercial oat flakes, 0·04 mg.; natural honey, none; grape and apple juice, trace; apple-juice concentrate, 0·1 mg.; finest wheat meal, none; whole-meal bread, 0·03 mg.; whole-meal rye bread, 0·1 mg.; hazel nuts, 0·1 mg. per 100 g. in each case; drinking water, 0·046 mg. per litre; human urine, 0·1 mg. per day; human fæces, 1·0 mg. per day; human blood up to 0·3 mg. per 100 g.; ox liver, 0·2 mg. per kg.; ox brain, 1·4 mg. per 100 g. (surprisingly large). P. W. Clutterbuck.

Volatile sulphide from muscle. W. A. Osborne (Biochem. J., 1928, **22**, 1312).—Volatile sulphide is formed in the muscle of well-nourished guinea-pigs when kept for about 24 hrs. even if precautions are taken to avoid bacterial decomposition. The volatile sulphide can be detected immediately after killing in the muscles of guinea-pigs which have previously been starved for 48 hrs. The flesh of sheep but not beef has been found to emit sulphide. S. S. Zilva.

Artificial preparation of the principal constituent of bones and teeth. T. Gassmann (Z. physiol. Chem., 1928, **178**, 62—66).—The preparation is described of phosphatocalcium carbonate (cf. A., 1911, ii, 129) by the treatment of calcium oxide under special conditions with atmospheric carbon dioxide, sodium phosphate solution, and acetic acid, followed by extraction with alcohol. The substance thus prepared had the composition and properties of the natural material (cf. A., 1913, ii, 320; 1914, i, 773). R. K. Callow.

Composition of bone. I. Analytical methods. M. J. Shear and B. Kramer. **II. Pathological calcification.** B. Kramer and M. J. Shear. **III. Physico-chemical mechanism.** M. J. Shear and B. Kramer. **IV. Primary calcification.** B. Kramer and M. J. Shear. **V. Properties of calcium citrate.** M. J. Shear and B. Kramer (J. Biol. Chem., 1928, 79, 105—120, 121—123, 125—145, 147—160, 161—175).—I. Bone was crushed and extracted in a Soxhlet apparatus with a mixture of alcohol and ether to which was added some sodium hydroxide to retain acid vapours; 50 mg. of the dried extracted powder were used for the determination of (*a*) carbonate by the method of Van Slyke and Neill (A., 1924, ii 872), (*b*) calcium by the method of Kramer and Tisdall (A., 1921, ii, 595), (*c*) phosphorus by the method of Briggs (A., 1922, ii, 718). The average ratio of non-carbonate calcium to total inorganic phosphorus was 2·0.

II. In pathologically calcified tissues the above ratio is the same as for normal bone except in calcified uterine fibroids, in which it is 2·2.

III. The probable mechanism of calcification is considered from a physico-chemical point of view. It is pointed out that there is no evidence for the existence of tertiary calcium phosphate in bone. Previous experiments on calcification *in vitro* and *in vivo* lead to the conclusion that the important factor is the ionic product $[Ca]^{++} \times [HPO_4]^{=}$; it is at least evident that no calcification occurs when the value of this product is less than that of the solubility product of secondary calcium phosphate, and this compound may first be precipitated and may be subsequently changed to one with a higher proportion of calcium.

IV. In primary calcification in rats undergoing healing of rickets, the non-carbonate calcium : inorganic phosphorus ratio is higher than in normal rat bones, indicating the presence of a basic calcium salt in the freshly-deposited bony tissue. The proportion of carbonate in rat bones increases with age, and in the condition of rickets. The theory expressed in the previous paper is modified to the view that, from an alkaline medium such as blood-serum, calcium is deposited as a mixture of secondary calcium phosphate and calcium hydroxide, which would give rise to the high Ca : P ratios observed.

V. Mixtures of sodium chloride and sodium citrate solutions have electrical resistances intermediate between those of solutions of the pure salts. Addition of sodium citrate to calcium chloride solution produces, however, anomalous results, the resistance first increasing and then decreasing; this affords evidence for the binding of the calcium ions by the sodium citrate. C. R. Harington.

***Bombyx mori*. I. Effect of hydrogen-ion concentration on the coagulation of liquid silk. II. Quantitative changes of cystine, tryptophan, and tyrosine in proteins of silkworms.** S. Nakajima (Bul. Sci. Fak. Terkultura Kjusu, 1926, 2, 20—32).—I. " Liquid silk " is negatively charged and is readily coagulated by addition of some acids. The optimal coagulation points are p_H 1·3 and 3·9; the latter approximates to the isoelectric point of sericin.

II. The cystine and tryptophan content gradually decreases during the development of the worms or silk formation, whilst that of tyrosine increases. Chemical Abstracts.

Significance of composition of the secreting and dry mammary gland to milk secretion. J. W. Gowen and E. R. Tobey (J. Gen. Physiol., 1928, 12, 123—128).—Values are given for the composition of the dry and lactating udder of the cow, and of the milk from the latter, with reference to fat, ash, nitrogen, and lactose. At all times there is a large excess of fat, ash, and nitrogen in the udder in proportion to that necessary for milk formation. This excess does not obtain during lactation in the case of lactose, and the non-lactating udder contains no lactose. These results are held to indicate that lactose in milk is formed from the blood only as needed in the formation of milk. E. A. Lunt.

Influence of freezing of milk on its acid fermentation. V. W. Winter (Chem. Listy, 1928, 22, 357—361).—The solid fraction of partly frozen milk has a lower specific gravity and a higher acidity than the original milk, whilst the contrary is the case with the liquid fraction. Both fractions on incubation at the ordinary temperature for 2—3 weeks exhibit a lower acidity than milk not previously frozen. R. Truszkowski.

Bufodeoxycholic acid in the bile of *Bufo vulgaris Japonica*. I. T. Okanura (J. Biochem. Japan, 1927, 8, 351—360).—The *bufodeoxycholic acid*, $C_{24}H_{36}O_4$, stimulates lipase action and is hæmolytic. Chemical Abstracts.

Fish bile. II. *Tetrodon porphyleus*, Sieb. N. Teraoka (J. Biochem. Japan, 1928, 8, 341—350).—The bile contains about 9% of taurocholic acid. Chemical Abstracts.

Solubility of cystine in urine. G. Blix (Z. physiol. Chem., 1928, 178, 109—124).—The causes of the relatively high solubility of cystine in urine as compared with water were investigated. The effect of different hydrogen-ion concentrations is small (cf. Sano, A., 1926, 345). Inorganic salts present in urine increase the solubility considerably; *e.g.*, in 0·25*N*-calcium chloride it is increased by 59%. The principal cause of the increased solubility is, however, the presence of colloids which inhibit the crystallisation of the cystine.

The influence of neutral salts on the solubility of amino-acids is discussed from the point of view of the activity theory. The effects are accounted for by Bjerrum's theory of the " zwitterion," which also accounts for changes in optical activity and depression of the f. p., rather than by Pfeiffer's theory. Pfeiffer's observation of the salting-out of cystine by ammonium sulphate (A., 1924, i, 378) could not be confirmed.

A method of determining sulphur, applicable to the determination of cystine, by oxidation with alkaline permanganate and precipitation with barium chloride in acid solution, is described. R. K. Callow.

Excretion of creatinine and the energy demand. L. Garot (Arch. Int. Physiol., 1927, 29, 326—341; Chem. Zentr., 1928, i, 1788).—The quantity of creatinine excreted per kg. body-weight falls with increasing age. The quantity is related to the muscle mass, and not to the energy demand. A. A. Eldridge.

Uric acid and creatinine in the urine of infants. O. S. Rougichitch (Amer. J. Dis. Children, 1926, 31, 504—513).—For infants, aged 1—22 months, on a diet free from purine, 14—25 mg. of uric acid per kg. of body-weight were excreted daily; the creatinine varied from 10 to 15 mg. per kg. Chemical Abstracts.

Uric acid in the urine of infants. O. S. Rougichitch (Amer. J. Dis. Children, 1926, 32, 530—535).—In boys aged 6—12 weeks the purine metabolism was regular throughout 24 hrs. Chemical Abstracts.

Test for alkalis [in urine]. C. Mitchell (Clin. Med., 1928, **35**, 167).—The urine is poured on to 20% nickel sulphate solution; in presence of alkalis a white ring or cloudiness appears at the interface. Albumin and sugar do not interfere.

Chemical Abstracts.

Dextrose in normal urine. A. Hassan (Biochem. J., 1928, **22**, 1332—1340).—Normal urines give crystal mixtures consisting of two simple osazones—glucosazone and an osazone which agrees in m. p. but not in crystalline structure with *iso*maltosazone. Examination of urines of more than 700 persons revealed that 20—30% of urines voided 1—2 hrs. after an ordinary meal yielded typical glucosazone crystals. The percentage dropped to 12—15 in urines passed 4—5 hrs. after meals. The presence of dextrose in the urine is not due to abnormal carbohydrate metabolism. 1 mg. of dextrose per 100 c.c. of water or urine from which the normal sugars have been removed could be detected by the method employed for the preparation of osazones.

S. S. Zilva.

Detection of sugar in urine. J. Schmid and E. Glorius (Süddeut. Apoth.-Ztg., 1928, **68**, 98—99; Chem. Zentr., 1928, i, 1896—1897).—In Schmidt and Rubner's reaction the mixture of urine, ammonia, and lead acetate is preferably heated at 85° at one point, or immersed in water at 40—50°, when the development of a salmon-pink colour will detect 0·05%; under these conditions lactose does not react similarly.

A. A. Eldridge.

Determination of sugar in normal urine. M. R. Everett and M. O. Hart (J. Lab. Clin. Med., 1927, **12**, 579—589).—Irregularities are recorded.

Chemical Abstracts.

Piperazine in the analysis of urine and blood. R. Gros (J. Pharm. Chim., 1928, [viii], **8**, 313—316). —By adding piperazine to urine, suspended uric acid and urates are dissolved, the bacteriological examination is simplified, and the determination of uric acid, purine bases, urea, chlorine, and phosphates by the usual methods is improved. In the preparation of standard uric acid solution in Grigaut's method for the determination of uric acid in blood, the addition of piperazine facilitates dissolution of the uric acid and has no effect on either the stability of the solution or the colorimetric determination.

E. H. Sharples.

Modifications of Katayama's formulæ for computing the fæcal nitrogen and fæcal organic matter in chicken excrement. H. W. Titus (Poultry Sci., 1928, **7**, 145—150).—Fæcal nitrogen= 0·9784×excrement-nitrogen−1·0253×uric acid nitrogen−1·2641×excrement ammonia-nitrogen−0·0554; urinary organic matter in the excrement=2·16× (urinary nitrogen %)+27·53%.

Chemical Abstracts.

Changes in composition of blood in pernicious anæmia treated by a diet rich in liver. W. P. Murphy, R. T. Monroe, and R. Fitz (J. Amer. Med. Assoc., 1927, **88**, 1211—1214).—Corpuscular-protein increased with increasing hæmoglobin concentration; no changes in plasma-protein or -non-protein-nitrogen were observed.

Chemical Abstracts.

Anaphylaxis in man and animals. VII. Potassium and calcium content of the blood and organs of the rabbit and dog and its changes in sensitised and anaphylactic animals. A. Schittenhelm, W. Erhardt, and K. Warnat (Z. ges. exp. Med., 1928, **58**, 662—682; Chem. Zentr., 1928, i, 1787).

Chemistry of healthy and of atherosclerotic aorta. II. Quantitative chemical changes in the atherosclerotic aorta. III. Atherosclerotic lipin mixture. R. Schönheimer (Z. physiol. Chem., 1928, **177**, 143—157).—II. The values for cholesterol, cholesteryl ester, and phosphatides in the atherosclerotic aorta support the infiltration theory previously advanced (A., 1926, 1269); the hypothesis of calcium deposition by way of the calcium salts of the hydrolysed fatty acids of the cholesteryl esters is rejected. The calcium salt corresponds in composition with that of bone.

III. From the lipins were isolated free cholesterol and the stearate, palmitate, and oleate. Indications of doubly-unsaturated esters were obtained. A galactoside, and substances not precipitated by digitonin, but apparently no neutral fats, were present.

J. H. Birkinshaw.

Composition of the blood of animals under pathological conditions. I. Broncho-pneumonia in cows. A. A. Horvath and R. B. Little (J. Clin. Invest., 1928, **5**, 541—546).—The blood-plasma chlorine is diminished and the globulin and fibrin fractions are increased.

Chemical Abstracts.

Analyses of blood in patients having senile cataract. C. S. O'Brien and V. C. Myers (Arch. Int. Med., 1928, **42**, 376—378).—Analyses made on the blood of 54 cases of cataract indicate no abnormality of composition except in the cholesterol content, which was high in 54% of the cases observed.

E. A. Lunt.

Effect of Karlsbad mineral water on diabetes mellitus. O. Kauffmann-Cosla and R. Zörkendörfer (Münch. med. Woch., 1928, **75**, 396—399; Chem. Zentr., 1928, i, 2103).

Diabetes. Mathematical derivation of the blood-dextrose curve. D. M. Ervin (J. Lab. Clin. Med., 1926, **12**, 318—325).—A mathematical expression for the blood-dextrose curve depends on the absorption from the intestinal tract, formation of glycogen, and oxidation. The curve depends only on a decreased rate of glycogen formation; there is no evidence of failure of dextrose combustion.

Chemical Abstracts.

Mechanism of the inflammatory process. III. Electrophoretic migration of inert particles and blood-cells in gelatin sols and gels with reference to leucocyte emigration through the capillary wall. H. A. Abramson (J. Gen. Physiol., 1928, **11**, 743—756).—The cataphoresis of particles of quartz and of silver as well as of air bubbles from 1·0 to 50·0 μ in diameter has been studied in 1·0% gelatin sols and gels. The apparent viscosity η' (measured using small shearing stresses) as well as the true viscosity η (measured using large shearing stresses) have also been determined for the sols and soft gels employed. The cataphoretic velocity remains constant during gelation, whilst the apparent viscosity is rapidly increasing. It appears therefore that the cataphoretic velocity in these sols and soft gels is dependent on the true viscosity which remains constant for a sol during the process of gelation. Leucocytes traverse soft gelatin-serum under cataphoresis with approximately the same velocity as quartz, viz., 0·5 μ per volt per cm., whilst red blood-cells move with double that speed. In both cases the velocity of migration remains constant during the process of gelation. With stiffer gels all three types of particles move at first with the same slow velocity which gradually increases as cataphoresis is continued, especially in the case of the red blood-cells. When leucocytes move in a fibrin gel they are frequently completely stopped apparently as the result of obstruction by the fibrin strands. Nickel particles suspended in a soft gelatin gel and acted on by a magnetic field show only elastic displacement if the field is sufficiently weak and apparently experience more resistance than the particles of the same size undergoing cataphoresis in a similar gel. The bearing of these results on the theory of the migration of leucocytes through the capillary walls is discussed. W. O. Kermack.

Blood-uric acid in nephritis. W. P. Holbrook and H. D. Haskins (J. Lab. Clin. Med., 1926, **12**, 10—15).—A diagnostic study.

Chemical Abstracts.

Value of the diazo-test on blood. S. M. Robson and L. Jacobs (Arch. Int. Med., 1928, **42**, 386—389).—Evidence is cited against the use of the diazo-test on blood as a specific means of differentiation between uræmic coma and that of other origin. A high creatinine content of the blood usually accompanies a positive diazo-test, although no definite creatinine value can be established as the point at which the positive diazo-test appears. E. A. Lunt.

Phosphorus and calcium in the blood in Parkinsonism after injection of ergotamine and hyoscine. C. I. Urechia and G. Popoviciu (Compt. rend. Soc. Biol., 1927, **97**, 1573—1575; Chem. Zentr., 1928, i, 1786).

Physiology of glands. L. Asher. **Prevention of over-compensation for loss of iron, through blockade of the reticulo-endothelial system, after extirpation of the spleen.** Y. Kojima (Biochem. Z., 1928, **197**, 84—104).—In order to find whether the decreased excretion of iron after splenectomy in guinea-pigs depends on over-compensation by the liver the method of blockade of the reticulo-endothelial system was employed. In normal guinea-pigs blockade with Chinese ink causes only insignificant increase in the amount of iron excreted daily. After splenectomy the blockade causes quite considerable increase in the excretion of iron, and this increase may become so great that all over-compensation is prevented and excretion is restored to its normal value. These results support the view that the spleen plays a part in the control of iron metabolism.

W. McCartney.

Physiology of glands. L. Asher. **Exchange of material between blood and tissues in [animals with] normal and denervated thyroid glands.** T. Honda (Biochem. Z., 1928, **197**, 72—83).—The change in the chloride content of the blood of rabbits and also the change in the volume of red blood-corpuscles following injection, at the same time, of sucrose solution and of solutions of a specific diuretic ("Euphyllin") have been followed. (The sugar was injected intraperitoneally, the diuretic intramuscularly.) After denervation of the thyroid gland the chloride content of the blood changed more rapidly and to a greater extent than before denervation. Complete removal of the gland caused only insignificant changes in the chloride content of the blood. W. McCartney.

Potassium, calcium, and choline content of the blood of dogs and its alterations following extirpation of the thyroid gland. M. Maxim and C. Vasiliu (Biochem. Z., 1928, **197**, 237—240).—There was a constant decrease in the potassium content in the first 4—7 days after the operation. The amount of calcium remained unchanged at first and then began to rise. There was also an immediate increase in the choline content, and during tetanic convulsions and also during respiratory crises it reached very high values, as also did the potassium. All analyses were made with whole blood.

W. McCartney.

Co-enzyme of glycolysis from tumours. H. Kraut and E. Bumm (Z. physiol. Chem., 1928, **177**, 125—142).—A highly active co-enzyme has been prepared from carcinomata and sarcomata capable of promoting glycolysis by sections of rat's kidney washed free from co-enzyme. A preparation of the tumour dried with acetone and ether is extracted with $0{\cdot}01N$-ammonia and precipitated by alcohol. The precipitate still contains an inhibitor which is removed by adsorption from concentrated solution by aluminium hydroxide. The final product is 125 times as active as the dried preparation. The co-enzyme content of extracts of liver, kidneys, embryo, and tumour increases in the order given. J. H. Birkinshaw.

Carbohydrate metabolism of certain pathological overgrowths. H. G. Crabtree (Biochem. J., 1928, **22**, 1289—1298).—The magnitude and relationships of the respiratory and glycolytic processes found by Warburg to be characteristic of malignant tissues are not specific for these tissues, but are a common feature of pathological overgrowth. Thus the magnitude of the respiration and aërobic and anaërobic glycolysis of the reactive tissue in experimental vaccinia in young chickens, in fowl pox and human warts approximates to that found for tumours. In the case of vaccinia lesions in rabbits where little or no epithelial hyperplasia is evident lower quotients are obtained, probably due to leucocytic invasion. In the brain of guinea-pigs dying of rabies where no abnormal cell division occurs there is no deviation from the normal metabolism. The metabolic activity of fowl-pox lesions exhibits a rough parallelism in its magnitude to the state of development or regression of the lesion. There is great variability in the values for respiration in the Rous chicken-sarcoma. After the injection of Rous sarcoma cell-free filtrate in the muscle of fowls a slight rise in the metabolism was noticed during 4½ hrs. followed by a return to the normal values obtained for resting muscle. During the subsequent development of the tumour in its early stages, the cells of this tumour assume on their first appearance the high metabolic activity characteristic of the fully grown tumour. S. S. Zilva.

Action of naturally occurring iron compounds on metabolism. Active iron. M. Kochmann and H. Seel (Biochem. Z., 1928, **198**, 362—378).—In prolonged experiments with young rats, a considerable acceleration of growth was obtained on administration of a naturally occurring mineral ("Liebenstein") water containing ferric hydrogen carbonate. This acceleration of growth was accompanied by increased oxygen utilisation. Animals receiving the same amount of ferrous sulphate showed a smaller acceleration of growth, but this was still greater than when distilled water free from iron was administered. No support could be obtained for the view that there exists a special form of iron, not as yet characterised, which shows great biological activity. P. W. Clutterbuck.

Growth-promoting influence of inorganic iron compounds. A. Bickel (Biochem. Z., 1928, **199**, 60—68).—Rats fed on a diet containing "siderac" (a magnetic benzidine-active ferric oxide) showed a greater increase in body-weight than controls receiving no "siderac." A second magnetic benzidine-active ferric oxide and a non-magnetic benzidine-active ferrous–ferric carbonate had no growth-promoting effect. "Siderac" also increased the iron content of the body. J. H. Birkinshaw.

Can the growth-promoting influence of iron be increased by ultra-violet irradiation ? P. M. Suski (Biochem. Z., 1928, **199**, 69—71).—Irradiation of ferrous sulphate produced no improvement in growth-promoting power. J. H. Birkinshaw.

(*a*) Inorganic iron of the organism. (*b*) Fate of inorganic iron in surviving organs. (*c*) Fate of inorganic iron in the organism after administration of ferrous and ferric compounds. E. Starkenstein and H. Weden (Arch. exp. Path. Pharm., 1928, **134**, 274—287, 288—299, 300—316).—(*a*) The inorganic iron present in the animal organism is only partly extracted by water or by dilute hydrochloric acid, but is almost completely extracted by boiling with 5*N*-hydrochloric acid followed by precipitation with trichloroacetic acid, a method which does not remove any hæmoglobin iron. The distribution of inorganic iron in the blood and organs of various animals has been investigated and the percentage present in the ferric and ferrous states has been ascertained. Inorganic iron for the most part appears to be present in a form insoluble in water. Of that extracted by hydrochloric acid, the greater portion is in the ferrous state, but of that extracted by water most is in the ferric state.

(*b*) The effect of the addition of ferrous chloride and of ferric hydroxide to blood has been investigated and the quantities of ferrous and ferric iron present at various times have been determined. Ferrous iron is oxidised to ferric and the ferric iron is reduced to ferrous, but the ferric iron formed from ferrous in the blood appears to have different physical and chemical properties from the ferric iron added as ferric hydroxide and in the same way the ferrous iron formed by reduction in blood of ferric hydroxide behaves differently from ferrous iron added as ferrous chloride.

(*c*) The various changes which ferrous chloride and ferric hydroxide undergo in the blood and in various organs have been investigated. W. O. Kermack.

Change of soluble ferrous salts in organisms. M. Messini (Arch. exp. Path. Pharm., 1928, **135**, 346—361).—The minimal lethal dose for colloidal ferrous phosphate was determined by intravenous injections into rabbits and compared with both simultaneous and consecutive injections of sodium phosphate and ferrous sulphate. The relative equivalence of the doses is assumed to justify the hypothesis that soluble ferrous salts are converted into insoluble ferrous phosphate *in vivo*. Subcutaneous injections of ferrous sulphate were made, the animals killed after measured time intervals, and the injection sites tested for iron and phosphate. The phosphate reaction increased with increase of time between injection and death to a maximum and then both iron and phosphate reactions decreased. This is claimed to support the hypothesis of conversion of soluble ferrous salts into phosphate *in vivo*. H. R. Ing.

Raw and prepared milks as sources of calcium and phosphorus for the human subject. M. M. Kramer, E. Latzke, and M. M. Shaw (J. Biol. Chem., 1928, **79**, 283—295).—Better retention of calcium and phosphorus in children was secured with fresh milk than with dried milk; for adults, fresh and condensed milks were about equally good, whilst pasteurised and dried milks were definitely poorer. C. R. Harington.

Relation of carbon quotient to oxidation quotient of urine. A. Bickel (Biochem. Z., 1928, **199**, 195—201).—The carbon quotient denotes the ratio total carbon/total nitrogen. The oxidation quotient is the reciprocal of that employed by Müller (A., 1927, 996) and denotes the ratio "oxygen requirement"/total nitrogen. J. H. Birkinshaw.

Carbon- and oxidation-quotients of urine after calcium administration. E. Goldschmidt (Biochem. Z., 1928, **199**, 207—211).—Rabbits received daily 0·03 g. or 0·06 g. of calcium *per os*. Whilst the carbon quotient in the first and second calcium periods was below normal, the oxidation quotient was above normal. J. H. Birkinshaw.

Carbon- and oxidation-quotients of urine after dextrose administration. T. Taslakowa (Biochem. Z., 1928, **199**, 212—215).—The daily oral administration to rabbits of 3 g. of dextrose per kg. body-weight caused a general movement of the two quotients in the same direction, both tending to increase. J. H. Birkinshaw.

Action of hypertonic dextrose solutions on the excretion of water and chlorides by the kidneys. I. J. M. Goldberg, S. M. Gamerow, and M. L. Pinchassik **Action of hypertonic dextrose solutions on the excretion of water and chlorides**

by the kidneys in thyroidectomised animals. II. J. M. Goldberg, M. L. Pinchassik, and S. M. Gamerow (Biochem. Z., 1928, **199**, 107—114, 115—120).—I. Hypertonic dextrose solutions introduced into the blood of rabbits cause the water content of the muscles to decrease, that of the blood and liver to increase. The chloride content remains unchanged. The secretion of urine usually diminishes, and the chloride content of the urine varies according to the total volume.

II. Hypertonic dextrose solutions have much less influence on the water distribution between blood, liver, and muscles of thyroidectomised rabbits than of normal animals; the decrease in the quantity of urine is, on the other hand, much more marked.

J. H. Birkinshaw.

Carbohydrate metabolism. H. Schur and A. Löw (Wien. klin. Woch., 1928, **41**, 225—229, 261—266; Chem. Zentr., 1928, i, 1886).—It is considered that the minimal quantity of carbohydrate for metabolism is smaller than is supposed. The function of the islets is discussed. A. A. Eldridge.

Overnutrition and the blood-sugar content. C. Schwarz and J. Smutny (Biochem. Z., 1928, **198**, 243—249).—The fasting blood-sugar value in normal dogs never exceeds 0·12% even after a period in which the diet has been increased by 200%.

P. W. Clutterbuck.

Carbohydrate metabolism in dried muscle. H. von Euler, E. Brunius, and S. Proffe (Z. physiol. Chem., 1928, **177**, 170—176).—Previous experiments had indicated that dried muscle preparations which were capable of producing glycolysis on addition of boiled yeast juice were not activated by purified co-zymase. A repetition of the work with new muscle preparations shows no difference between the action of boiled juice and that of chemically purified co-zymase. J. H. Birkinshaw.

Enzyme experiments with dried muscle. E. Brunius (Z. physiol. Chem., 1928, **177**, 201—204).—Experiments were carried out on lactic acid formation from dextrose by means of the activator prepared according to Meyerhof. The best phosphate concentration was 1—1·3%; the presence of toluene had no effect. Extraction of the active preparation with water weakened its power; the filtrate was inactive. On treatment with alcohol and hydrochloric acid the dried muscle lost its activity and this was not restored by addition of the extract.

J. H. Birkinshaw.

Regulation of carbohydrate metabolism. II. Rôle of lactic acid in intermediary carbohydrate metabolism. III. Action of electrolytes on blood-sugar. A. Partos (Fermentforsch., 1928, **10**, 50—65, 66—71; cf. this vol., 1049).—II. The rate of glycogenolysis which occurs in minced liver *in vitro* is increased by the presence of lactic acid and also by adrenaline and extracts of the pituitary and ovary. Insulin has a retarding action, whilst thyroxine has no material influence. In presence of the above substances, lactic acid has always an accelerating influence *in vitro*, but *in vivo* it accentuates the hypoglycæmia brought about by insulin and decreases or converts into a hypoglycæmia the hyperglycæmia resulting from the administration of adrenaline, or extracts of pituitary or ovary. On the other hand, the hyperglycæmia resulting from administration of thyroxine is scarcely affected by lactic acid.

III. The action which is exhibited by certain acids in raising the concentration of sugar in the blood is not dependent on an increase in hydrogen-ion concentration, but is rather a specific effect of the anion and is exhibited by the sodium salt as well as by the acid itself. W. O. Kermack.

Determination of lactic acid in the vessels of the uterus and umbilicus. F. Wind and K. von Oettingen (Biochem. Z., 1928, **197**, 170—174).—A method of measuring the lactic acid metabolism of tissues in the living animal is described.

W. McCartney.

Metabolism of body-cells. A. Fujita (Biochem. Z., 1928, **197**, 175—188).—Suprarenal, pituitary, and parathyroid glands, sympathetic ganglia, embryonic lenses, testes, ovaries, placentas, spleens, and bone-marrow were investigated. The animals used were rats, rabbits, mice, and guinea-pigs. The serum method of determination was employed. Except the lenses, all the organs and cells investigated, under anaërobic conditions, display glycolysis, but this disappears almost completely on saturation with oxygen. This holds also for placenta and leucocytes, neither of which is comparable with carcinoma cells as regards metabolism.

W. McCartney.

Behaviour of aldol in the animal body and in fresh organ pulp. F. Lieben and G. Ehrlich (Biochem. Z., 1928, **198**, 317—327).—Ripper's method for the determination of aldehydes (A., 1900, ii, 319) may be used for aldol and paraldol, the presence of acetone interfering but of sugar not. The presence of aldol does not interfere with the determination of sugar by the Pavy–Kumagawa–Suto method. Aldol administered subcutaneously does not pass into the urine in significant amounts either in normal or phloridzinised dogs. The conversion of aldol into sugar in phloridzinised dogs is possible, but owing to the high excretion of sugar and the small permissible amount of aldol administered (high toxicity), the extra sugar cannot be determined. The D/N ratio is not affected by these small amounts of aldol, and no increase in urinary β-hydroxybutyric acid occurs. Aldol must therefore either be burnt or built up into glycogen or fat. It does not appear to be detoxicated by combination with glycuronic acid. Organ pulp has the power to destroy aldol in large or small concentration, β-hydroxybutyric acid being in part formed; the activity of the organs decreases in the following order: liver, spleen, muscle of warm-blooded animals, muscle of cold-blooded animals. Aldol is very quickly destroyed on perfusion through a surviving tortoise. P. W. Clutterbuck.

Importance of lipins in cell permeability. N. Okuneff (Biochem. Z., 1928, **198**, 296—310).—Lecithin and cholesterol are shown to be capillary-active at benzene–water and water–olive oil interfaces both when dissolved in the lipin solvent and when emulsified or suspended in water, the activity being in general greater in the former case. Lecithin is considerably more active than cholesterol, especially at a water–benzene interface, concentrations of 1 in 400,000 still causing a lowering of surface tension. When trypan-blue is added to the aqueous layer and lipin simultaneously to the benzene or olive oil the surface tension developed at the interface is only that of the constituent which is most capillary-active at the concentration employed. P. W. Clutterbuck.

Lipoid metabolism of the stomach. S. M. Ling, A. C. Liu, and R. K. S. Lim (Chinese J. Physiol., 1928, **2**, 305—327).—Although subcutaneous injection of histamine results in a considerable increase in gastric secretion in dogs, the concentration of total fatty acid remains unchanged, whereas that of the lipoid phosphoric acid decreases. Calculation of the phospholipin fatty acid from the lipoid and acid-soluble phosphoric acid shows it to be only 9% of the total fatty acids. Phospholipin appears to be derived chiefly from the peptic secreting cells and the non-phosphorus fatty acid from the oxyntic cells. The total lipoid content of gastric mucosa before and after injection of histamine is constant, but the phospholipin content increases and the phosphorus-free fat decreases after injection.

The phospholipin fraction of mucosa lipoid appears to consist of lecithins and kephalins, since about 70% is fatty acid, and of these 50% are liquid fatty acids which become more unsaturated during activity. L. C. Baker.

Chloride metabolism of the stomach. C. L. Hou, T. G. Ni, and R. K. S. Lim (Chinese J. Physiol., 1928, **2**, 299—303).—The average basal chlorine intake of the viviperfused stomach is 0·029 mg./g. of gastric mucosa per min. and is greater than can be accounted for by the amount in the basal secretion. Injection of histamine increases the chlorine intake two- to fifteen-fold, which is again greater than the secretion demands. Since the maximum intake is reached before the maximum output occurs, there is an accumulation of chlorine in the tissues, although as it falls the intake may finally be less than the output. L. C. Baker.

Degradation of fatty acid in surviving dog's muscle. W. Griesbach (Z. ges. exp. Med., 1928, **59**, 123—132; Chem. Zentr., 1928, i, 1788).—The lower extremities and the liver of dogs were perfused with blood to which *iso*valeric and *n*-butyric acid were added. Only in liver perfusion were acetic and β-hydroxybutyric acids formed; the acids formed were rapidly decomposed when the liver perfusion blood was passed through the lower extremities. A. A. Eldridge.

Nitrogen metabolism of man after total resection of the stomach. L. Soloviev (Biochem. Z., 1928, **199**, 121—135).—The removal of the stomach had no marked effect on protein assimilation or on the excretion of the chief products of nitrogen metabolism. After 6 months, nitrogen retention was observed and a progressive increase in body-weight. The proportion of bound sulphate to total sulphate in the urine was twice that of the normal subject. J. H. Birkinshaw.

Decomposition of *d*- and *l*-alanine, glycyl-*dl*-alanine, and *dl*-alanylglycine by the organism of the dog. E. Abderhalden and K. Franke (Fermentforsch., 1928, **10**, 39—49).—*d*-Alanine administered to a dog is completely decomposed, whilst *l*-alanine is only partly decomposed, part of it being excreted in the urine unchanged. From experiments in which *dl*-alanylglycine and glycyl-*dl*-alanine were administered it appears that the peptides containing *d*-alanine are utilised by the animal organism, whilst the peptides containing *l*-alanine are excreted in part unchanged. The observation was made that the lead salt of *d*- or *l*-alanine has an optical rotation greater than the original acid and opposite in sign. The same appears to be true for other α-amino-acids, whereas lead salts of dipeptides have an increased rotation but of the same sign as that of the original dipeptide. W. O. Kermack.

Purinolytic enzymes of the leech (*Hirudo medicinalis*) and the fresh-water mussel (*Anodonta*). R. Truszkowski (Biochem. J., 1928, **22**, 1299—1301).—From the determinations of purine-nitrogen before and after autolysis of the tissues of leeches and of fresh-water mussels, it is concluded that the end-product of their purine catabolism is xanthine, or hypoxanthine, or a mixture of the two. S. S. Zilva.

Absorption of uric acid by tissue. II. Relation between absorbed urate and concentration of perfusion liquid. S. La Franca (Ann. Inst. Physiol., 1927, **29**, 291—297; Chem. Zentr., 1928, i, 1788).

Action of the sympathetic on the formation of ammonia in muscle. H. E. Büttner (Biochem. Z., 1928, **198**, 478—486).—The traumatic formation of ammonia in frogs is about 50% higher on the sympathectomised side than on the control and, on stimulating electrically, is about 60% greater on the denervated side. The resting ammonia values are not regularly increased after sympathectomy. P. W. Clutterbuck.

New aminophosphoric acid [in invertebrate muscle]. O. Meyerhof and K. Lohmann (Naturwiss., 1928, **16**, 47; Chem. Zentr., 1928, i, 1674—1675).—Argininephosphoric acid, analogous to creatinephosphoric acid in vertebrate muscle, is present in invertebrate (crab) muscle. The latter is less readily decomposed, especially at the neutral point, by the muscle enzyme, and at slightly alkaline reaction is more readily resynthesised from its components; it contains a free amino-group. The effect of increasing acid concentration and of catalysts (molybdate) on the rate of decomposition is reversed in the two cases. A. A. Eldridge.

Transformation of phosphagen in muscle. O. Meyerhof and O. Nachmansohn (Naturwiss., 1928, **16**, 726—727).—The reversible decomposition of phosphagens (guanidino-, creatine-, and arginine-phosphoric acids) has been shown to be concerned in muscle activity (cf. A., 1927, 75, 274, 990; this vol., 917). The decomposition is now shown to occur only or at least principally in the excitation process rather than in the contraction. The ratio of the amount of phosphagen decomposed to the amount of lactic acid formed is much reduced by curarising the muscle. Paralysing the nerves with tetramethylammonium chloride further hinders the phosphagen decomposition; muscle treated in this way shows a transient decomposition on contraction, but resynthesis occurs practically completely on relaxation. Indirect confirmation of the view that the normal excitation process is intimately connected with the phosphagen decomposition is given by suspending muscle in a phosphate concentration higher than the inorganic phosphate content of the muscle itself; excitability and phosphagen concentration are thereby increased. R. A. Morton.

Tryptophan and the thyroid gland. H. C. Chang and W. C. Ma (Chinese J. Physiol., 1928, **2**, 329—335).—Addition of tryptophan to the food of rats fed on a gelatin diet did not improve the condition of the thyroid gland, except in one case where the loss in body-weight was small. There was usually a loss in body-weight as in inanition and the appearance of the glands in both cases is similar. L. C. Baker.

Determination of tryptophan and tyrosine in proteins: application to the most important food-proteins. J. Tillmans, P. Hirsch, and F. Stoppel (Biochem. Z., 1928, **198**, 379—401).—A method is described for the determination of tryptophan and tyrosine in proteins, the protein being nitrated and the colour tones at two widely different $p_{\rm H}$ being compared with those of solutions containing known amounts of these acids similarly nitrated. A table summarises the tyrosine and tryptophan contents of a large number of proteins along with the values obtained by the methods of other authors. The albumin and globulin fraction of human, cow's, and goat's milk contains about the same amounts of tyrosine and tryptophan, but the whey protein of human milk contains more tryptophan and less tyrosine than that of goat's and cow's milk. The tyrosine and tryptophan contents of the myosin of the muscle of different animals are about the same. The protein extractable by saline from wheat meal contains a large amount of tryptophan, but this is absent from zein. Considerable differences were obtained between the tyrosine and tryptophan contents of rye and wheat proteins. The globulin fraction of legumes contains 1—2% of these acids. Of the food proteins egg- and blood-albumins contain 4—5% of tyrosine, but other albumins and globulins have a low content (0·7—2%). Gliadin and glutelin have a high tyrosine content (5—8%). P. W. Clutterbuck.

Muscle-protein. V. Nutritive value of the muscle-protein. 2. Amount of lysine in the muscle-protein and its effect on the growth of young rats. H. Sekine (J. Imp. Fish. Inst., 1926, **22**, 42—43).—Experiments with proteins from *Oncorhynchus masou* and *Meretrix meretrix* indicate that the lysine, but not the tryptophan or histidine, content of muscle-protein is directly related to the growth of young animals. Chemical Abstracts.

Quantitative methods of measuring the nutritive value of proteins. H. H. Mitchell (Biochem. J., 1928, **22**, 1323—1326).—Polemical. The author objects to Kon's statement (this vol., 324) that it is inherent in the author's method to give higher biological values in the periods immediately following the standardising nitrogen-free or low-nitrogen periods and also that the method is not a measure of the capacity of a protein to build new tissues. S. S. Zilva.

Determination of coefficients of utilisation of foodstuffs. V. G. Heller, C. H. Breedlove, and W. Likely (J. Biol. Chem., 1928, **79**, 275—282).—The method of Bergeim (A., 1926, 1170) for determining the coefficients of utilisation of foodstuffs compares well with standard methods so long as the mixing of the ferric oxide with the diet be perfectly even; this is difficult to obtain, and since most diets contain sufficient iron for the purpose, the best results are obtained by applying the method of analysis of Bergeim without the addition of any extraneous iron. C. R. Harington.

Effect of varying amounts of oxygen, anoxæmia, and anæsthetics on the sugar metabolism of animal cells. A. M. Estes and W. E. Burge (Amer. J. Physiol., Proc. Amer. Physiol. Soc., 1927, **81**, 474).—Experiments on paramœcia are described. Chemical Abstracts.

Lactic acid and carbohydrate in sea-urchin eggs under aërobic and anaërobic conditions. W. A. Perlzweig and E. S. G. Barron (J. Biol. Chem., 1928, **79**, 19—26).—The mature unfertilised eggs of the sea-urchin, *Arbacia punctulata*, contain 2—5 mg. of lactic acid per g. of protein; this amount is considerably increased by treatment of the eggs with potassium cyanide, and a smaller increase is observed after fertilisation. No free reducing sugars were detected in the eggs, nor was glycogen isolated, but acid hydrolysis of the eggs yielded dextrose in amounts more than sufficient to serve as precursor for the lactic acid. C. R. Harington.

Effect of certain electrolytes and non-electrolytes on permeability of living cells to water. M. McCutcheon and B. Lucke (J. Gen. Physiol., 1928, **12**, 129—138).—Permeability to water in unfertilised eggs of *Arbacia punctulata* is found to be greater in hypotonic solutions of dextrose, sucrose, and glycine than in sea-water of the same osmotic pressure. The addition to dextrose solution of small amounts of calcium or magnesium chloride reduces the permeability approximately to the value obtained in sea-water. Further addition of sodium or potassium chloride increases the permeability. E. A. Lunt.

Retarding action of metallic silver on the development of sea-urchin eggs. A. Drzewina and G. Bohn (Compt. rend. Soc. Biol., 1927, **97**, 1522—1524; Chem. Zentr., 1928, i, 1789).

Changes in the cholesterol content of rabbit's serum after intracardial injection of peptone. X. Chahovitch, V. Arnovljevitch, and M. Vichnjitch (Arch. Int. Physiol., 1927, **29**, 298—301; Chem. Zentr., 1928, i, 1786).—A fall in the cholesterol content is followed by persistently high values. A. A. Eldridge.

Activity and toxicity of the vapours of the lower aliphatic alcohols. H. Weese (Arch. exp. Path. Pharm., 1928, **135**, 118—130).—The narcotic and toxic action of the vapours of methyl, ethyl, propyl, *iso*propyl, *n*-, *sec*-, *tert*.-, and *iso*-butyl alcohols have been investigated by ascertaining their action on white mice. W. O. KERMACK.

Toxic action of fatty acids in relation to the adaptation of the organism. J. BĚLEHRÁDEK and F. SCHWARZ (Bull. Soc. Chim. biol., 1928, **10**, 909—919).—The toxic action of normal fatty acids (formic to valeric) on *Anguillula aceti*, *Daphnia*, and the larvæ of *Rana fusca* and similar organisms is examined. The time of survival may be expressed as the reciprocal of a constant power of the concentration of the acid. The toxic action is apparently not determined by adsorption or by surface tension. G. A. C. GOUGH.

Alimentary glycæmia in phloridzin diabetes. Action of phloridzin on the liver. C. SCHWARZ and H. SASSLER (Biochem. Z., 1928, **198**, 250—258).—Blood-sugar values are tabulated for dogs over prolonged periods with normal diet, after phloridzin and fasting. Hypoglycæmia becomes strongly developed during administration of phloridzin to fasting animals, whilst in subsequent fasting the blood-sugar values rise again, but the glycogen-forming capacity of the liver is still disturbed, as is seen by the administration of a carbohydrate-rich diet, which causes a considerable glycæmia. P. W. CLUTTERBUCK.

Influence of section of the vagus and of morphine on the respiratory exchange. H. MELTZER and M. STEUBER (Arch. exp. Path. Pharm., 1928, **134**, 259—273).—Subcutaneous administration of morphine accelerates the breathing, decreases the absolute respiratory volume, strongly increases the alveolar carbon dioxide tension, and markedly decreases the intake of oxygen. W. O. KERMACK.

Influence of narcotics on the blood-sugar concentration. K. STEINMETZER and F. SWOBODA (Biochem. Z., 1928, **198**, 259—267).—All the narcotics (ether, morphine, chloral hydrate, "hedonal") investigated caused hyperglycæmia in dogs which on the average persisted for 6 hrs. and always lasted longer than the duration of narcosis. The mean blood-sugar was 30—50% above normal. Hyperglycæmia caused by small doses of chloral hydrate and "hedonal" persists for a considerable time. P. W. CLUTTERBUCK.

Effect of various substances of the quinine group on the enzymic functions of the organism. IX. Effect of quinine on the dynamics of carbohydrate and fat metabolism. I. A. SMORODINCEV (Biochem. Z., 1928, **197**, 160—169).—In general, carbohydrate metabolism is increased in the presence of quinine. The hydrolysis of starch is, in most cases, accelerated by quinine, but that of sucrose and of maltose is almost unaffected. At $p_{\rm H}$ 8·0 and higher quinine checks the hydrolysis of fats, but the process is accelerated if the medium in which it takes place is acid. Probably the inhibition is produced by adsorption of free quinine on the enzyme molecule, whilst the accelerating effect is due to the action of quinine salts. W. MCCARTNEY.

Effect of parasympathetic poisons on the blood-sugar. II. T. SAKURAI (J. Biochem. Japan, 1928, **8**, 365—370).—The combined effect of ergotoxin and pilocarpine is to lower the blood-sugar; the effect can be prevented by atropine. CHEMICAL ABSTRACTS.

Effect of illumination on the proteins of the lens of the eye. F. LIEBEN and P. KRONFELD (Biochem. Z., 1928, **197**, 136—140).—On illuminating lenses of fresh intact pig eyes with diffused daylight in the presence of a sensitising agent and with a quartz lamp with and without the presence of the agent no decrease in the tryptophan content of the proteins of the lenses could be observed. Under the same conditions, in solutions of the lenses in sodium hydroxide containing the equivalent of 0·5% of proteins, considerable destruction of tryptophan took place, but, since such destruction did not occur in solutions four times as concentrated, it may be assumed that the protein material in the lens is able to protect itself, by its high concentration, from chemical changes caused by light. Normal human lenses and lenses affected by cataract exhibit no differences in so far as the tryptophan content of their proteins is concerned. W. MCCARTNEY.

Influence of peroral and intravenous administration of radium bromide on the urinary C : N quotient. A. A. GOLDBLOOM (Biochem. Z., 1928, **197**, 14—19).—Daily peroral administration to rabbits of radium bromide increases the urinary C : N quotient, whilst single intravenous injections cause a gradually developing increase; in both cases this is mainly due to decrease of nitrogen excretion. There is great similarity between radium and radiothorium as far as their actions on metabolism are concerned. W. MCCARTNEY.

Prophylactic and sterilising properties of organic arsenicals and mercurials in syphilis. G. E. WAKERLIN and A. S. LOEVENHART (J. Pharm. Exp. Ther., 1928, **34**, 15—22).—One intravenous injection of the following drugs 24 hrs. after the inoculation of rabbits with *Treponema pallidum* showed their protective power to run parallel to their sterilising power; 25 mg./kg. of salvarsan, 40 mg./kg. of neosalvarsan, and 750 mg./kg. of tryparsamide afforded complete protection, 200 mg./kg. of proparsanol (monosodium salt of *p*-γ-hydroxypropylaminophenylarsinic acid) delayed symptoms 2 weeks and 30 mg./kg. of "flumerin" and 100 mg./kg. of sodium 1-mercuribis-3-nitronaphthalene-8-carboxylate did not protect. The determination of prophylactic power requires only 3 months, as against 8 months for sterilising power, and is therefore recommended for assessing the therapeutic efficacy of these drugs. L. C. BAKER.

Therapeutic action of organic mercurials in syphilis. G. E. WAKERLIN and A. S. LOEVENHART (J. Pharm. Exp. Ther., 1928, **34**, 23—28).—Mercuric salicylate shows definite healing power of syphilitic lesions in rabbits with 3 weekly intramuscular injections of 10 mg./kg. (one third of the tolerated dose), but little sterilising power, whilst the maximum dose tolerated affords no protection. Two doses of 15 mg./kg. (half the tolerated dose) and two of 7·5 mg./kg. of "flumerin" are effective in healing, but one fourth of the tolerated dose is much less effective; it has no sterilising or protective power. Sodium

1-mercuribis-3-nitronaphthalene-8-carboxylate shows no healing power in two doses of 25 mg./kg. and two of 50 mg./kg. (half the tolerated dose) and it has no sterilising or prophylactic properties.

L. C. Baker.

Toxicity of lead compounds. F. Bischoff, L. C. Maxwell, R. D. Evans, and F. R. Nuzum (J. Pharm. Exp. Ther., 1928, 34, 85—109).—Details are given for the preparation of colloidal suspensions of various lead compounds by adding the sodium salt of the particular anion required to a solution of lead chloride containing 1·5—2·0% of gelatin. The toxicity of lead given intravenously to rabbits depends entirely on the form of lead and four groups may be distinguished. Most toxic is ionic lead such as colloidal lead hydroxide, metallic lead, and lead glycerophosphate, oleate, and stearate, for which the lethal dose is 3—10 mg./kg. body-weight. To produce a fall in hæmoglobin comparable to that produced by a dose of ionic lead, two to four times that dose of colloidal lead oxychloride, oxycarbonate, or carbonate is necessary, 4—16 mg. being the lethal dose. Lead tetraethyl and lead triethyl chloride produce only a very slight fall in hæmoglobin even when the lethal dose, which, except in pregnancy, for lead tetraethyl is of the same order as for lead oxycarbonate and for lead triethyl chloride as for ionic lead, is approached. Tri- and di-lead phosphate and lead sulphide do not appear to affect the red cells nor does the first appear to be toxic. Lead phosphate and ionic lead are practically removed from the blood-stream in 2 hrs. Colloidal lead phosphate and lead tetraethyl seem suitable for trial in cancer therapy.

L. C. Baker.

Toxicology of bismuth. R. Fabre and M. Picon (J. Pharm. Chim., 1928, [viii], 8, 249—258, 297—308).—The distribution of bismuth in the organism after intramuscular and intravenous injection of an oil solution of bismuth camphocarbonate into dogs and rabbits has been examined. The method of destruction of the organs for bismuth determination is given and colorimetric and microelectrolytic methods for the determination of bismuth are described and compared. Whatever method of injection is used most of the bismuth is found in the liver and kidneys and a notable proportion is present in the blood. The salivary secretion, teeth, and hair contain considerable amounts and evidently act as auxiliaries to the usual methods of elimination, especially in animals in which perspiration does not play a large part. The brain retains only a small amount of bismuth even after long treatment.

E. H. Sharples.

Structure and enzyme reactions. VII. The system glycogen–amylase–liver tissue. S. J. Przylecki and J. Wójcik (Biochem. J., 1928, 22, 1302—1306).—Liver tissue has an exceptionally high adsorptive action on glycogen which, as in the case of egg-white, is reversible, elution taking place when the concentration of glycogen in solution falls. The addition of protein to the system glycogen–amylase retards but does not inhibit the reaction of glycogenolysis. The biological reaction is: adsorbed glycogen $\rightleftharpoons$ free glycogen $\rightleftharpoons$ dextrose. S. S. Zilva.

Inter-relation of hydrogen-ion activity and concentration of salt in the activation of pancreatic amylase. H. C. Sherman, M. L. Caldwell, and M. Adams (J. Amer. Chem. Soc., 1928, 50, 2529—2535).—The above inter-relation was investigated for pancreatic amylase in presence of buffers of sodium phosphate, which salt, like sodium sulphate, does not influence the activity. The optimum hydrogen-ion activity depends on the nature and concentration of the salt, or salts, present. It decreases with increasing salt concentration until the latter reaches a certain value depending on the nature of the salt, beyond which the activity is practically uninfluenced. Sodium salts and potassium chloride were used. S. K. Tweedy.

Influence of concentration of neutral salt on the activation of pancreatic amylase. H. C. Sherman, M. L. Caldwell, and M. Adams (J. Amer. Chem. Soc., 1928, 50, 2535—2537).—The optimum concentrations for certain sodium salts and potassium chloride together with the corresponding optimum hydrogen-ion activities for pancreatic amylase are recorded. The activity of pancreatic amylase is favoured by more acid solutions in the presence of those salts which must be present in higher concentrations to produce complete activation.

S. K. Tweedy.

Quantitative comparison of the influence of neutral salts on the activity of pancreatic amylase. H. C. Sherman, M. L. Caldwell, and M. Adams (J. Amer. Chem. Soc., 1928, 50, 2538—2543).—This comparison was made in the presence of chlorides of sodium, potassium, and lithium and several sodium salts, each at its optimum concentration. The anions have much more influence than the cations. If sodium sulphate, or more especially sodium nitrate, is added to amylase containing sodium chloride, the activity of the enzyme is diminished to an extent which increases as the concentration of the added salt is increased. The salt concentration necessary for producing the optimum hydrogen-ion activity seems to be independent of the concentration of the enzyme solution and of the starch present (2—4%). The presence of a neutral salt is essential to the activity of pancreatic amylase; its effect may be due to some influence on the colloidal state of the enzyme, since, except in the case of sodium sulphate, those neutral salts having the most favourable influence on the activity are also the most effective precipitating agents for proteins. In all probability the effect is the result of a specific reaction between the enzyme and the salt rather than of the influence of salt on the total ionic strength and activity of the solution. S. K. Tweedy.

Complement of the amylases. VI. H. Pringsheim, J. Bondi, and E. Thilo (Biochem. Z., 1928, 197, 143—151).—In order that proteins may become energetic activators of the amylases it seems to be necessary for the proteins to undergo digestion with trypsin. W. McCartney.

Glycogenase in fish muscle. I. T. Oya and K. Shimada (J. Imp. Fish. Inst. Tokyo, 1926, 22, 24—28).—The action of glycogenase in muscle of

Scomber japonicus, *Paralichthus olivaceus*, and *Pagrosomus mayor* is optimal at p_H 7.

Chemical Abstracts.

Specific nature of invertase. R. Weidenhagen (Z. Ver. deut. Zucker-Ind., 1928, 406—418).—The sucrose-splitting enzymes in *Aspergillus oryzæ* (the source of taka-diastase), *A. niger*, *Penicillium glaucum*, and pigs' intestine are all capable of decomposing raffinose into melibiose and lævulose at rates which are of the same order as those observed in the hydrolysis of sucrose. There are therefore no grounds for assuming that the invertase of taka-diastase or the other materials mentioned represents a different type (gluco-invertase) from that present in yeast (fructo-invertase). J. H. Lane.

Hydrolysis of sucrose by enzymes. R. Weidenhagen (Z. Ver. deut. Zucker-Ind., 1928, 539—542).—A more detailed account of work already published (this vol., 1157).

Preparation of substance taking part in the enzymic decomposition of dextrose to lactic acid (Meyerhof's "activator"). E. Brunius and S. Proffe (Z. physiol. Chem., 1928, **178**, 164—168).—A strain of top-yeast, treated according to Meyerhof's method (A., 1927, 590), yielded no substance capable of forming lactic acid from dextrose unless autolysis of the yeast was previously carried out in presence of dextrose. A second strain of bottom-yeast, however, did not need this preliminary treatment. The explanation of the difference is uncertain. A solution of the "activator" was found to possess undiminished activity after dialysis.

R. K. Callow.

Succinoxidase. II. Influence of phosphate and other factors on the action of succinodehydrogenase and the fumarase of liver and muscle. P. W. Clutterbuck (Biochem. J., 1928, **22**, 1193—1205; cf. A., 1927, 693).—The fumarase activity of rabbit's liver pulp is about eight times that of the same weight of muscle pulp. An amount of the enzyme with an activity approximately equal to that of the tissue pulp itself can be removed from liver or muscle by steeping in water or 0·25% saline solution. Succinodehydrogenase could not be detected in these extracts, possibly because it became inactivated in the manipulation. After this extraction a further quantity of fumarase equal in activity to about six times the original pulp can be obtained from the muscle residue, but not from the liver residue, by elution with $M/15$-phosphate. $0{\cdot}052M$-Phosphate activates fumarase from muscle and liver, but not succinodehydrogenase. The temperature coefficient for fumarase activity of liver pulp is 2—2·4, and of muscle pulp 1—4, but the coefficient of the aqueous extract of the latter tissue is nearer normal. Sodium chloride inhibits the action of succinodehydrogenase considerably, but of fumarase only slightly. Sodium fluoride inhibits the action of fumarase considerably. The presence of fumarase has been detected in the muscle of *Pecten maximus* and *Anodonta cygnea*, but not in baker's yeast. It was present in the corpuscles but absent from the serum of fresh defibrinated blood. A very active fumarase solution is obtained by precipitating the phosphate extract of washed muscle with ammonium sulphate, filtering, and dialysing the solution of the precipitate. S. S. Zilva.

Specificity of the dehydrases. Separation of the citric acid dehydrase from liver and of the lactic acid dehydrase from yeast. F. Bernheim (Biochem. J., 1928, **22**, 1178—1192).—The finely-minced liver tissue is extracted with acetone and dried in a vacuum. The dried powder is extracted with water, the extract is dialysed and precipitated by half saturation with ammonium sulphate, leaving the hæmoglobin in solution, and the active precipitate is finally dissolved in water. A further yield of the enzyme can be obtained from the hæmoglobin solution by fully saturating with ammonium sulphate. The citric acid dehydrase thus prepared did not act with the sodium salts of the following acids as donators: succinic, malic, fumaric, lactic, tartaric, formic, glutamic, maleic, acetic, α-hydroxybutyric, oxalic, saccharic acids, or with acetaldehyde. It also did not utilise aconitic acid as a donator, but this compound, like citric acid, is capable of inhibiting the citric acid–enzyme system beyond certain concentrations.

The lactic acid dehydrase was prepared by treating baker's yeast with acetone, extracting the zymin thus obtained with $M/15$-disodium hydrogen phosphate for 4 hrs., and dialysing the active solution against distilled water. The enzyme is specific for lactic and α-hydroxybutyric acids. The following did not act as hydrogen donators: β-hydroxybutyric, malic, maleic, formic, citric, glutamic, succinic, fumaric, oxalic, acetic, tartaric, and pyruvic acids and acetaldehyde and dextrose. Pyruvic acid is the product of the action of the enzyme on lactic acid, but not on α-hydroxybutyric acid. Pyruvic, oxalic, and lactic acids inhibit the action of the dehydrase. Oxygen could not replace methylene-blue as a hydrogen acceptor, nor did the enzyme produce pyruvic acid when, instead of the dye, xanthine oxidase, hypoxanthine, and a concentrated solution of peroxidase were added to the system and oxygen was bubbled through the solution for several hours at 37°.

S. S. Zilva.

Dehydrogenation of lactic acid. A. Hahn, E. Fischbach, and W. Haarman (Z. Biol., 1928, **88**, 89—90).—Washed, minced muscle in presence of methylene-blue as hydrogen acceptor was able to dehydrogenate lactic acid to pyruvic acid. Semicarbazide was used to protect the pyruvic acid from further oxidation by the formation of semicarbazone. The pyruvic acid was finally isolated and weighed as the phenylhydrazone. J. H. Birkinshaw.

Dehydrogenation of malic acid. A. Hahn and W. Haarman (Z. Biol., 1928, **88**, 91—92).—Washed muscle in presence of methylene-blue was shown to dehydrogenate malic to oxalacetic acid, which was isolated as the semicarbazone. On hydrolysis of the latter the free acid formed lost carbon dioxide, giving pyruvic acid, which was isolated as the phenylhydrazone. J. H. Birkinshaw.

Influence of intravenous injections of hepatocatalase on the catalase and anticatalase content of rabbit tissues. I. Catalase and anticatalase content of tissues from normal rabbits.

L. G. Belkina, L. L. Kremlev, and R. V. Falk. **II. Changes in the catalase and anticatalase content of blood and tissues following injection of massive doses of catalase into the blood.** L. G. Belkina and L. L. Kremler (Zhur. Exp. Biol. Med., 1928, 8, 322—328, 329—341).—I. Considerable variations are observed. The order of catalase content is: blood, kidney, liver, spleen, lungs, heart, brain, muscles. The order of anticatalase content is nearly the same.

II. The injected catalase disappears completely in 3 hrs. The catalase accumulates chiefly in the kidneys and muscles. Anticatalase changes are not parallel with catalase changes.

Chemical Abstracts.

Oxidising enzymes. X. Relationship of oxygenase to tyrosinase. M. W. Onslow and M. E. Robinson (Biochem. J., 1928, 22, 1327—1331).—The view of Pugh and Raper (this vol., 202) that, since tyrosinase has all the properties ascribed by Onslow to oxygenase, it seems unnecessary to retain the term oxygenase, is opposed. S. S. Zilva.

Tyrosinase of *Beta vulgaris*. R. Weidenhagen and F. Heinrich (Z. Ver. deut. Zucker-Ind., 1928, 499—538).—The tyrosinase–tyrosine reaction is best followed by the disappearance of tyrosine as determined by the bromine absorption method of Raper and Wormall. Haehn and Stern's rapid modification (A., 1927, 699) is not trustworthy, but the following gives good results. The test portion is heated with acetic acid, made alkaline without filtration, kept for 1 day, re-acidified, and the necessary potassium bromide added. On filtration a water-white liquid is obtained, in which the tyrosine can be readily determined. The tyrosinase–tyrosine reaction is not unimolecular, the velocity coefficient usually increasing with time. The velocity increases from p_H 5 to 8 in phosphate-buffered solutions. Borate buffers are unsuitable, as strong acidity is developed by boric acid in presence of dihydroxyphenylalanine, the first product of the reaction. Phosphate buffers exert an inhibiting effect at concentrations much above $M/15$. Tyrosinase is inactivated by heating in solution for 5—10 min. at 70—80°, and slightly weakened in 7 hrs. at 30°. The reaction proceeds more slowly at 40° or 30° than at 20°; in the former case the velocity coefficient decreases with time, indicating probable destruction of enzyme. The relative velocity is greater with low concentrations of substrate, but not in strict proportion, and at the highest concentration employed, 0·1% of tyrosine, the coefficient decreased with time. The time value for tyrosinase is defined as the time taken to bring about the disappearance of 50 mg. of tyrosine from a solution containing 100 mg. in 200 c.c. of phosphate buffer of p_H 6·81. Beet tyrosinase cannot be purified by precipitation by alcohol, or by adsorption on kaolin or alumina. It is precipitated with the proteins, but damaged by the use of metallic salts or tannin for this purpose. Precipitation with phosphotungstic acid (p_H 4·4), rapid separation and washing of the precipitate, and elution with very dilute ammonia (p_H 7·5—8) gives a 7·5-fold increase in activity calculated on the dry matter, with a 45% loss of total activity. Better results are obtained by treating beet slices with the phosphotungstic acid, and after washing and pulping, treating with dilute ammonia, evaporating in a vacuum, and dialysing. This treatment gives a forty-fold increase in the activity of the preparation. It is essential to use fresh material, and the use of rootlets from seed germinating in sand is recommended. The sap from these after dialysis shows a higher tyrosinase activity than the raw sap, apparently owing to removal of inhibiting impurities. F. E. Day.

Stalagmometric determination of lipases. B. J. Krijgsman (Natuurwetensch. Tijdschr., 1928, 10, 137—144).—The apparatus and method of Rona and Michaelis (A., 1911, ii, 302) have been modified to permit of quicker and more accurate determination of lipase. An examination of the hydrolysis of tributyrin by lipase from the middle intestine of the snail, *Helix pomatia*, showed that at first the time required to hydrolyse a definite quantity of the fat was inversely proportional to the quantity of enzyme used. The quantity of fat hydrolysed was directly proportional to the time. Magnesium chloride had no influence on the speed of the reaction within the limits of concentration used. S. I. Levy.

Acceleration of lipase activity by substances containing vitamin-*A*. B. L. Johnson (Iowa State Coll. J. Sci., 1928, 2, 145—153).—Addition of vitamin-*A* concentrates to a mixture of ethyl butyrate, lipase, and sea sand greatly increases the amount of butyric acid liberated. Sodium oleate and palmitate accelerate lipase activity. Chemical Abstracts.

Metaphosphatase. T. Kitasato (Biochem. Z., 1928, 197, 257—258).—Sodium hexametaphosphate in 2% solution in the presence of 1·5% of taka-phosphatase and toluene gives in 68 hrs. at 37° a yield of 20% of orthophosphate, whereas in this time a solution of the metaphosphate alone gives only traces of orthophosphate. This change can also be produced by animal organs (liver and kidney) and by yeast. W. McCartney.

Action of rennin on the proteins of milk. IV. Enzymes in the stomach contents of calves of various ages. J. Zaykovski, O. Fedorova, and V. Ivankin (Fermentforsch., 1928, 10, 83—87).—Pepsin and rennin are both present in the stomach of embryonic calves. Both are increased in amount after birth, but pepsin proportionately more than rennin, from which it appears that rennin and pepsin are not identical. W. O. Kermack.

Nature of proteases. I. Behaviour of amino- and carboxyl groups in various pepsin preparations. J. A. Smorodincev and A. N. Adova (Z. physiol. Chem., 1928, 177, 187—200).—A relationship was found to exist between the total nitrogen, the ratio of amino- to carboxyl groups, the amino-acid and polypeptide content, and the effect on the p_H of the solvent on the one hand and the proteoclastic action of various pepsin preparations on the other. The activity is directly proportional to the nitrogen, amino-nitrogen, and carboxyl group content. The ratio NH_2/CO_2H varies from 0·75 in strong to less than 0·5 in weak preparations, the ratio polypeptide

CO_2H/amino-acid CO_2H varies from 2·64—3·41 in strong to 0·8—1·5 in weak preparations.

J. H. Birkinshaw.

Modification of Congo-red method for determination of pepsin. E. Beer and O. Peczenik (Fermentforsch., 1928, **10**, 88—90).—A modification of the method of Kawahara (Arch. ges. Physiol., 1924, **206**, 360) for the determination of pepsin is described, consisting in the substitution of rose-bengal B for Congo-red. A solution of albumin coloured by rose-bengal B is not decolorised by the addition of hydrochloric acid. If, however, hydrolysis of the protein by pepsin is allowed to take place, the rose-bengal becomes decolorised when insufficient protein is left to keep it in the coloured form. By this modification the time required for a determination is reduced from 16 to 2—4 hrs. W. O. Kermack.

Degradation of caseinogen, serum-globulin, and serum-albumin by dilute alkali, dilute acid, pepsin and hydrochloric acid, and pancreatic enzymes. E. Abderhalden and W. Kröner (Fermentforsch., 1928, **10**, 12—35).—The hydrolyses have been followed using Sørensen's formol titration in order to determine the degree of decomposition which occurs after various periods of time. Albumin is split more slowly by alkali than is caseinogen or serum-globulin. *N*-Hydrochloric acid effects no detectable hydrolysis in the cases of caseinogen or of serum-globulin, although with these proteins the results are complicated owing to the precipitation of the proteins by the acid. Caseinogen is hydrolysed slowly by pepsin and hydrochloric acid, with the production of equal numbers of free amino- and of free carboxyl groups, whilst serum-albumin and especially serum-globulin are practically unattacked. Caseinogen and serum-globulin are extensively hydrolysed by pancreatic enzymes, whereas serum-globulin is unattacked. Protein previously treated with pepsin and hydrochloric acid is more extensively hydrolysed by *N*-sodium hydroxide solution than is untreated protein. Caseinogen after treatment with trypsin is more intensively hydrolysed than is fresh caseinogen, but serum-albumin is not affected by previous treatment. The action of *N*-hydrochloric acid is not greater on caseinogen and serum-albumin after the action of tryptic enzymes. Preliminary treatment with pepsin and hydrochloric acid increases the susceptibility of all proteins to tryptic digestion, a phenomenon particularly noticeable in the case of serum-globulin, which by the method used shows no evidence of decomposition by pepsin and hydrochloric acid, or by trypsin separately. Trypsin is also effective to some extent if the globulin is previously treated with 0·1*N*-hydrochloric acid alone. In the case of no protein is pepsin and hydrochloric acid rendered more effective by previous treatment with trypsin. Trypsin causes no increase in amino-nitrogen when it acts on serum-albumin or serum-globulin previously treated for a considerable time with *N*-sodium hydroxide solution and only a slight increase in the case of serum-globulin. W. O. Kermack.

Action of erepsin and of trypsin-kinase on *l*-leucylpentaglycyl-*l*-tryptophan. E. Abderhalden and H. Sickel (Fermentforsch., 1928, **10**, 91—94).—l-*Leucylpentaglycyl*-l-*tryptophan* is hydrolysed by purified erepsin in such a way that no tryptophan is set free, whereas when this polypeptide is acted on by pure trypsin-kinase, tryptophan is liberated. α-Bromo*iso*hexoyltetraglycylglycine, decomp. 210°, $[\alpha]_D^{20}$ +12·21°, is converted into the acid *chloride* and allowed to react with *l*-tryptophan in dilute sodium hydroxide solution under definite conditions with the formation of *α-bromo*iso*hexoylpentaglycyl*-l-*tryptophan*, and this is converted into l-*leucylpentaglycyl*-l-*tryptophan* by treatment with liquid ammonia at the ordinary temperature. This amorphous polypeptide begins to decompose at 135°, but has no definite m. p., is precipitated by mercuric salts and by phosphotungstic acid, and gives the biuret reaction. W. O. Kermack.

Action of erepsin and trypsin-kinase on polypeptides containing *d*-glutamic acid. E. Abderhalden and E. Rossner (Fermentforsch., 1928, **10**, 95—101).—The three new polypeptides, d-valyl-*l*-leucylglycyl-*d*-glutamic acid, *d*-alanyl-*d*-valyl-*l*-leucylglycyl-*d*-glutamic acid, and *l*-leucyl-*d*-alanyl-*d*-valyl-*l*-leucylglycyl-*d*-glutamic acid as well as the phenylcarbimide derivative of the last have been prepared and subjected to the action of purified erepsin and of trypsin-kinase. The tetrapeptide was almost completely resistant to erepsin, whilst the pentapeptide was slightly, and the hexapeptide considerably, attacked by that enzyme. All three polypeptides were hydrolysed by trypsin-kinase. The phenylcarbimide compound was not attacked by erepsin, but was definitely hydrolysed by trypsin-kinase. α-Bromo*iso*valeryl chloride and *l*-leucylglycylglutamic acid react in dilute sodium hydroxide solution with the formation of *α-bromo*iso*valeryl*-l-*leucyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ +16° in absolute alcohol, which by the action of aqueous ammonia is converted into d-*valyl*-l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ +11·4° in water. Similarly, d-*α-bromopropionyl*-d-*valyl*-l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ +0·36° in alcohol, −18·2° in water, is converted by aqueous ammonia into d-*alanyl*-d-*valyl*-l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{19}$ −10·7 in water, and d-*α-bromo*iso*hexoyl*-d-*alanyl*-d-*valyl*-l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{21}$ +12·6° in alcohol, is converted into l-*leucyl*-d-*alanyl*-d-*valyl*-l-*leucylglycyl*-d-*glutamic acid*, $[\alpha]_D^{20}$ −9·5° in water, which couples normally with phenylcarbimide to yield the *compound* $C_{34}H_{53}O_{10}N_7$.

W. O. Kermack.

Proof of the enzymic nature of the phenomena underlying the Abderhalden reaction. E. Abderhalden and S. Buadze (Fermentforsch., 1928, **10**, 111—144).—Serum dried at a low temperature is treated with 87% glycerol, which extracts the enzymes responsible for the Abderhalden reaction. The enzymes can be purified by adsorption on kaolin or alumina followed by elution with ammonium phosphate solution. Of sera from cases of pregnancy 76% gave extracts showing the presence of enzymes, whilst of other sera none gave a positive result.

W. O. Kermack.

Urease. M. Jacoby (Fermentforsch., 1928, **10**, 1—11).—Discussion and bibliography.

W. O. Kermack.

Relation between protein and urease. H. Ishibashi (Bul. Sci. Fak. Terkult. Kjusu, 1928, 2, 287—291).—Pepsin and trypsin produce from urease some amino-acid, and the activity of the urease is diminished, although not proportionally. Urease is closely related to proteins. Chemical Abstracts.

Influence of structure on the kinetics of desmolases. I. Uricase. Systems uricase–uric acid–active and inactive charcoal or protein. S. J. von Przyłecki (Z. physiol. Chem., 1928, **178**, 19—38).—See this vol., 1055.

Enzymes and biocatalysts in relation to adaptation and inheritance. I. Effect of iron-containing media on yeast. H. von Euler and E. Eriksson (Z. physiol. Chem., 1928, **178**, 39—51).—Yeast was grown in media containing iron as ferrous sulphate, and the iron and the amino-, peptide-, and cyclic nitrogen contents, rate of fermentation, rate of reduction of methylene-blue, and oxygen absorption were measured. By growth in a succession of media containing ferrous sulphate the iron content of the yeast was raised to 0·04%. The rate of reduction of methylene-blue and the oxygen absorption decreased with increasing iron content. A decrease in the peptide-nitrogen appeared to take place, but was not definitely established. The rate of reduction of methylene-blue by normal yeasts treated with sulphur, hydrogen sulphide, or thiolactic acid was little affected. R. K. Callow.

Yeast amylase. A. Gottschalk (Z. physiol. Chem., 1928, **178**, 139—147; cf. A., 1926, 759).—A juice poor in co-zymase, prepared by maceration of dried yeast, fermented glycogen very slowly in comparison with dextrose, showing that glycogen requires a relatively larger quantity of co-zymase. On the other hand, a juice rich in co-zymase, prepared by maceration of dried yeast with an extract of yeast by hot water, fermented glycogen more rapidly, but still at a lower rate than dextrose. The results were affected by the concentration of carbohydrate and by the age of the yeast. The induction period of the glycogen fermentation was longer. The aqueous extract supplies, in addition to co-zymase for the fermentation of the hexoses from glycogen, an activating agent for the action of the amylase. The amylase, as previously shown (*loc. cit.*), is extracted with difficulty from yeast, and the addition of a little of the residue from maceration accelerated the fermentation of glycogen considerably. Takadiastase fermented glycogen nearly as rapidly as dextrose, but the results obtained with saliva were similar to those with yeast amylase. Comparison was made of the autolysis of fresh yeast with that of yeast the structure of which had been destroyed by chemical or mechanical treatment. No difference was found, and it was concluded that the yeast-cell contained no excess of diastase adsorbed on the cell-wall. R. K. Callow.

Second form of fermentation of sugar under the influence of carbamic acid hydrazide and thiocarbamic acid hydrazide. Isolation of acetaldehyde and glycerol. M. Kobel and A. Tychowski (Biochem. Z., 1928, **199**, 218—229).—Carbamic acid hydrazide and thiocarbamic acid hydrazide were used as interceptors of acetaldehyde in the second form of fermentation; yields of acetaldehyde up to 15% of the theoretical were attained. Acetaldehyde and glycerol were formed in equivalent amounts. Where the sulphur content of the mash prevented a direct determination of the glycerol by the original Zeisel–Fanto method the *iso*propyl iodide was absorbed in pyridine. The pyridine solution was treated with silver nitrate solution, strongly acidified with nitric acid, and boiled for 2—3 hrs. The excess of silver in solution was then determined by Volhard's method. J. H. Birkinshaw.

Supposed interception of methylglyoxal in alcoholic fermentation. C. Neuberg and M. Kobel (Biochem. Z., 1928, **199**, 230—231).—Kostytschev and Soldatenkov (this vol., 923) have now retreated from their original position with regard to the isolation of methylglyoxal as the disemicarbazone, but still claim the isolation of pyruvic acid as the semicarbazone. This has been anticipated by several authors. J. H. Birkinshaw.

Difference between the processes of alcoholic fermentation and of acetaldehyde dismutation. C. Neuberg and E. Simon (Biochem. Z., 1928, **199**, 232—247).—Boiled suspensions of acetic bacteria capable of producing strong dismutation (*B. ascendens* and *B. pasteurianum*) were quite unable to replace co-zymase. When the suspension was added to a system of washed dried yeast (apo-zymase) and dextrose no fermentation occurred until co-zymase was added. Thus the view of Euler and Myrbäck (A., 1927, 484) that the initiator of fermentation (co-zymase) and the agent causing dismutation of acetaldehyde are of the same nature is not substantiated. J. H. Birkinshaw.

Co-zymase and its determination. K. Myrbäck (Z. physiol. Chem., 1928, **177**, 158—169).—Recent work casting doubt on the existence of Harden's co-zymase is criticised. According to the author the essentials for cell-free fermentation are: the enzyme system (apo-zymase); inorganic phosphate; small amounts of hexosediphosphate; co-zymase; a suitable acidity. For quantitative measurements of fermentation velocity the experiments must be carried out at constant temperature and the vessels shaken. J. H. Birkinshaw.

Mechanism of enzyme action. II. Action of ethylene. F. F. Nord and K. W. Franke (J. Biol. Chem., 1928, 79, 27—51).—Treatment of a zymase solution (which could be preserved in the cold with unimpaired activity for 65 days), or of yeast suspensions with ethylene caused an increase in the ability to ferment dextrose; in the latter case the increase was observed after contact with ethylene during 1 min. only, and is regarded as being due to formation of a film of ethylene on the cells with increasing permeability of the latter. A similar increase in the activity of the catalase of tobacco leaves was found after treatment of these with ethylene. In the fermentation of pyruvic acid by yeast, preliminary ethylene treatment increased both the permeability (and hence the enzymic activity of the yeast) and its power of resisting the harmful effects of high concentrations of the acid. C. R. Harington.

Trehalosemonophosphoric ester isolated from the products of fermentation of sugars with dried yeast. R. Robison and W. T. J. Morgan (Biochem. J., 1928, **22**, 1277—1288).—The *ester* $C_{12}H_{21}O_{11}\cdot PO_3H_2$, $[\alpha]_{5461}$ +185° (*barium* salt, $[\alpha]_{5461}$ +132°; *brucine* salt, $[\alpha]_{5461}$ +31°), was isolated from the products of fermentation of lævulose in presence of phosphate by zymin and dried yeast by fractional alcohol precipitation (30—70%) of the aqueous solution of the barium salts and by purification as the brucine salt. It is also produced by fermentation of dextrose in the presence of phosphates. It is non-reducing and from it the bone phosphatase liberates trehalose. Hydrolysis with boiling mineral acid slowly converts the ester into dextrose and dextrosemonophosphoric ester, the latter being still more slowly hydrolysed to dextrose and phosphoric acid. Barium dextrosemonophosphate was isolated, but in a slightly impure condition. Trehalosemonophosphoric ester is readily fermented by dried yeast and more slowly by yeast juice and zymin. The examination of dried yeast used in the fermentation showed that neither trehalosemonophosphoric ester nor free trehalose was present in quantities sufficient to account for the amount of the ester found in the fermentation products. This ester was not found in the products of fermentation by yeast juice. S. S. Zilva.

Alcoholic fermentation of sugars by acetic acid bacteria. C. Neuberg and E. Simon (Biochem. Z., 1928, **197**, 259—260).—When *B. ascendens* or *B. pasteurianum* was allowed to act, under anaërobic conditions, on a 1·2% dextrose solution typical alcoholic fermentation occurred, the yield of alcohol amounting to 25% of the theoretical quantity. Addition of sterile extract of bottom yeast doubled this yield. Since the amounts of alcohol and carbon dioxide produced were nearly equivalent and since only about 45% of the unfermented sugar was recovered, part of it had apparently been decomposed in some other way. W. McCartney.

Respiratory pigment, cytochrome, in bacteria. H. Yaoi and H. Tamiya (Proc. Imp. Acad. Tokyo, 1928, **4**, 436—439).—The absorption spectra of the respiratory pigment cytochrome have been examined microspectroscopically in a large number of strains of aërobic, facultative aërobic, and anaërobic pathogenic bacteria. The first class exhibit all four bands (*a*) (614—593 μμ), (*b*) (567—561 μμ), (*c*) (550 μμ), and (*d*) (532 and 521 μμ), the second show only (*b*) and (*d*) and occasionally (*a*), whilst the pigment is absent in anaërobic bacteria. In addition, in all strains of *B. dysenteriæ*, excluding the Shiga bacillus, and in *B. coli*, a new characteristic band at 623—637 μμ was detected. J. W. Baker.

Formation of catalase by *Bacillus coli*. O. Fernández and T. Garméndia (Z. Hyg. Infekt.-Krankh., 1928, **108**, 329—335; Chem. Zentr., 1928, i, 1783).—In aërobic cultures of *B. coli* in synthetic media containing various sugars (2%) and amino-acids (0·5%), the formation of catalase depends on the sugar. It is particularly marked with lævulose in presence of alanine, asparagine, or glycine, and with tyrosine and ammonium lactate. With leucine, optimal catalase formation takes place in presence of galactose and dulcitol; with glutamic acid, in presence of sucrose. In anaërobic cultures peroxidase, but seldom catalase, is formed. A. A. Eldridge.

Quantitative enzyme measurements with micro-organisms. II. Effect of some factors on the catalase content of bacteria. A. I. Virtanen and A. O. Winter (Biochem. Z., 1928, **197**, 210—221).—The factors considered were: effect of hydrogen-ion concentration, effect of concentration of iron, effect of different sources of carbon and nitrogen, and effect of aërobic and anaërobic growth. Inconclusive results were obtained as regards the effect of concentration of iron, but catalase formation by *B. coli* is independent of the other factors. The great decrease in the catalase content of bacteria grown in media containing dextrose is due to destruction of the catalase resulting from the formation of acid. No agreement could be found with the general view that the catalase content of cells grown under aërobic conditions is greatly increased. W. McCartney.

Sulphate-reducing bacteria in Californian oil waters. R. Gahl and B. Anderson (Zentr. Bakt. Par., 1928, II, **73**, 331—338; Chem. Zentr., 1928, i, 1783).

Oxidations by *Bacterium xylinum*. I. Formation of dihydroxyacetone from glycerol. K. Bernhauer and K. Schön (Z. physiol. Chem., 1928, **177**, 107—124).—A bacterium resembling *B. xylinum* can convert quantitatively glycerol into dihydroxyacetone. In order to prevent mould contaminations, it was found advisable to acidify the medium. Acetic acid was found to be superior to formic, propionic, and butyric acids for this purpose, the best concentration being 0·02—0·03*N*. The process gives the highest yields when the medium is in shallow layers (1—2 cm.) and contains not more than 6—8% of glycerol. J. H. Birkinshaw.

Biochemical nature of *B. paratyphosus B.*, Schottmüller, and *B. enteritidis*, Breslau, and a new differentiating medium for these. M. N. Fischer and A. J. Bunte (Biochem. Z., 1928, **198**, 428—441).—Autoclaving milk or Seitz's medium causes the condensation of amide-nitrogen with sugar, giving a humin-like substance the nitrogen of which is difficultly assimilable by micro-organisms, *B. paratyphosus*, Schottmüller, being probably unable and *B. enteritidis*, Breslau, able to assimilate it. P. W. Clutterbuck.

Pyocyanine, the blue colouring matter of *Bacillus pyocyaneus*. III. Constitution of hemipyocyanine. F. Wrede and E. Strack (Z. physiol. Chem., 1928, **177**, 177—186).—In continuation of previous work (A., 1925, i, 844) the authors prepared a further quantity of hemipyocyanine by the action of sodium hydroxide solution on pyocyanine and purified it by sublimation. It had m. p. 158° and the formula $C_{12}H_8ON_2$. Its constitution as 1-*hydroxyphenazine* was proved by synthesis. The 1-methyl ether of pyrogallol was oxidised with lead peroxide in benzene solution to the *o*-quinone and the latter treated with *o*-phenylenediamine in acetic acid. Condensation occurred with elimination of 2 mols. of water, the monomethyl ether of 1-hydroxyphenazine being produced. This was identical with hemipyocyanine monomethyl ether. It was demethylated by hydrobromic acid. J. H. Birkinshaw.

Influence of the medium on the growth of tubercle bacilli. V. M. Kulikov and Z. I. Nikolskaja (Zhur. exp. biol. Med., 1928, **8**, 73—77).—Copper ions and guaiacol are much more toxic to tubercle bacilli in an alkaline than in an acid medium. Chemical Abstracts.

Chemotherapy of tuberculosis. I. E. Hesse, G. Meissner, and G. Quast (Arch. exp. Path. Pharm., 1928, **135**, 82—110).—Certain dyes of the triphenylmethane, azine, and thiazine series show special affinity for the tubercle bacillus and stain the living organism. When tested under particular conditions certain of these dyes have marked bactericidal power. Experiments are described the aim of which is to correlate such results obtained *in vitro* with the chemotherapeutic activity of the dye administered to the animal organism. W. O. Kermack.

Influence of ultra-violet radiation on some physico-chemical and biological properties of tuberculin. S. M. Mikhailovski (Zhur. Exp. Biol. Med., 1928, **9**, 12—22).—The p_H of solutions is shifted towards the acid side, and the surface tension increases. Chemical Abstracts.

Oxidation–reduction equilibria in biological systems. I. Reduction potentials of sterile culture bouillon. C. B. Coulter (J. Gen. Physiol., 1928, **12**, 139—146).—The time–potential curves of sterile culture bouillon during deaëration with nitrogen indicate a negative drift to —0·060 volt as a limiting value. It is suggested that this is due to the glutathione, from the chopped meat, acting as a catalyst in the oxidation of the muscle residue by molecular oxygen. E. A. Lunt.

Isoelectric state of bouillon containing toxin. A. S. Raewsky (Biochem. Z., 1928, **197**, 8—13).—The point at which the precipitate of maximum toxicity is obtained should not be regarded as the isoelectric point of the toxin itself, and the isoelectric points found by the author were those either of the proteins of the bacillus or of a compound of these with the proteins of the bouillon. The proteins of the nutrient medium, when they react with the proteins of the bacilli, displace the isoelectric point of the latter, the degree of displacement being proportinal to the amount of protein present in the medium. W. McCartney.

Diphtheria toxin. A. Leulier, P. Sédallian, and J. Gaumont (Compt. rend. Soc. Biol., 1927, **97**, 1543—1545; Chem. Zentr., 1928, i, 1973).—By acidification of the filtrate from bouillon cultures of the diphtheria bacillus with hydrochloric or acetic acid to p_H 4—7, a precipitate containing all the toxic principle is obtained. This is considered to be a nucleoprotein; it contains 0·5—1·5% P. A. A. Eldridge.

Action of adrenaline. I. Carbohydrate metabolism of fasting rats. II. Carbohydrate metabolism of rats in the post-absorptive state. III. Utilisation of absorbed dextrose. C. F. Cori and G. T. Cori (J. Biol. Chem., 1928, **79**, 309—319, 321—341, 343—355).—I. During the second 24 hrs. of a fasting period, the total glycogen content of rats is decreased by only 22 mg.; the authors explain this small deficit on the basis of intermediary formation of sugar from fat in the course of oxidation, a process distinct from true gluconeogenesis in which the sugar newly formed is stabilised in the body. Injection of adrenaline into 24-hr. fasting rats produced a rise in oxygen consumption, but no change in the respiratory quotient; the liver-glycogen was increased and the muscle-glycogen decreased by a more than equivalent amount. In view of the facts that oral administration of lactic acid leads to increased deposition of glycogen, and that the disappearance of muscle-glycogen could not be accounted for by oxidation, it is thought that the action of adrenaline may involve the degradation of muscle-glycogen to lactic acid, and the re-synthesis of the latter into liver-glycogen.

II. Whilst in the normal rat in the post-absorptive state the glycogen which disappears from the animal is derived partly from the liver and partly from the muscles, after injection of adrenaline the whole of the glycogen disappearing comes from the muscles, and after insulin a larger proportion comes from the liver than in the normal. The hyperglycæmia following adrenaline administration is due in part to mobilisation of muscle-glycogen and in part to diminished utilisation of blood-sugar; in the latter respect, therefore, adrenaline and insulin are directly antagonistic.

III. The above hypothesis is confirmed by the observation that rats injected with adrenaline fail to utilise as much dextrose (both by oxidation and by conversion into liver-glycogen) after feeding with dextrose as do normal animals. The extra heat production of the adrenaline-treated rats is accounted for entirely by oxidation of fats. C. R. Harington.

Relation between concentration and action of adrenaline. D. Wilkie (J. Pharm. Exp. Ther., 1928, **34**, 1—14).—The isometric and isotonic response to adrenaline of strips of sheeps' carotid arteries, prepared by cutting 5 mm. rings of the artery longitudinally, may be expressed by the formula $Kx=y/(A-y)$, where x is the concentration of adrenaline, A maximum response, y response produced, and K is a constant. The arterial flow, rise in blood-pressure, and cardiac frequency are also fairly well expressed by this formula. L. C. Baker.

Action of insulin. IV. Effect on the metabolism of the tortoise. B. v. Issekutz and F. v. Végh (Magyar Orvosi Arch., 1928, **29**, 1—7).—Insulin increases the oxygen consumption and carbon dioxide production. The respiratory quotient does not change. Chemical Abstracts.

Action of insulin. I and II. H. Handovsky (Arch. exp. Path. Pharm., 1928, **134**, 324—338, 339—346).—I. Administration of insulin to rabbits causes a decrease in the carbohydrate present in the muscle and particularly in the muscle-glycogen.

II. The action of insulin is greater in animals to which calcium dithioglycollate has been administered than in untreated animals. It is suggested that the sulphydryl group of insulin plays an important part in its action. W. O. KERMACK.

Pancreatic hormone and mineral metabolism. I. Influence of the pancreatic hormone on the excretion of different urinary constituents (particularly inorganic salts) by normal and by pancreas-diabetic dogs. S. TAKEUCHI (Tôhoku J. Exp. Med., 1928, **10**, 388—407).—Subcutaneous injection of pancreatic hormone into dogs increased the daily excretion of chlorine, potassium, and nitrogen. In two depancreatised dogs the daily quantity of urine, phosphorus, chlorine, calcium, magnesium, potassium, sodium, nitrogen, sulphate, and sodium/potassium ratio were decreased and the phosphoric acid/nitrogen ratio was increased by injection of the hormone. CHEMICAL ABSTRACTS.

Relation between hormonal and enzymic phenomena in the mechanism of regulation of the carbohydrate metabolism. V. A. ENGELHARDT and A. N. PARSHIN (Zhur. exp. biol. Med., 1928, **8**, 573—580).—Fatal doses of insulin caused an average increase of only 10% in the blood-amylase. CHEMICAL ABSTRACTS.

Physiological changes of the inner secretion of the pancreas. I. Proof of the existence of a physiological insulinæmia. II. Vagus as nerve inducing insulin secretion. III. Rôle of the nervous system in regulation of physiological insulinæmia. J. LA BARRE. **IV. Hyperinsulinæmia after hyperglycæmia caused by injection of dextrose. V. Hyperinsulinæmia after injection of adrenaline.** E. ZUNZ and J. LA BARRE (Arch. Int. Physiol., 1927, **29**, 227—290; Chem. Zentr., 1928, i, 1785).

Hormonal action of dextrose on production of insulin. E. GEIGER (Arch. exp. Path. Pharm., 1928, **134**, 317—323).—A sodium chloride or urea solution isotonic with 60% dextrose solution is as effective as the latter in stimulating the production of insulin by the pancreas. The conclusions of Grafe and Meythaler (A., 1927, 1115; cf. this vol., 925) that dextrose specifically stimulates the production of insulin is not rigorously proved. This conclusion is supported by the fact that if dextrose is administered in a concentration isotonic with blood no stimulation of insulin production is apparent. W. O. KERMACK.

Destructive action of heat on insulin solutions. A. KROGH and A. M. HEMMINGSEN (Biochem. J., 1928, **22**, 1231—1238).—The destruction of insulin at a constant temperature follows fairly well the law of unimolecular reactions. The relation of rate of destruction to temperature can be expressed by the formula of Arrhenius. The critical thermal increment amounts to 28,300. The rate of destruction is not appreciably altered by changes in the p_H between 2 and 4. S. S. ZILVA.

Behaviour of the urinary C : N quotient following parenteral administration of extract of the anterior lobe of the pituitary body. A. A. GOLDBLOOM (Biochem. Z., 1928, **197**, 20—30).—The chief effect produced is a limitation of the oxidations, but the extract also has a certain hyperoxidising function. Almost always there is increase in the amount of dysoxidisable carbon in the urine, whilst the nitrogen generally increases in amount with small doses but decreases with large ones. W. McCARTNEY.

Carbon- and oxidation-quotients of urine after injection of "praephysone." A. A. GOLDBLOOM (Biochem. Z., 1928, **199**, 202—206).—Rabbits receiving a daily subcutaneous injection of "praephysone" (extract of anterior lobes of the pituitary corresponding to 0·66 g. of fresh organ) showed a general increase in both carbon- and oxidation-quotients, but the increases were irregular. J. H. BIRKINSHAW.

[Lack of] effect of pituitary preparations on phosphorus and calcium metabolism. F. NAKAZAWA (Biochem. Z., 1928, **198**, 350—361).—In dogs which have been fed on a diet of sugar, starch, fat, and salts sufficient calorifically but practically free from nitrogen, calcium, and phosphorus, the daily excretion (urine and fæces) of phosphorus is 14—26 mg./kg. and of calcium 2—6 mg./kg. Subcutaneous injection of various pituitary preparations did not affect the excretion of phosphorus and calcium. P. W. CLUTTERBUCK.

Parallelism in behaviour of the pancreatic secretin and of enterokinase at the b. p. I. P. RASENKOW (Fermentforsch., 1928, **10**, 72—77).—From the observation that the behaviour of enterokinase and secretin at the b. p. under various conditions of reaction shows very great similarity, it is considered possible that these two substances are identical. W. O. KERMACK.

Influence of boiling on pancreatic secretin. I. P. RASENKOW (Fermentforsch., 1928, **10**, 78—82).—Secretin resembles enzymes in that under certain conditions it is largely destroyed by boiling. W. O. KERMACK.

Tissue respiration. IV. Influence of thyroxine, adrenaline, and insulin on the oxygen consumption of surviving liver-cells. H. REINWEIN and W. SINGER (Biochem. Z., 1928, **197**, 152—159).—Both thyroxine and commercial extract of thyroid gland cause increase in the oxygen consumption of surviving liver-cells. Adrenaline in concentrations above 10^{-5} checks the consumption of oxygen by the cells, and there is no stimulating effect on the consumption even at the lowest concentrations. In high concentrations insulin has a damaging effect on tissue respiration, and an increase, due to insulin, in the respiratory activity of surviving liver-cells is never observed. W. McCARTNEY.

Thyroid and tissue respiration. M. MAEDA (Fol. pharmacol. japon., 1927, **3**, 796—824).—The thyroid hormone promotes tissue respiration of almost all organs except the thyroid. CHEMICAL ABSTRACTS.

Thyroid gland and mineral metabolism. Influence of disodium hydrogen phosphate and calcium salts on the action of the thyroid. I. ABELIN (Biochem. Z., 1928, **199**, 72—106).—The action of thyroid substances on the basal metabolism of the rat is increased by phosphate and diminished by calcium, although these have no effect without thyroid. The over-excitability caused by thyroid feeding is diminished by calcium. Glycogen formation by the liver can often be maintained, in spite of thyroid administration, if calcium is supplied, preferably as carbonate; the chloride is unsuitable. Attention is directed to the old lime theory of goitre, since there is actually an antagonism between thyroid gland function and excess of calcium.

The action of adrenaline on the basal metabolism is not noticeably influenced by calcium.

J. H. Birkinshaw.

Rôle of the iodine component of the thyroxine molecule. B. Zavadovski, N. Raspopova, T. Rolitch, and E. Umanova-Zavadovski (Zhur. exp. biol. Med., 1928, 8, 600—611).—The minimum quantity of iodine necessary to produce metamorphosis in axolotls (8—15 g.) is 0·5 mg., and of thyroxine 0·003—0·010 mg. Di-iodotyrosine cannot replace thyroxine; hence it is doubtful if the former is an intermediate in the synthesis of the latter. Chemical Abstracts.

Extraction of ovarian hormone. II. S. Thayer, C. N. Jordan, and E. A. Doisy (J. Biol. Chem., 1928, 79, 53—64).—The ovarian hormone is readily destroyed by traces of peroxides; it is necessary therefore that the ether and light petroleum employed in its extraction (A., 1926, 1064) should be free from these compounds, and that the stages of the preparation involving the use of these solvents should be carried through as rapidly as possible. A clear aqueous solution of the hormone may be obtained by diluting the concentrated alcoholic solution of the purified material with water, distilling off the alcohol, flocculating the colloidal impurities by addition of a little hydrochloric acid, and finally filtering through asbestos. Crude extracts are stable in ethereal solution, but the purified material deteriorates more or less rapidly in solution in ether or light petroleum; the more active preparations are best stored in aqueous or alcoholic solution, in which, provided that no oxidising agent be present, they are stable at least for 3—4 years. C. R. Harington.

Avitaminosis. VIII. Influence of avitaminosis of normal and thyroidectomised rabbits on the nitrogen-, creatine-, and creatinine-excretion and on the blood-sugar. A. Palladin, A. Utewski, and D. Ferdmann (Biochem. Z., 1928, 198, 402—419).—Thyroidectomised rabbits when placed on a diet free from vitamins develop the usual symptoms of avitaminosis, and the duration of life and the course of the blood-sugar curve are the same as with normal rabbits on the same diet. The excretion of nitrogen by thyroidectomised rabbits in avitaminosis is lower than for non-operated animals under the same conditions. Creatine appears in the urine of thyroidectomised animals in avitaminosis 2—3 days, and in non-operated animals 1·5—2 weeks, before death. P. W. Clutterbuck.

Rickets in rats. VII. Calcium and phosphorus metabolism of rats on non-rachitic diets. A. T. Shohl, H. B. Bennett, and K. L. Weed. **IX.** p_H **of the fæces.** A. T. Shohl and F. C. Bing (J. Biol. Chem., 1928, 79, 257—267, 269—274).—VII. To a basal rachitic diet were made graded additions of phosphates and vitamins-*A* and -*D*, and the behaviour of young rats on the various diets so produced was observed. The gradual improvement in the quality of the diet was accompanied by increased intake of food, resulting in better growth, and there was increased retention of calcium and phosphorus with improved histological condition of the bones.

IX. The cure of rickets in rats by agents other than cod-liver oil is not necessarily accompanied by change in the p_H of the fæces from alkaline to acid (cf. Jephcott and Bacharach, this vol., 332).

C. R. Harington.

Protein and vitamin-*B*. G. A. Hartwell (Biochem. J., 1928, 22, 1212—1220).—Many young rats die on a diet containing 20% of edestin and 5 g. of yeast extract per 100 g. of dry solid, showing typical kidney abnormality. Older rats are not affected by this diet. These symptoms can be prevented by the addition of more yeast extract to the diet. The "protective" factor in yeast extract is not destroyed by autoclaving at 120° for 4½—5 hrs. Edestin requires more yeast extract than either caseinogen or egg-albumin for normal metabolism in young growing rats. S. S. Zilva.

Minimum amount of vitamin-*D* required for a positive antirachitic effect in the "line" test. K. H. Coward (Biochem. J., 1928, 22, 1221—1222).—The daily dose which gives this positive result is 2×10^{-5} mg., which confirms the prediction of Fosbinder, Daniels, and Steenbock (this vol., 557).

S. S. Zilva.

Photochemical activation of sterols in the cure of rickets. II. S. K. Kon, F. Daniels, and H. Steenbock (J. Amer. Chem. Soc., 1928, 50, 2573—2581).—Cholesterol purified by fractional oxidation with permanganate in acetone cannot be activated antirachitically by irradiation (cf. Bills, Honeywell, and McNair, this vol., 332). The results of Bills (A., 1926, 645) on activation by means of "floridin" are confirmed. The photochemical formation of vitamin-*D* from ergosterol has been studied quantitatively (cf. this vol., 557). The minimum amount of radiation necessary to produce sufficient vitamin to cause deposit of calcium in the bones of a rachitic rat is 700—1000 ergs, corresponding with the formation of 6×10^{-8} g. of vitamin-*D*. For monochromatic light from the mercury lines 256, 265, 280, and 293 μμ, the quantum efficiency is independent of the wave-length and of the continuous or intermittent nature of the irradiation. The same value is obtained with ergosterol, solid or in alcoholic solution, and with ergosteryl acetate. The quantum efficiency of ordinary cholesterol is variable and may be nearly as high as that of ergosterol. H. E. F. Notton.

Irradiation of ergosterol. T. A. Webster and R. B. Bourdillon (Biochem. J., 1928, 22, 1223—1230).—Ergosterol was irradiated at 77·8°, 30·6°, 1°, −18°, −183° (approx.), and −195° (approx.). With the exception of the products obtained at the last two temperatures, which were less active, all the activated products showed about equal activity. 0·1% Solutions of ergosterol irradiated by rays which were passed through a filter which cut off all rays of wave-length shorter than 265 μμ showed a maximum activity after exposure for 1 or 4 hrs., whilst after 63 hrs. they were less than one quarter as active. The products remaining after removal of unchanged ergosterol by precipitation with digitonin show strong absorption for wave-lengths shorter than 290 μμ with no maximum between 265 and 280 μμ, in contrast to ergosterol and other products which have a maximum between 300 and 330 μμ. The absorption is much greater than that of ergosterol. Ergosterol examined after short periods of irradiation shows an increase in absorption which is at a maximum after a period depending on the concentration of the solution and on the intensity of radiation. On further irradiation the absorption decreases steadily to almost complete disappearance. The antirachitic activity and absorption are produced at approximately the same rate. On further irradiation of active products after the removal of ergosterol, the antirachitic activity and absorption decrease and eventually disappear entirely after irradiation for 3—5 hrs. The irradiation of ergosterol probably produces two substances in succession, one with maximum absorption at 280 or 290 μμ and a second with a maximum at about 230 μμ, the former of which is probably vitamin-*D*. S. S. Zilva.

Factor *H* in the nutrition of trout. C. M. McCay and W. E. Dilley (Trans. Amer. Fish Soc., 1927, 57, 250—260).—Fresh meat contains a thermolabile factor (*H*) which is essential for life and growth. Raw liver (5%) causes marked increase in growth. Lactose cannot replace starch. The factor in liver responsible for growth is different from that concerned in blood regeneration.

Chemical Abstracts.

Spectrophotometric studies of penetration. IV. Penetration of trimethylthionine into *Nitella* and *Valonia* from methylene-blue. M. Irwin (J. Gen. Physiol., 1928, 12, 147—165).—Spectrophotometric measurements indicate that the dye present in the sap extracted from uninjured cells of *Nitella flexilis* and *Valonia macrophysa* which have been placed in methylene-blue solution, is chiefly trimethylthionine. The mechanism of the penetration is discussed. E. A. Lunt.

Photo-oxidation with anthraquinone. K. Pfeilsticker (Biochem. Z., 1928, 199, 8—11).—Anthraquinone in the light acts as oxygen carrier, the carbonyl groups becoming reduced to carbinol. On shaking with air the anthraquinone is regenerated. This action can also occur in the dark with dextrose as oxygen acceptor. J. H. Birkinshaw.

Theory of photo-synthesis. K. Pfeilsticker (Biochem. Z., 1928, 199, 12—20).—The view is held that chlorophyll-*B*, activated by four quanta, produces electrolysis of aqueous protein–carbon dioxide solution. Two carbonyl and two methine groups add on four hydrogen atoms, and a hydrogen carbonate and three hydroxyl ions are electrically discharged at the magnesium anode. Dipercarbonic acid is formed which decomposes catalytically, giving formaldehyde and oxygen. The chlorophyll-*A* regenerates chlorophyll-*B* with the formation of hydrogen peroxide from which catalase liberates oxygen.

J. H. Birkinshaw.

Maintenance of seeds in a medium deprived of oxygen as a means of prolonging their germinative faculty. A. Guillaumin (Compt. rend., 1928, 187, 571—572).—An atmosphere from which oxygen has been removed is as efficient as a vacuum for the purpose of prolonging the germinative faculty of seeds (soya). J. Grant.

Angiosperm seeds and factors in germination. III. Surface-active substances. A. Niethammer (Biochem. Z., 1928, 199, 175—185).—Various seeds were shown to contain saponins. The influence of saponin substances on the germination of saponin-containing and of saponin-free seeds was examined, but no marked differences were found between the two types. The action of various alkaloids was also tested. J. H. Birkinshaw.

Enzyme content of germinating wheat. N. Prokopenko (Nauch. Agron. Zhur., 1927, 4, 346—354).—Catalase, peroxidase, and amylase values were determined. Chemical Abstracts.

Carbohydrate metabolism and its relation to growth in the edible canna. J. C. Ripperton (Hawaii Agric. Exp. Sta. Bull., 1927, 56, 1—35).—The distribution of sugars in the leaves, stem, and root is recorded. The hexoses are considered to be sugars of translocation and the starch in the rootstocks to be formed from sucrose.

Chemical Abstracts.

Nutrition of plants with aldehydes. VIII. T. Sabalitschka (Biochem. Z., 1928, 197, 193—196).—The author discusses results communicated in the previous papers and comments on the views of Bodnár and co-workers (this vol., 207).

W. McCartney.

Enzymic oxidation of oxalic acid by higher plants. V. Zaleski and A. Kucharkova (Ukraine Chem. J., 1928, 3, 139—152).—The velocity of aërobic or anaërobic oxidation of oxalic acid by wheat seeds, as measured by the quantity of carbon dioxide produced, is unaffected by the addition of hydrogen acceptors, such as methylene-blue, potassium nitrate, or hydrogen peroxide, whilst quinone and quinol have a distinctly inhibitory influence on oxalase, the enzyme responsible for this oxidation. The inhibitory action of the latter is due probably to their greater affinity for oxygen, the supply of which is thereby greatly diminished for the oxidation of oxalic acid. Cyanides and ethylurethane do not inhibit the action of this enzyme, showing that neither surface action nor active centres containing iron are responsible for its action. Potassium iodide has a marked inhibitory influence, probably as a result of combination with the enzyme. It is concluded that, in spite of the above observations, oxalase is a dehydrogenase, able to use only molecular oxygen as a hydrogen acceptor. R. Truszkowski.

Carbohydrate transformations in carrots during storage. H. Hasselbring (Plant Physiol., 1927, 2, 225—243).—On storage at 0—14° inversion of sucrose and hydrolysis of dextrins and hemicelluloses took place; little change took place after 10 weeks. Chemical Abstracts.

Losses in mangels during storage. G. T. Pyne (J. Dep. Lands Agric. Ireland, 1927, 27, 33—35).—The losses (5 months) were: water 8·8, dry matter 27·0, protein 22·2, fibre 3·8%. The sucrose decreased 29·5% during 2 months. Chemical Abstracts.

Origin of camphor in camphor trees. T. Yahagi (Japan. J. Chem., 1928, 3, 109—129).—The different parts of the camphor tree have been chemically examined at various stages of growth. It is shown that the formation of camphor, and of the oil of which it is the chief constituent, takes place, even in the earliest stages of growth, in nearly all tissues of active growth, especially just beneath the cambial layer. The sap, however, contains no appreciable amount of camphor. The rate of formation of camphor and oil is very closely related to the growth of the tree; the more vigorous the growth the more rapid is the rate of formation. Once the formation of oily matter is started in the cell it proceeds fairly rapidly until the cell is filled with camphor products. The lining of the oil cells has been shown to contain an enzyme, of the nature of a peroxidase, which appears to be responsible for the formation of the oil and disappears when the cell is full of oil. The peroxidase lining has been found in the cells of other oil-bearing plants. M. S. Burr.

Flower coloration and nitrogen fertilisation. M. von Wrangell and H. von Bronsart (Naturwiss., 1928, **16**, 169—172; Chem. Zentr., 1928, i, 1973).—Unlike that of leaves, the colour of flowers is not markedly brightened by nitrogen fertilisation. A. A. Eldridge.

Behaviour of cyanogenetic glucosides of cherry laurel during starvation. H. Godwin and L. R. Bishop (New Phytol., 1927, 24, 295).—The cyanogenetic glucosides represent a fairly large fraction of the stored carbohydrate of the leaves. During starvation, the glucoside disappears, the rate of disappearance becoming maximal, and then decreasing. Protoplasm is present as gel in young cells; hence the available water at enzyme centres may be so small that accumulation of enzyme results. Chemical Abstracts.

Relation of boron to the growth of the tomato plant. W. H. Dore (Science, 1928, 67, 324—325).—The presence of boron is essential for the normal growth of tomato plants. Plants deficient in boron exhibit an excessive accumulation of sugar in the leaves, which become purple. A. A. Eldridge.

Influence of sulphur on the nitrogen and phosphoric acid utilisation of plants. A. Kalushski (Nauch. Agron. Zhur., 1927, 4, 643—656).—By addition of 0·03—0·04% S the p_H of soil was changed from 7 to 6·6—6·8. Utilisation of nitrogen, and particularly of phosphoric acid, was increased. Chemical Abstracts.

Nitrate reduction by plant roots. A. Schmuck (Nauch. Agron. Zhur., 1927, 4, 155—170).—Marked reduction of nitrate to nitrite takes place in the root substrate. Aromatic nitrogen compounds are also reduced. Chemical Abstracts.

Effect of light on nitrate assimilation in wheat. W. E. Tottingham and H. Lowsma (J. Amer. Chem. Soc., 1928, 50, 2436—2445).—Comparative experiments show that the absorption of nitrate and the synthesis of protein by maize in water-cultures is decreased by the removal from sunlight of those rays which are absorbed by ordinary greenhouse glass. The growth of wheat in sand- or water-cultures has been followed at a total intensity of illumination of 200—8000 ft.-candles, using various distributions of spectral energy. When the blue, violet, and long ultra-violet rays of the tungsten lamp are increased some 50—400% by the use of carbon arcs, absorption of nitrate and, to a smaller extent, synthesis of protein are increased, whilst sugar content and total dry matter are decreased. The same effects are observed when an intensity of illumination greater than that required for maximum tissue formation is employed. Using as standard this combined illumination from which light of lower wave-length than 4000 Å. has been excluded, the effect of successive extensions of the spectrum into the ultra-violet are: 4000—3700 Å., no change; 3700—3000 Å., increase in absorption, but not in assimilation of nitrates; 3000—2800 Å., decrease in formation of tissue and protein. H. E. F. Notton.

Microchemistry of *Illicium verum*, Hook, and *I. religiosum*, Sieb. E. Siersch (Pharm. Zentr., 1928, 69, 581—585, 601—605).—The crystals obtained by extraction with solvents of the carpel and seeds of *I. verum* and *I. religiosum* have been examined microchemically and their solubilities and colour reactions are described. Shikimic acid, m. p. 184°, was isolated from the carpel of both plants, but those from *I. verum* contained much smaller quantities than those of *I. religiosum*. The acid could not be detected in the seeds of either plant but from the seeds of *I. religiosum* a crystalline substance was isolated which agreed in colour reactions with the shikimin of Eykman (A., 1891, 919). Combe's saponin reaction indicated the presence of a saponin in the fruits of *I. religiosum* but in much smaller amount than in *I. verum*. E. H. Sharples.

Seed of *Euphorbia verrucosa*, Jacq. P. Gillot (Mat. grasses, 1928, **20**, 8166—8168).—The seed contains: water 8·84, fat 25·74, crude protein 21·12, nitrogen-free extract 1·30, ash 5·80, crude fibre 37·20%. Cold-pressed oil has α (200 mm.)+0° 10′, d_{15}^{15} 0·9356, n^{22} 1·4855, Crismer value (alcohol d 0·7967) 65°, f. p. −24°, acid value 2·4, acidity (as oleic) 1·24%, soluble fatty acids (Planchon) 0·7 c.c. 0·1N-potassium hydroxide per 150 c.c., soluble fatty acids (as butyric) 0·12%, Hehner value 95·60%, Reichert–Wollny value 0·2 c.c. 0·1N-potassium hydroxide (soluble), 0·3 c.c. (insoluble), saponification value 190·4, acid [? iodine] value 209·0, acetyl value (André) 10·4, unsaponifiable matter 1·04%, ether-insoluble brominated glycerides (Hehner and Mitchell) 60·56%, degree of oxidation (Bishop) 21·20%. The total fatty acids have n^{22} 1·4740, iodine value 218·1, neutralisation value 197·5, solid acids 2·5%, liquid 97·5%; the liquid acids have n^{22} 1·4745, iodine value 222·3. Chemical Abstracts.

Variations in the constants of the oils of certain *Leguminosæ*. G. Halden (Mat. grasses, 1928, 20, 8168—8171).—A discussion. Chemical Abstracts.

Jerusalem artichoke. L. E. Dunton (Forecast, 1927, **34**, 295—296, 332).—Average values are: moisture 81·2, ash 1·26, phosphorus 0·099, calcium 0·023, iron 0·003%. Chemical Abstracts.

Chemical constituents of the fruit of *Ginkgo biloba*. I. J. Kawamura (Japan. J. Chem., **3**, 89—108).—From the ethereal extract of the fruit of *Ginkgo biloba* the unsaturated acid, *ginkgolic acid*, $C_{21}H_{30}(OH)\cdot CO_2H$, m. p. 42—43°, has been isolated. On catalytic reduction with palladium or platinum-black this acid yields dihydroginkgolic acid, $C_{21}H_{34}O_3$, m. p. 86—88° (identical with *cyclo*galliparic acid, cf. Kunz-Krause and Schelle, A., 1904, i, 587; acetyl derivative, m. p. 73—74·5°; p-*nitrobenzoyl* derivative, m. p. 87—89°; *methyl* ester, m. p. 41—42·5°; *silver*, *lead*, and *alkali* salts), which on nitration yields the *derivatives* $C_{21}H_{33}O_3\cdot NO_2$, m. p. 66—68°, and $C_{15}H_{22}N_2O_5$, m. p. 55—56°. Ginkgolic acid possesses an aromatic nucleus and a phenolic hydroxyl group. When heated at 240° it loses carbon dioxide with the formation of *ginkgol*, $C_{20}H_{31}\cdot OH$, b. p. 221—223°/4 mm., which when reduced catalytically in presence of platinum-black yields dihydroginkgol, $C_{20}H_{33}\cdot OH$ (identical with *cyclo*gallipharol, *ibid.*, 588; p-*nitrobenzoyl* derivative, m. p. 60—61·5°). Methylation of ginkgol yields *ginkgol methyl ether*, $C_{20}H_{31}\cdot OMe$, b. p. 200—203°/3 mm., which on oxidation with potassium permanganate gives rise to a *dihydroxy*-derivative, $C_{20}H_{31}(OH)_2\cdot OMe$, m. p. 98—98·5°, as well as to a compound probably identical with butyric acid.

Besides ginkgolic acid the ethereal extract contains (*a*) a secondary alcohol, *ginnol*, $C_{27}H_{55}\cdot OH$, m. p. 82·5°, which on oxidation with potassium dichromate yields a ketone, *ginnone*, $C_{27}H_{54}O$, m. p. 74—75° (*oxime*, m. p. 49·5°; *semicarbazone*, m. p. 45—46°); (*b*) *bilobol*, $C_{21}H_{32}(OH)_2$, m. p. 36—37°, which on catalytic reduction using platinum-black yields *dihydrobilobol*, m. p. 89—90° (*dinitro*-derivative, m. p. 68—71° with previous sintering; *diacetyl* derivative, m. p. 56°); (*c*) an *acid*, $C_{21}H_{42}O_3$ (?), m. p. 63°.

The alkali salts of ginkgolic acid are strong hæmolytic agents. Ginkgolic acid, ginkgol, and ginkgol methyl ether strongly inflame the skin, whilst bilobol is even more active in this respect than ginkgolic acid.

[With N. Fujita.] Phosphoric acid and asparagine have also been isolated from the fruit juice of *Ginkgo biloba*. W. O. Kermack.

Nuclear materials in *Nostoc*. F. A. Mockeridge (Brit. J. Exp. Biol., 1927, **4**, 301—304).—Nucleic acid was not found, but phosphate, pentose, adenine, guanine, cytosine, and uracil were identified.

Chemical Abstracts.

Influence of temperature on the growth of fungi. R. Meyer (Biochem. Z., 1928, **198**, 463—477).—Curves show the growth of *Aspergillus niger* (dry weight plotted against time) on a medium containing different amounts of ammonium sulphate at different temperatures. With rising temperature the time to attain maximal growth decreases, more strongly with larger than with smaller amounts of ammonium sulphate. Curves showing minima are obtained by plotting the time to attain maximal values against the temperature for a particular concentration of ammonium sulphate.

P. W. Clutterbuck.

Dependence of the slope of the nitrogen growth curve on the phosphoric acid supply for *Aspergillus niger*. R. Meyer (Biochem. Z., 1928, **199**, 171—174).—The Mitscherlich law defining action of growth factors cannot be reconciled with the author's results showing influence of nitrogen and phosphorus supply on the yield of *A. niger*.

J. H. Birkinshaw.

New enzyme, glucose-oxidase. I. D. Müller (Biochem. Z., 1928, **199**, 136—170).—Active enzyme preparations were obtained from *Aspergillus niger* capable of promoting dextrose oxidation. These were (1) the expressed juice from the ground mycelium, (2) a dry powder obtained by treating the juice with 12 vols. of 96% alcohol–ether (2 : 1), (3) a dried mycelium preparation obtained by treating the pressed mass with alcohol-ether. Approximately one atom of atmospheric oxygen was absorbed per mol. of dextrose, giving rise to 1 equivalent of fixed acid. This was shown to consist, probably entirely, of *d*-gluconic acid. J. H. Birkinshaw.

Effect of stimulation on [the production of] invertase by *Penicillium glaucum*. II. Z. I. Kertész (Fermentforsch., 1928, **10**, 36—38; cf. this vol., 1063).—*P. glaucum* was grown first on dextrose, then on sucrose, and again on dextrose solution. The invertase activity of the solution measured during the last period rises during the first 8 days and then decreases. It appears therefore that the production of invertase within the mould is stimulated by sucrose and that this enzyme slowly diffuses into the dextrose solution. W. O. Kermack.

"Lead disease" [of plants]. C. M. Albizzati (Anal. Soc. cient. Argentina, 1927, **103**, 38—42; Chem. Zentr., 1928, i, 1973).—In "lead disease" the leaves contain more soluble and less insoluble oxalate than normally, and a greater quantity of a diastase.

A. A. Eldridge.

Spike disease of sandal (*Santalum album*, L.). II. Analysis of leaves from healthy and spiked trees. II. Physico-chemical study of the leaf sap. A. V. V. Iyengar (J. Indian Inst. Sci., 1928, **11A**, 97—102, 103—109).—Sandal leaves affected with spike disease have a higher content of reducing sugars, total carbohydrates, starch, total nitrogen, and dry matter and a lower moisture content than healthy leaves. Diseased leaves are also deficient in calcium, potassium, and ash content.

The p_H values of the sap of healthy and diseased leaves were 5·15—5·71 and 4·69—4·99, respectively. The titratable acidity and osmotic pressure are higher in diseased leaves, and the specific conductivity and the ratio of specific conductivity to f.-p. depression lower in "spiked" sap than in normal.

A. G. Pollard.

New respirometer apparatus. S. Steffenburg (Z. physiol. Chem., 1928, **178**, 75—80).—An apparatus is described consisting of a capillary gas-burette attached to a reaction vessel, by means of which absorption or evolution of gas during fermentation etc. may be measured at constant pressure.

The accuracy is fifty times that of the Euler–Myrbäck apparatus. R. K. Callow.

Micro-determination of carbon dioxide tension. A. Beck (Biochem. Z., 1928, **199**, 21—28).—Into a syringe containing the sample of liquid (5—10 c.c.) an air bubble (0·05—0·1 c.c.) is introduced. Equilibrium is attained by shaking and the bubble is then transferred by way of an intermediate vessel to the absorption apparatus, where the gas is contained in a graduated capillary tube and enclosed by mercury. After absorption of the carbon dioxide by potassium hydroxide the contraction is measured. An accuracy of 0·1% is claimed. J. H. Birkinshaw.

Two-colour colorimetry. E. Kaufmann (Biochem. Z., 1928, **197**, 141—142).—A description of a modified form of the Autenrieth colorimeter is given. The instrument may be used for the determination of blood-sugar and of the oxygen capacity of blood. W. McCartney.

Measurement of chlorine-ion potentials in the presence of proteins. R. S. Aitken (Biochem. J., 1928, **22**, 1239—1245).—The chlorine-ion potentials in pure potassium chloride solutions as measured by means of silver–silver chloride electrodes are steady and reproducible. The readings obtained in potassium chloride solutions containing serum-protein are steady but not reproducible and indicate a higher concentration of chlorine ions than is known to be present. The readings obtained in oxalated human plasma were neither steady nor reproducible. Immersion in plasma " poisoned " the electrode. S. S. Zilva.

Determination of soluble carbohydrates. C. O. Appleman, W. E. Loomis, T. G. Phillips, W. E. Tottingham, and J. J. Willaman (Plant Physiol., 1927, **2**, 195—204).—A report of a committee of the American Society of Plant Physiologists. Chemical Abstracts.

Behaviour of various sugars in the Bang micro-method. Reducing power of lævulose in the Bertrand method. B. Róhny (Biochem. Z., 1928, **199**, 48—52, 53—59).—The Bang factor corresponding with c.c. of $0·01N$-residual thiosulphate/mg. of sugar was determined for xylose, lævulose, galactose, lactose, and maltose. This is compared with Bertrand's factor representing mg. of copper/mg. of sugar for the same series.

The Bertrand factor for pure lævulose is found to be lower than that for dextrose, contrary to the statement of Bertrand; however, in presence of dextrose both lævulose and galactose factors become identical with that for dextrose. Thus invert-sugar and inverted lactose have the same factor as dextrose. J. H. Birkinshaw.

Determination of pyruvic acid. B. H. R. Krishna and M. Sreenivasaya (Biochem. J., 1928, **22**, 1169—1177).—The proteins are eliminated from biological fluids either by the Folin and Wu method or by precipitation with alcohol. Acetone, acetaldehyde, or other volatile compounds are removed from the neutralised solution by evaporation under diminished pressure at 40—50°. After acidification and extraction with ether the extract is treated with sodium hydrogen sulphite and extracted again with ether, which removes lactic acid, β-hydroxybutyric acid, phenols, etc. The residue containing the pyruvic acid is reduced by sulphuric acid and zinc with a trace of copper to lactic acid and the latter compound determined by Friedemann, Cotonio, and Shaffer's modification of Fürth and Charnass' method (A., 1927, 800). S. S. Zilva.

Determination of nitrogen in relatively simple compounds. C. O. Appleman, W. E. Loomis, T. G. Phillips, W. E. Tottingham, and J. J. Willaman (Plant Physiol., 1927, **2**, 205—211).—A report of a committee of the American Society of Plant Physiologists. Chemical Abstracts.

Determination of carnosine. W. M. Clifford and V. H. Mottram (Biochem. J., 1928, **22**, 1246—1252; cf. Hunter, A., 1922, ii, 328, 885; 1924, i, 791).—A reinvestigation of Clifford's method of determination of carnosine (A., 1921, ii, 604) shows that the method is accurate to within 1%. The carnosine content of skeletal muscle of a species is constant but varies from species to species. S. S. Zilva.

Determination of small amounts of bismuth in urine and organs. J. Bodnár and A. Karell (Biochem. Z., 1928, **199**, 29—40).—The bismuth is determined colorimetrically in presence of potassium iodide. Since the chloride ion has a detrimental effect the organic matter is ashed in presence of nitric acid. The ash from 20—100 g. of material is heated with 5 c.c. of 10% nitric acid to boiling, to the cooled filtrate and washings are added 6 drops of 1% sodium hydrogen sulphite solution, 3 drops of 1% starch solution (to be certain that the solution contains no free iodine), 2 c.c. of 20% potassium iodide solution, and water to 20 c.c. The yellow colour produced is compared with the standards; 0·02 mg. of bismuth can be determined. J. H. Birkinshaw.

Detection of minute traces of lead in biological material. R. Berg (Biochem. Z., 1928, **198**, 420—423).—The ash after heating with sulphuric acid and igniting is treated with nitric acid and electrolysed, when the lead, as peroxide, is deposited on a platinum wire, acting as the positive pole, which becomes brownish-black. The method detects 0·01 mg. of lead (cf. A., 1922, ii, 659). P. W. Clutterbuck.

Micro-determination of potassium. A. T. Shohl and H. B. Bennett (J Biol. Chem., 1928, **78**, 643—651).—Organic matter is destroyed by incineration with sulphuric acid in presence of hydrogen peroxide; from the hydrochloric acid solution of the ash potassium is precipitated as chloroplatinate; the precipitate is re-dissolved and treated with potassium iodide, the colour of the potassium iodoplatinate formed being determined against standards. Alternatively, the excess of iodide may be titrated with thiosulphate. The error of the method is ±4% for 0·1 mg. and ±2% for 0·4 mg. of potassium. C. R. Harington.