

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

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General, Physical, and Inorganic Chemistry.

Excitation of spectra by atomic hydrogen. F. L. MOHLER (Physical Rev., 1927, [ii], 29, 419—425).—When hydrogen from a Wood discharge tube is passed into a tube containing the metallic vapour, sodium and cadmium strongly emit their first resonance lines, potassium faintly emits the first resonance doublet, mercury gives the complete hydride spectrum and faint emission of the line 2537 Å., caesium, magnesium, thallium, and zinc give no line spectra. Atomic hydrogen is evidently formed, but it is considered that two atoms cannot radiate away the energy of recombination, the presence of a third substance being necessary. A three-body collision of two hydrogen atoms and a metal atom may accomplish this, with excitation of the metal atom, or a metal hydride may first be formed, yielding a hydrogen molecule and an excited metal atom in a two-body collision with a hydrogen atom.

A. A. ELDRIDGE.

Relativistic fine structure of spectral lines. F. PASCHEN (Ann. Physik, 1927, [iv], 82, 689—696).—Leo (this vol., 82) found the value 0.3459 cm.^{-1} for $\Delta_{\nu H}$ for the 4686 He II line, whereas on the basis of Sommerfeld's theory the value 0.3647 cm.^{-1} was to be expected, and is now actually observed within the limits of error. The author's earlier measurements (Ann. Physik, 1916, [iv], 50, 913) are shown to be in agreement with theory in regard to wave-length. Leo's work with reference to the 3203 line is discussed.

R. A. MORTON.

Some infra-red spectra. H. G. SMITH and (MISS) M. E. WESTMAN (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 323—325).—The spectrum of beryllium has been studied from 4000 to 10,500 Å. and that of gold from 7000 to 10,500 Å., using a spark source. Some new air lines of wave-length greater than 8000 Å. have also been observed.

R. CUTHILL.

Structure of arc spectra of germanium and carbon. J. C. McLENNAN and A. B. McCLAY (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 355—363).—The Ge I spectrum has been analysed from the point of view of the Heisenberg-Hund theory by the method previously described (A., 1926, 874), and its structure found to be similar to those of the arc spectra of silicon, tin, and lead, as Bohr's arrangement of the periodic table would require. The C I spectrum is also apparently of the same type.

R. CUTHILL.

Spectrum of the third order of oxygen. C. MIHUL (Compt. rend., 1927, 184, 874—875; cf. this vol., 177).—Five new multiplets, (${}^3D' - {}^3P'$), (${}^3D' - {}^3D$), (${}^3D - {}^3D'$), (${}^3P' - {}^3D'$), and (${}^3P' - {}^3P$), have

been discovered in the third order spectrum of oxygen, and are described.

J. GRANT.

Red and blue argon spectra in extreme ultra-violet. H. B. DORGELO and J. H. ABBINK (Z. Physik, 1927, 41, 753—768).—The red and blue spectra of argon between 1800 and 400 Å. have been examined with a vacuum spectrograph. The results are discussed in relation to theory and to other experimental results.

W. E. DOWNEY.

Measurements of the *P.D.* between the positive strata [in a discharge tube] of argon and neon. F. M. PENNING (Z. Physik, 1927, 41, 769—774).—The *P.D.* between stationary positive strata in argon and neon is almost independent of the pressure of the gas and of the current strength. The value of the difference for argon was found to be 11.9 volts, approximately the excitation potential of the 1s state, whilst for neon it is 18.5 volts, approximately the excitation potential of the 2p state. The *P.D.* between moving positive strata in argon is proportional to the current strength.

W. E. DOWNEY.

Spectrum of doubly-ionised scandium. S. SMITH (Proc. Nat. Acad. Sci., 1927, 13, 65—67).—Twelve lines between 730 and 4070 Å. in the Sc III spectrum are given, together with their intensities, wave-numbers, separations, and term combinations. Assuming for $4F$ the value 62,570, which is suggested by the values of the $4F$ terms of K I and Ca II, term values have been calculated. It is concluded that the lines 2012 and 1993 Å., which were considered by Gibbs and White (A., 1926, 1185) as $4^2P_{1,2} - 5^2S_1$, together with the line 2011, form a triplet in which the line 2012 is the satellite of the strongest member 2011. The triplet at 2011 is considered to be the first normal member of the diffuse series of Sc III.

J. S. CARTER.

Multiplets in two-electron systems of the first long period. R. C. GIBBS and H. E. WHITE (Physical Rev., 1927, [ii], 29, 426—432).—Multiplets appearing when an electron in a $4p$ orbit jumps to a $4s$ orbit in the presence of another valency electron in a $3d$ orbit have been observed for V IV and Cr V, and the wave-lengths of the lines have been measured. The regular and irregular doublet laws hold fairly accurately for two-electron systems when one of the electrons jumps between two orbits, p and s , having the same total quantum number.

A. A. ELDRIDGE.

Spark spectrum of copper (Cu II). A. G. SHENSTONE (Physical Rev., 1927, [ii], 29, 380—390).—The spark spectrum of copper consists of a set of

terms 3D and 1D from the electron structure (d^9s), the letters denoting the k -values of the orbits and the indices the numbers of electrons, only the last eleven being given, since the others remain in closed groups; a set 3P , $^3D'$, 3F , 1P , $^1D'$, 1F due to the configuration (d^9p); a set 3D , 1D , from the configuration (d^9s), the notation indicating that the s -electron is in an excited level; and probably 1S (d^{10}). All but the last have been identified. The value of 1S is about 22,224 wave-numbers lower than 3D_3 . A comparison is made with corresponding terms in Ni I and Pd I. An ionisation potential for Cu II is computed to be about 20.5 volts.

A. A. ELDRIDGE.

Arc spectrum of zinc. N. K. SUR (Z. Physik, 1927, 41, 791—793).—The absorption spectrum of zinc measured by Zumstein (A., 1926, 453) is explained in terms of Hund's theory of spectra.

W. E. DOWNEY.

Spectra of doubly-ionised gallium and indium. K. R. RAO (Proc. Physical Soc., 1927, 39, 150—160).—Investigation of the second spark spectra of indium and gallium has been extended for long wave-lengths. The spark spectra of the elements in hydrogen and in air under different conditions of excitation were studied, and lines corresponding with the second series in the spectra of doubly-ionised indium and gallium identified. The results obtained are in excellent accord with the quantum theory of spectral line emission.

C. J. SMITHELLS.

Spectrum of ionised tin (Sn III). K. R. RAO (Proc. Physical Soc., 1927, 39, 161—168).—A search for regularities in the spectrum of Sn III has been made. Varying conditions of excitation revealed a strong triplet at 5100. The detection of two more triplets confirms this identification. A member of the first fundamental series was also found with the aid of the corresponding members in In II and Ga II (see preceding abstract).

C. J. SMITHELLS.

Arc and spark spectra [of yttrium, zirconium, lanthanum, cerium, neodymium, and beryllium] in the lower quartz spectral region. (Miss) M. C. McDONALD, (Miss) E. E. SUTTON, and A. B. MCLAY (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 313—322).—The arc and spark spectra of the above elements in the region between 1850 and 2300 Å. have been investigated and the results tabulated. Most of the important wave-lengths are apparently in the visible region of the spectrum. R. CUTHILL.

Arc and spark spectra of rare elements in the fluorite region. J. C. McLENNAN and M. J. LAGAKT (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 377—383).—The arc and spark spectra of yttrium, niobium, lanthanum, cerium, neodymium, praseodymium, beryllium, scandium, and gold in the fluorite region have been investigated and the results obtained tabulated.

R. CUTHILL.

Flash arc spectrum of caesium. F. H. NEWMAN (Phil. Mag., 1927, [vii], 3, 843—848).—With an applied potential of 100 volts and at a pressure less than 10^{-4} mm., an intermittent arc could be struck between caesium-coated iron electrodes. The radiation obtained contained none of the iron lines, and in

addition to the ordinary arc spectrum of caesium showed 149 lines between 6648 and 2267.8 Å. All these lines, with the exception of those at 6648, 6078, 5845, 5664, 5102, 5086, 4622 Å., and some very faint lines are included in the induction spectral lines observed by Dunoyer (A., 1922, ii, 729). The spectrum also includes all the lines found by Mohler (A., 1926, 877) to be excited at 24 volts. The flash arc spectrum can be divided into two groups. The first group extends from 5400 to 3780 Å., contains practically all the first spark spectral lines, and has an optical centre at 4350 Å. It is much more intense than the second group, which extends from 3700 to 2268 Å., and contains many lines of a second spark spectrum found by Mohler to be excited between 40 and 80 volts. The two groups are analogous to the two different types of xenon arc spectra, and point to a similarity in structure between the singly-ionised caesium and the normal xenon atoms.

A. E. MITCHELL.

Fine structure of the spark spectrum of caesium. A. FILIPPOV and E. GROSS (Z. Physik, 1927, 42, 77—80).—The fine structure of the following caesium lines has been determined: 5371, 5274, 5249, 5227, 4953, 4830, 4604, and 4527 Å.

R. W. LUNT.

New lines in the arc spectrum of europium at normal pressure between 3100 and 2200 Å. S. PIÑA DE RUBIES (Anal. Fis. Quím., 1927, 25, 47—51; cf. this vol., 82).—A description of the arc spectrum of europium at normal pressure between the above limits, including some new lines.

G. W. ROBINSON.

Arc spectrum of gadolinium. Measurements made at normal pressure between 3100 and 2200 Å. S. PIÑA DE RUBIES (Compt. rend., 1927, 184, 593—596).—A list of 250 new lines found in the arc spectrum of gadolinium oxide is given, with their intensities.

J. GRANT.

Radiations of mercury, krypton, and xenon from the point of view of their meteorological applications. A. PÉRARD (Compt. rend., 1927, 184, 681—683; cf. this vol., 285).—Exact measurements of the wave-lengths of the most intense rays in the spectra of mercury, krypton, and xenon have been made with the object of enabling them to be used for meteorological purposes. Correction curves have been constructed as for neon and helium (*loc. cit.*). The wave-lengths measured (in m μ) are as follows: mercury, 435-8325, 491-60686, 546-07430, 576-95996, 579-06638; krypton, 557-02892, 587-09154; xenon, 462-4275, 467-1225, 473-4154. For xenon, the rays were feeble, and situated in a portion of the spectrum to which the eye is insensitive. J. GRANT.

Arc spectrum of lead. N. K. SUR (Phil. Mag., 1927, [vii], 3, 736—739).—An explanation of the arc spectrum of lead from the point of view of Hund's theory of complex spectra.

A. E. MITCHELL.

X-Ray spectrometer with which wave-lengths are read directly on an ordinary micrometer screw. W. W. NICHOLAS (J. Opt. Soc. Amer., 1927, 14, 61—70; cf. A., 1926, 215).—The accuracy and some details of construction of the instrument are discussed.

L. F. GILBERT.

Selective displacement of 0.0153 Å. in X-ray spectral lines. III and IV. F. H. LORING (Chem. News, 1927, 134, 130—131, 193—194).—III. Explanatory.

IV. In view of the different values recorded for the Cu $K\beta_1$ line, revised tables have been prepared showing the deviations of certain X-ray spectral lines of a number of the elements from the values calculated on the basis of a selective displacement of 0.0153 Å., or a multiple of this, from a standard α -value (cf. this vol., 87, 287). M. S. BURR.

Chemical constitution and K absorption spectra. IV. Chloro-compounds. O. STELLING (Ber., 1927, 60, [B], 650—655; cf. A., 1924, ii, 139; 1925, ii, 935, 936).—Determinations are recorded of the X-ray K absorption spectra of lithium, sodium, potassium, rubidium, caesium, cuprous, silver, ammonium, magnesium, calcium, strontium, barium, manganese, ferrous, nickel, cerium, cobalt, and cupric chlorides, of a series of cobalt and chromium amines, and of the chlorates and perchlorates of sodium and potassium. Attention is directed to the characteristic effect of water of crystallisation and to the different action of ionic and non-ionic chlorine. The results are interpreted in accordance with the deformation theory. H. WREN.

Intensity dissymmetry for the Stark effect in hydrogen. R. WIERL (Ann. Physik, 1927, [iv], 82, 563—575).—The long-wave and short-wave components in the hydrogen Stark effect exhibit intensity differences which are reversed when the field is reversed both with moving hydrogen particles and with "stationary" hydrogen excited by means of nitrogen canal-rays. In the same field, the intensity difference of the components in the "stationary" emission is the reverse of that found in the "moving" light. To explain these results, it is assumed that the emission centres of the long-wave and short-wave components are on different sides of the nucleus of the atom and that the orientation depends on the electric vector. The components of the emission from retarding hydrogen are symmetrically resolved in the field, and although unequal intensities are observed if the canal ray is projected in nitrogen in a direction transverse to the field, a symmetrical resolution is obtained if the last few mm. of its trajectory occur in a high vacuum. R. A. MORTON.

Intensity dissymmetry for the Stark effect in hydrogen. F. G. SLACK (Ann. Physik, 1927, [iv], 82, 576—584).—An explanation of Wierl's work (preceding abstract) in terms of Schrödinger's wave-mechanics. R. A. MORTON.

Ionisation and resonance potentials in gallium and indium. C. W. JARVIS (Physical Rev., 1927, [ii], 29, 442—450).—Ionisation potentials (probably ± 0.5 volt) were observed in gallium vapour at 5.8 and 13.2 volts, and in indium vapour at 6.3 and 14.1 volts. Critical potentials below ionisation were observed in gallium vapour at 3.07, 4.22, 2.70, and 3.8 volts, and in indium vapour at 0.30, 3.03, 4.07, and 2.8 volts. A. A. ELDRIDGE.

Relation between ionisation potential and certain physico-chemical properties. N. PERRAKIS

(J. Chim. phys., 1927, 24, 120—128).—The ionisation potential varies approximately inversely with the atomic radius, and thus also inversely with the cube root of the atomic volume, since the work required to remove the valency electron will diminish as its distance from the nucleus increases. A marked periodic relationship also exists between the ionisation potential and the atomic number; this also applies to the "atomic number" of some compounds, since hydrogen chloride, hydrogen bromide, and hydrogen iodide have ionisation potentials which are identical respectively with those of argon, krypton, and xenon, in agreement with the respective identity of atomic numbers. With the rare gases and oxygen and nitrogen, the ionisation potential diminishes as the critical temperature and pressure increase, since the work required to remove an electron decreases as the gas becomes further removed from the ideal state. For the same gases, the ionisation potential $V = 28.57e^{-0.07147T}$, where T is the b. p. on the absolute scale, whilst for elements boiling between 200° and 2200° Abs., the relationship between T and V is linear. For elementary gases of n atoms per molecule, each having an ionisation potential V_i , the molecular ionisation potential V_m (i.e., the P.D. necessary to remove one optical electron from the molecule) is given by $V_m = nV_i - D$, where D is the dissociation potential for the molecule.

S. J. GREGG.

Photo-electric ionisation of mercury vapour. F. G. HOUTERMANS (Z. Physik, 1927, 41, 619—635).—The ionisation of saturated mercury vapour in the temperature range 19—170° (0.002—5 mm.) varies as the square of the intensity of the exciting radiation for the line 2537 Å. In the temperature range 65—150°, the addition of hydrogen greatly reduces the ionisation, the reduction being approximately 50% for a partial pressure of 10⁻² mm. of hydrogen. The results are held to demonstrate a linear relationship between the ionisation and the number of mercury atoms in the 2³P₀ state. R. W. LUNT.

Photo-electric properties of thoroughly out-gassed platinum. L. A. DUBRIDGE (Physical Rev., 1927, [ii], 29, 451—465).—The photo-electric emission from platinum foil heated at 1200—1400° at 10⁻⁸ mm. decreased to a minimum value which could not be further reduced; this value is characteristic of the gas-free platinum. The long wavelength limit reached a final steady value of 1958 \pm 15 Å. The photo-electric effect is independent of the temperature only in the region below 500°. At higher temperatures up to 1200°, the photo-electric currents increase with rise of temperature, and the threshold shifts slightly towards the red. A. A. ELDRIDGE.

Photo-electric emission, thermionic emission, and Peltier effect from the point of view of dual electric conduction. E. H. HALL (Proc. Nat. Acad. Sci., 1927, 13, 43—46).

Comparison of the thermionic and photo-electric work functions for clean tungsten. A. H. WARNER (Proc. Nat. Acad. Sci., 1927, 13, 56—60).—The thermionic and photo-electric work functions for clean tungsten are identical within the experimental error. J. S. CARTER.

Electron scattering in helium. E. G. DYMOND (Physical Rev., 1927, [ii], 29, 433—441).—The velocity and angular distribution of electrons scattered by single collisions in helium have been measured. For initial velocities of not less than 100 volts, the principal energy loss is due to the excitation of the 2^1S state, corresponding with 20.5 volts. For still higher velocities, the energy change probably ceases to be quantised. A. A. ELDRIDGE.

Energy loss of slow electrons in collisions with molecules. W. HARRIES (Z. Physik, 1927, 42, 26—42).—An apparatus is described in which determinations with an estimated accuracy of 3% have been made of the energy loss suffered by electrons, of a velocity corresponding with 5.2 volts, in collisions with gas molecules. For a hundred collisions, the values 0.26 and 0.83 volt have been obtained for the energy loss in nitrogen and carbon monoxide, respectively. The values correspond with the absorption of one vibration quantum in 110 collisions in nitrogen, and with 31 in carbon monoxide; this result is to be anticipated from the fact that carbon monoxide has an electric moment and nitrogen has none. R. W. LUNT.

Cluster-formation in gas ions. W. BUSSE (Ann. Physik, 1927, [iv], 82, 697—712).—A detailed reply to Nolan's criticisms. R. A. MORTON.

Potential gradient in the positive column of the glow discharge. I. Nitrogen, hydrogen, neon. A. GÜNTHER-SCHULZE (Z. Physik, 1927, 44, 718—736).—The usual methods of examining the connexion between the gradient in the positive column of a glow discharge and the pressure of the gas fail to show any law. The two quantities are not connected. The mean free path l is taken as the variable, and is calculated from the measured pressure and from the partly measured, partly calculated rise in temperature of the discharge space. It is found, for a glow discharge in nitrogen or hydrogen, for constant l , that the gradient is independent of the current strength. In neon, for higher current densities, the gradient slightly decreases for increasing current strength. The equation, gradient $= Cl^{m-1}/r^m$, where r is the radius of the tube, deduced on theoretical grounds, applies to all three gases. For nitrogen and hydrogen, $m = \frac{1}{2}$; for neon, $m = 1$. Thus, for neon the gradient is independent of both l and the gas pressure. The relations between potential gradient and r agree with the equation, gradient $= C/r$, which Schottky deduced from his theory of the ambipolar diffusion of the positive column. The relationship fails, first, with decrease of gas pressure when the mean free path is large compared with the diameter of the tube, so that the diffusion law no longer holds, and, secondly, when the pressure is so great that the positive column detaches itself from the walls of the vessel and becomes an independent tube or thread-like structure. Thus, the law applies between the same pressure limits as give a true glow discharge. W. E. DOWNEY.

Effect of velocity distribution on the deflexion of atoms in an inhomogeneous magnetic field. W. H. RODEBUSH (Proc. Nat. Acad. Sci., 1927, 13, 50—52).

Definition of an element according to the International Commission on Chemical Elements. G. URBAIN (Bull. Soc. chim. Belg., 1927, 36, 124—136).—A *résumé* of the discoveries which in 1923 led the International Commission to define an element in terms of an atomic number. J. S. CARTER.

Density of boron trichloride and the suspected variation in the atomic weight of boron. H. V. A. BRISCOE, P. L. ROBINSON, and H. C. SMITH (J.C.S., 1927, 282—290).—The densities of samples of boron trichloride derived from different sources have been determined by the method of calibrated glass floats (A., 1926, 771). The boron trichloride in each case was the same as that used in the determination of the ratio $BCl_3 : 3Ag$ (A., 1925, ii, 346), and was subjected to further purification. The densities so determined reveal a real difference of approximately 0.01 in the mean atomic weights of boron from California and from Asia Minor. W. E. DOWNEY.

Constitution of mercury derived from coal tar. F. W. ASTON (Nature, 1927, 119, 489).—Mercury obtained from coal tar, where it is present in the lightest fractions, gives isotopic lines indistinguishable from those of ordinary mercury. A. A. ELDRIDGE.

Straggling of α -particles from radium-C. G. H. BRIGGS (Proc. Roy. Soc., 1927, A, 114, 313—340).—By means of the magnetic deflexion method, measurements have been made of the distribution of the velocities for α -particles from radium-C after passing through sheets of mica of varying thickness. The stopping power of the mica, measured by the scintillation method and expressed as the air equivalent, ranged from 0.315 to 5.056 cm. The distribution of density in the deflected and undeflected bands produced on a photographic plate was measured with a microphotometer, applying the null method of Dobson and measuring the density directly in terms of a neutral grey wedge; results are given for emergent velocities from 0.98 to 0.22 V_0 . The distribution of energies on emergence is very approximately Gaussian in form, as indicated by Bohr's theory of the phenomenon. From the data for the energy distribution, it is shown that the straggling of the ranges can be calculated at any point in the region investigated, and the contribution to the total straggling of various parts of the range can be determined. It is found that the straggling is proceeding at a maximum rate near the beginning of the range, half the total occurring in the first 2.4 cm. It is everywhere found to be about 1.4 times that predicted by Bohr's theory. This indicates that for a small element of path, ΣQ^2 , where Q is the energy transferred to an electron, is approximately twice as great as in Bohr's theory. The experimental and theoretical results are compared, and it is suggested that the simplest explanation which accounts for the discrepancy between theory and experiment is that the large transfers of energy from the α -particles to the electrons, which account for nearly all the straggling, occur twice as frequently as predicted by Bohr's theory of the stopping of α -particles. L. L. BIRCUMSHAW.

Decrease in velocity of α -particles from radium-*C*. G. H. BRIGGS (Proc. Roy. Soc., 1927, A, 114, 341—354; cf. preceding abstract).—Using the apparatus employed in the investigation of the straggling of α -particles in radium-*C* (*loc. cit.*), data can be obtained on the photographic plates from which the mean value of V/V_0 for the beam of α -particles can be calculated. The values of V/V_0 , over a range of velocity from 0.98 to $0.22V_0$, have been deduced from values of r/r_0 (r being the radius of curvature of the path), which were calculated from the appropriate formula for the deflexion in terms of r and the dimensions of the apparatus. For velocities less than $0.55V_0$, the decrease in velocity was much more rapid than that found by Marsden and Taylor (*ibid.*, 1913, A, 88, 443), but was in good agreement near the end of the range with the results found by indirect methods by Kapitza (*ibid.*, 1924, A, 102, 48) and by Curie (A., 1925, ii, 834). The ratio λ_2/λ_1 of the number of singly- to doubly-charged α -particles at various velocities is given by the ratio of the areas of the density curves of the corresponding bands, and from the values obtained it is deduced that $\lambda_2/\lambda_1 = 5.3 \times 10^{-3} V^{-4.3}$. The homogeneity of the initial velocities of the α -particles was also investigated by means of the same apparatus. No evidence was found of velocities greater than the average by more than 1 in 3000. Velocities of less than the maximum were present, probably due to absorption in the source.

L. L. BIRCUMSHAW.

Relation between the atomic weight of the isotopic radio-elements and the speed of the α -particles they emit. G. FOURNIER (Compt. rend., 1927, 184, 878—880).—If the atomic weights (A) of the isotopic radio-elements are plotted as a function of the speeds of the α -particles they emit (v), all the points (except that of polonium) fall on five parallel straight lines, each of which corresponds with a determined atomic number, *i.e.*, with a group of isotopes. Thus, the speeds of the α -particles decrease proportionally with their atomic weights to the same extents for the different isotopic groups. This is expressed by the relation $v = v_0 - kA$, where v_0 varies with the group of isotopes and k is a constant. An atomic weight of 227 is indicated for actinium, which is probably derived from an isotope of uranium ($A = 239$). Possibly v depends on the force existing between the α -particle and the layer from which it is emitted.

J. GRANT.

Passage of α -rays and β -rays through matter. E. J. WILLIAMS (Nature, 1927, 119, 489—490).—Much of the discrepancy between the results of the application of classical mechanics to the calculation of possible energy transfers during encounters between the moving particle and the atomic electrons and the corresponding experimental results disappears when the motion of the atomic electrons is allowed for. For primary ionisation in hydrogen, the values agree to within 5%. A corrected value for the stopping power is given.

A. A. ELDRIDGE.

Relative intensities of the groups in the magnetic β -ray spectra of radium-*B* and radium-*C*. C. D. ELLIS and W. A. WOOSTER (Proc. Roy. Soc., 1927, A, 114, 276—288).—Previous work

on β -ray spectra of radioactive substances has been concerned almost entirely with the energies of the individual groups forming the spectra, but many important questions are connected with relative intensities. These have been measured for radium-*B* and radium-*C* by photometric measurement of the density of the lines recorded photographically by the standard focussing method. Intensities of the groups in the two spectra are measured on the same scale, and refer to equal numbers of disintegrating atoms. It is found that the ratio of the intensities of the groups due to conversion of the same frequency γ -ray in the *K* and *L* levels is independent of the frequency and approximately equal to that occurring in the ordinary external absorption of X-rays. The bearing of this result on the mechanism of emission of the groups is discussed. From Gurney's measurements of the number of electrons in the stronger groups of radium-*B* and radium-*C* (A., 1926, 5), the numbers of electrons in the other groups are deduced.

L. L. BIRCUMSHAW.

Ionising powers of radium-*B* and radium-*C*. H. JEDRZEJOWSKI (Compt. rend., 1927, 184, 596—598).—The ratio of the amounts of radium-*B* and radium-*C* in an active deposit of radium is constant when these are in equilibrium with the radon, but varies with the time when they are separated from it. A formula is deduced for the determination of the percentage, due to each of these constituents, of the total ionisation produced by γ -rays from such a deposit. The method has been confirmed by measurements of the ionising power of the deposit when that due to radium-*B* is excluded by lead screens. A table also is given for the decrease in ionising power when screens of increasing thicknesses of aluminium are used. The action of the γ -rays of radium-*B* cannot be detected through aluminium screens more than 60 mm. thick.

J. GRANT.

Discoloration and luminescence due to Becquerel rays. II. K. PRZIBRAM (Z. Physik, 1927, 41, 833—847; cf. A., 1924, ii, 85).—The discoloration produced in various salts of the alkali metals when exposed to β - and γ -radiations is discussed at length from the point of view of the author's theory (*loc. cit.*). Following an account of the effect of pressure on these phenomena, an equation, involving four constants, is developed relating the absorption coefficient (assumed proportional to the density of neutral atoms produced by the radiation) with the intensity of the radiation and the time of exposure. By a suitable choice of constants, this equation can be used to represent the data of Bělař on the coloration produced in rock-salt; for a constant intensity, the coloration increases logarithmically with the time to a limiting value. Data are tabulated referring to the coloration, the absorption maximum, and the stability of the coloration of the hydrides and halides of sodium, potassium, rubidium, and caesium.

R. W. LUNT.

Experiments to test the possibility of transmutation by electronic bombardment. M. W. GARRETT (Proc. Roy. Soc., 1927, A, 114, 289—292; cf. A., 1926, 1015).—Negative results were obtained in an attempt to transmute tin into indium in a

quartz tube apparatus with sealed-in tungsten leads similar to that used with mercury (*loc. cit.*). It was found impossible to obtain tin free from all traces of indium, the most persistent line in the spectrum being the 4102. Unsuccessful attempts were made to transmute titanium into scandium by bombardment in a vacuum with high-speed electrons capable of penetrating the innermost electronic orbits of the titanium atom.

L. L. BIRCUMSHAW.

Existence of sub-electrons. F. EHRENFHART (*Z. Physik*, 1927, 41, 708—709).—A reply to Mat-tauch's criticism (this vol., 87) of the author's paper (*A.*, 1926, 880).

R. W. LUNT.

The Main Smith-Stoner scheme of atomic orbits. M. N. SABA and B. B. RAY (*Physikal. Z.*, 1927, 28, 221—225).—Theoretical. A combination of Bohr's scheme of atomic orbits with Pauli's principle of electron-orbit synthesis gives better agreement with experimental results than those obtained by the use of the scheme of Main Smith and Stoner.

W. E. DOWNEY.

Atomic number and atomic structure. G. PICCARDI (*Atti R. Accad. Lincei*, 1927, [vi], 5, 169—174).—It is suggested that the difference between the atomic weight and twice the atomic number in the higher elements is to be attributed to a neutral zone of protons and electrons exterior to the nucleus, and therefore relatively easily detached. Attempts are made on this basis to explain the occurrence of hydrogen in positive-ray apparatus, and in the experiments of Rutherford and Chadwick.

R. W. LUNT.

Quantum theory of the emission and absorption of radiation. P. A. M. DIRAC (*Proc. Roy. Soc.*, 1927, A, 114, 243—265).—The problem is considered of an assembly of similar systems satisfying the Einstein-Bose statistics, which interact with another different system, a Hamiltonian function being used to describe the motion. The theory is applied to the interaction of an atom with an assembly of particles moving with the velocity of light, and it is shown that it gives Einstein's laws for the emission and absorption of radiation. The interaction of an atom with electro-magnetic waves is also considered, and it is shown that by taking the energies and phases of the waves to be q -numbers satisfying the proper quantum conditions instead of c -numbers, the Hamiltonian function takes the same form as in the light-quantum treatment. The theory gives the correct values for Einstein's A 's and B 's.

L. L. BIRCUMSHAW.

Theoretical prediction of physical properties of many-electron atoms and ions. Mole refraction, diamagnetic susceptibility, and extension in space. L. PAULING (*Proc. Roy. Soc.*, 1927, A, 114, 181—211).—The wave mechanics of Schrödinger provides an atomic model which suggests that the method of treatment used to evaluate the screening constant s_0 (*cf.* this vol., 88) can be adapted to derive theoretical values of screening constants to be used in the equations representing the mole refraction or polarisability, diamagnetic susceptibility, extension in space, and other properties of atoms and monatomic ions. In following this procedure, the

assumption is made that the nuclear charge is large in comparison with that of an electron shell. Since this requirement is not fulfilled by actual atoms and ions, an empirical correction is introduced, obtained from a consideration of the mole refraction and mole refraction-screening constant of the rare gases and of some ions in aqueous solution. Theoretical values are thus obtained for the mole refraction and diamagnetic susceptibility of a large number of atoms and ions, the values being in good agreement with such experimental data as are available. A third screening constant is also evaluated, which permits the calculation of the electronic distribution in atoms and ions and the determination of inter-atomic distances. It is shown in this connexion that the study of the diffraction of X-rays by crystals provides a method for the direct experimental verification of the form of Schrödinger's *eigen* functions. It is stated that the general method followed in this communication is capable of refinements which should render possible the accurate prediction of the properties of any atom or ion.

L. L. BIRCUMSHAW.

Ionised hydrogen molecule and [Schrödinger's] wave mechanics. W. ALEXANDROV (*Ann. Physik*, 1927, [iv], 82, 683—688).—An extension of previous work (this vol., 5).

R. A. MORTON.

Radiation and the photo-electric effect. F. H. LORING (*Chem. News*, 1927, 134, 129—130).—An extension of some theoretical considerations on the fundamental ideas of radiation.

R. A. MORTON.

Spinning electron in wave mechanics. A. CARRELLI (*Nature*, 1927, 119, 492—493).—Mathematical.

A. A. ELDRIDGE.

Structure of an atom of nitrogen. H. COLLINS (*Chem. News*, 1927, 134, 209—212, 273—277).—Speculative.

Photographic method of spectrophotometry in the red and infra-red. A. L. SCHOEN (*J. Opt. Soc. Amer.*, 1927, 14, 179—186, and *Z. wiss. Phot.*, 1927, 24, 326—336).—A method is described which permits the use of suitable photographic plates for spectrophotometric measurements throughout the range 200—900 $m\mu$.

L. F. GILBERT.

Electronic states and band spectrum structure in diatomic molecules. III. Intensity relations. R. S. MULLIKEN (*Physical Rev.*, 1927, [ii], 29, 391—412).—The correspondence principle predicts definite intensity relations for P , Q , and R band lines in molecules having a rotational energy term $F(j) = B(j^2 - \sigma^2) + \dots$, provided σ is an electronic quantum number correlated with a precession about the inter-nuclear axis (along which the angular momentum $\sigma h/2\pi$ is directed). Hönl and London's equations for the three possible cases $\Delta\sigma = 0, \pm 1$, have been altered in form. Theoretical and experimental results are in qualitative agreement for various electronic emission bands, and for oscillation-rotation absorption bands corresponding with $\sigma' = \sigma'' = 0$.

A. A. ELDRIDGE.

Bands in the secondary spectrum of hydrogen. H. S. ALLEN and I. SANDEMAN (*Proc. Roy. Soc.*, 1927, A, 114, 293—313; *cf.* *A.*, 1925, ii, 909).—The band with head at 4582.58 Å., comprising a P , Q , and R combination, which was described in

a previous communication (*loc. cit.*) and attributed to triatomic hydrogen, has been found to be one of a large number of similar bands. These bands occur in groups, the bands of a group being spaced out at intervals of about 92 wave-numbers, the spacing being in some cases approximately constant and in others conforming to a quadratic law. The bands are found both in the range of wave-lengths measured by Merton and Barratt (A., 1922, ii, 461) and by Tanaka (A., 1925, ii, 909), and also in the infra-red region investigated by Allibone (A., 1926, 873). Two groups occurring in the latter region have been considered in detail. Experiment has shown that in some cases the lines of the group are enormously enhanced in the spectrum of the arc in hydrogen at higher pressures. The bands must originate in molecules with large moments of inertia, and other considerations are advanced which support the view that they are due to triatomic hydrogen.

L. L. BIRCUMSHAW.

Structure and origin of the Swan band spectrum of carbon. R. C. JOHNSON (Phil. Trans., 1927, A, 266, 157—230).—The Swan band spectrum has been studied both experimentally and theoretically. The sources used were a carbon arc burning in hydrogen and the discharge through a vacuum tube containing traces of carbon gases and filled with 20—50 mm. of one of the inert gases. The spectrum was photographed in the second order of a twenty-one foot grating, and about 2000 lines were measured. Eleven bands have been assigned to series and the rotational energy functions evaluated. The moments of inertia and internuclear distances deduced therefrom have values appropriate to an HC-CH molecule. The bands consist each of a *P* and *R* branch typical of a dipolar emitter. The fine structure multiplicity classes the bands as of the Heurlinger triplet type. The distribution of energy among the vibrational states shows the Swan bands to be a high-temperature, non-thermal system. A new band system with its strongest head at 4770 Å. was found associated with the Swan bands.

The analysis of the spectrum points to an HC-CH molecule as the emitter. Experimental evidence is also adduced to show that the earlier view that the Swan bands are due to carbon monoxide is extremely improbable; the fine structure analysis indicates that two carbon atoms are present; the singlet character of the levels classes the Swan emitter as an even-valency electron model; the close analogy to the second positive nitrogen bands (due to neutral N₂ molecule) points to its origin in an HC-CH molecule. It is probable that in the molecule each carbon atom retains its *K*-electrons, which are shared by the CH group and move in 1₁ orbits. Common to the whole molecule is the complete *L*-shell of the four 2₁ electrons and four 2₂ electrons. Outside, but penetrating to between the nuclei, are the two valency electrons in 3₁ orbits. The ground level is 1S, as in the magnesium atom. W. E. DOWNEY.

Spectra excited by active nitrogen. A. E. RUARK, P. D. FOOTE, P. RUDNICK, and R. L. CHENAULT (J. Opt. Soc. Amer., 1927, 14, 17—27).—The facts bearing on the constitution of active nitrogen

are discussed, and it is concluded that the balance of evidence is in favour of the older view that the active gas is composed of neutral unexcited atoms, and not, as has been recently suggested, of excited diatomic molecules. Full references are given, and the following new facts adduced. (1) Active nitrogen has no absorption spectrum between 6500 and 3200 Å.; absorption in this region would be expected from an activated molecule, but not necessarily from an atom. (2) Mercury atoms can receive at least 10 volts energy from active nitrogen. This energy corresponds with the lower limit for the heat of association of two nitrogen atoms. It was also observed that the usual intensity rules for the mercury multiplets do not hold for after-glow spectra; and two new bands of the β-system of nitric oxide, near 2400 and 2300 Å., are recorded. The nitrogen was excited by the electrodeless discharge, and an apparatus is described suitable for the introduction of metal vapours into the active gas.

The after-glow spectra of zinc, magnesium, platinum, sodium, cadmium, and thallium, and of silicon and titanium tetrachlorides, are discussed.

S. BARRATT.

Absorption bands of nitrogen. H. SPONER (Z. Physik, 1927, 41, 611—618).—The absorption of nitrogen has been examined in the range 1700—1200 Å. by a vacuum grating spectrograph. Two different band systems are observed, commencing at 1544 and at 1450 Å. The results are discussed at length, with particular reference to the spectra of carbon monoxide and of nitric oxide.

R. W. LUNT.

[Spectrochemistry of compounds containing nitrogen. II.] K. VON AUWERS and W. ERNST (Z. physikal. Chem., 1926, 124, 464).—A concession of priority to Colson (J.C.S., 1917, 111, 554) in the application of spectrochemical methods to the question of the structure of cyanamide (cf. A., 1926, 994), and a correction.

R. CUTHILL.

Rotational terms in the MgH bands. W. W. WATSON and P. RUDNICK (Physical Rev., 1927, [ii], 29, 413—418).—Wave-numbers for the first six branches in the band 5211 Å., to which are assigned the vibrational quantum numbers $n' = n'' = \frac{1}{2}$, are tabulated, together with values of ΔF for initial and final electron levels and several vibrational levels. The Kratzer, Kramers, and Pauli formula is applied.

A. A. ELDRIDGE.

Ultra-violet absorption spectra of nickel, cobalt, and tellurium. J. C. McLENNAN and R. F. B. COOLEY (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 349—353).—The absorption spectra of the vapours of the above elements in the lower quartz and fluorite regions have been examined. In the region 2402—1524 Å., 26 wave-lengths of nickel, and possibly 4 additional ones, were shown to be absorbed by the normal vapour of nickel. Between 2000 and 1448 Å., 15 wave-lengths of the spectrum of cobalt were found to be totally absorbed and 10 partly so by cobalt vapour. Between 2000 and 1650 Å., 11 wave-lengths were found to be absorbed by tellurium vapour.

R. CUTHILL.

Absorption spectra of metallic vapours. J. C. McLENNAN, (MISS) E. COHEN, and M. J. LIGGETT

(Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 365—376).—The absorption spectra of the vapours of manganese, nickel, palladium, platinum, lanthanum, neodymium, praseodymium, and uranium have been mapped between 1450 and 6000 Å. Numerous new lines are recorded. No absorption by the vapour of cerium or thorium could be detected. R. CUTHILL.

Ultra-violet spectrograms of carbohydrates. P. NIEDERHOFF (Z. physiol. Chem., 1927, 165, 130—139).—Ultra-violet absorption curves are given for dextrose, lævulose, galactose, and lactose; sucrose shows no absorption in the ultra-violet. The results are in general agreement with those of Bielecki and Henri (Ber., 1914, 46, 3627). The form of the curve for dextrose suggests the presence of a carbonyl group. C. R. HARRINGTON.

Spectrochemical studies of hydroxyazo-compounds. III. T. UEMURA, N. YOKOJIMA, and T. ENDO (Bull. Chem. Soc. Japan, 1927, 2, 48—51; cf. this vol., 238, 291).—The following substances have been examined spectrochemically, and possess the forms assigned: benzeneazopyrogallol, *A*-form in neutral solution, a mixture of the *A*- and *R*-forms in alkaline solution; *p*-nitrobenzeneazopyrogallol, *A*-form in neutral solution, *R*-form in alkaline solution; benzeneazophloroglucinol, *A*-form in both solutions; *p*-nitrobenzeneazophloroglucinol, *A*-form in neutral solution, *R*-form in alkaline solution.

S. J. GREGG.

Absorption spectra and the constitution of benzene derivatives. IX. Dihydroxybenzaldehydes. Theory of auxochromes. N. VALASCHKO (Ukraine Chem. J., 1926, 2, 183—235).—It has been shown (A., 1910, ii, 1015; 1913, ii, 367) that the isomeric hydroxybenzaldehydes give two types of absorption spectra. These two types consist of the α_1 and α_2 -bands characteristic of benzaldehyde, and the ϕ -band characteristic of phenol. When the hydroxyl group is in the *para* position, a phenolic type of absorption spectrum is produced; in the *ortho* or *meta* positions, the ϕ -line is very weak or is missing, and the spectra of the α -type are produced with a very strong α_2 -band.

Curves of absorption spectra for 2 : 4-, 3 : 4-, 2 : 5-, and 2 : 6-dihydroxybenzaldehydes and their methoxy-derivatives have been compared in aqueous, alcoholic, alkaline, and acid solutions, with the corresponding curves for the hydroxybenzaldehyde derivatives. With the 2 : 4-dihydroxybenzaldehyde derivatives, the α_2 -band is shifted towards the ultra-violet, and is greatly intensified as compared with the corresponding 2-hydroxybenzaldehyde. The ϕ -band in neutral or acid solution is shifted towards the ultra-violet as compared with 4-hydroxybenzaldehyde. In alkaline solution, the band is shifted somewhat towards the red end, whilst its intensification either remains constant or is slightly decreased. Both the neutral and alkaline solutions are colourless. In neutral or acid solution, 3 : 4-dihydroxybenzaldehyde derivatives give α -lines shifted either greatly towards the blue or slightly towards the red, as compared with 3-hydroxybenzaldehyde. In strong alkaline solution, the bands are shifted greatly towards the red and are very much intensified. The ϕ -band is shifted towards the

blue in neutral solution; in alkalis, towards the red, with a great diminution of intensity. 2 : 3-Dihydroxybenzaldehyde derivatives show a great shift of the α_2 -band towards the red, with no change of intensity. The ϕ -band is missing. The alkali solutions of the compounds are lemon-yellow. Derivatives of 2 : 5-dihydroxybenzaldehyde resemble the 2 : 3-derivatives.

On the basis of Auwers' work, (A., 1915, ii, 297) the probable mechanism by which the above results are obtained is discussed, and it is concluded that the various spectra are due to the different kinds of conjugation of the double linkings with the hydroxyl groups. The effects of placing the auxochromes in various positions as compared with the chromophores with regard to the formation of colour are discussed and various corrections to the rules formulated by Kauffmann and Franck (A., 1906, i, 841) are made. Finally, it is suggested that the presence of the three bands can be explained by attributing the α_2 -band to the carbonyl group, the ϕ -band to the phenolic group, and the α_1 -band to the benzene ring.

From the facts that in *o*-hydroxybenzaldehyde the α_2 -band is increased in intensity 120 times, in *m*-hydroxybenzaldehyde 80 times, whilst in *p*-hydroxybenzaldehyde the α_2 - and the α_1 -bands disappear and the ϕ -band is increased 20 times, all the types of absorption spectra for the dihydroxybenzaldehydes can be explained. In the last case, the disappearance of the α_1 -band is attributed to the fact that it has been shifted towards the ultra-violet and is lost in the much stronger ϕ -band. E. ROTHSTEIN.

Excitation of fluorescence in fluorescein. E. H. KENNARD (Physical Rev., 1927, [ii], 29, 466—477).—The fluorescence curves show a maximum at about 5240 Å.; the excitation curve shows a maximum at 5000 Å. for fluorescence at 5270 Å., and at shorter wave-lengths for other points in the fluorescence spectrum. Maximum absorption occurs around 4750 Å. A. A. ELDRIDGE.

Fluorescence of chlorine and of bromine. L. BLOCH and E. BLOCH (Compt. rend., 1927, 184, 744—746).—In the course of experiments on the effect of an oscillating electric discharge on sodium chloride and bromide (this vol., 178), a fluorescence characteristic of the anion of the salt employed has been observed to appear at a particular pressure. Photographs of the spectra have shown that the fluorescence of chlorine consists of groups of channelled bands of complicated structure situated chiefly between 3960 and 4920 Å., those in the middle of the spectrum being most intense. The intense orange fluorescence of bromine yielded 25 bands, similar in structure and arrangement to those of chlorine, between 6400 and 5100 Å. (cf. A., 1926, 884). The phenomena are attributed to the effect of soft X-rays, since the bands of nitrogen, water vapour, and the first and third negative groups of carbon are also present.

J. GRANT.

Intensity distribution in the *D*-line of the chemiluminescence of sodium vapour. R. L. HASCHE, M. PÓLÁNYI, and E. VOGT (Z. Physik, 1927, 41, 583—610).—Measurements of the absorption by sodium vapour of the *D*-line emitted from sodium

vapour, at pressures in the range 5×10^{-4} — 10^{-2} mm., burning in mercuric chloride vapour have shown that the half width of the line varies from 0.055 to 0.08 Å.; this variation is attributed to absorption in the burning mixture. It has also been shown that the broadening of the line so observed is the same as that in the light emitted by sodium vapour at corresponding temperatures and pressures. The mechanism of the reaction is discussed on the basis of these results, and it is concluded that the observed light emission is excited by the vibrational energy of the sodium chloride molecules formed in the reaction.

R. W. LUNT.

Effect of X-rays on thermoluminescence. (Miss) F. G. WICK (J. Opt. Soc. Amer., 1927, 14, 33—44; cf. A., 1924, ii, 714; 1925, ii, 262).—The effect of (a) variation of temperature on the rate of decay of the thermoluminescence of natural specimens of fluorite and calcite, natural specimens after exposure to X-rays, and specimens heated to remove all thermoluminescence before being exposed to X-rays, of (b) time of exposure to X-rays on maximum brightness of thermoluminescence and rate of decay, and of (c) keeping specimens for varying lengths of time after exposure to X-rays before observations were made has been investigated. Specimens of fluorite which were not naturally thermoluminescent became so to a greater or less degree on exposure to X-rays. Crystals which were naturally active had the intensity at a given temperature greatly increased, and many of them acquired, in addition to the luminescence of the original colour, a new and entirely differently coloured luminescence, which flashed up before the thermoluminescence characteristic of the natural crystal appeared. The results suggest a complicated mechanism.

L. F. GILBERT.

Effect of exposure to X-rays on the thermoluminescence of some synthetically prepared materials. (Miss) F. G. WICK and (Miss) M. K. SLATTERY (J. Opt. Soc. Amer., 1927, 14, 125—132; cf. preceding abstract).—Small amounts (0.2—0.4%) of manganese mixed with calcium sulphate induce a green thermoluminescence on exposure to X-rays. The decay of luminescence at 120° is of the "persistent" type (cf. Nichols and Howes, Proc. Nat. Acad. Sci., 1918, 4, 305). The brightness of the maximum after exposure increases linearly with the temperature. Saturation is reached at 260° with an exposure of 1 hr. Synthetic thermophosphors show an increase in activity on keeping a few minutes after exposure. Less energy is stored in a specimen of manganese calcium sulphate if the temperature of exposure is decreased slightly.

L. F. GILBERT.

Ionic mobilities for ion rays. F. KOETHER (Ann. Physik, 1927, [iv], 82, 639—663).—With a large surface and high temperatures the emission of positive ions from salts is reasonably constant. Rutherford's alternating current method leads to mobilities of the order of a few cm. per sec. for the positive ions from silver and cadmium halides over the temperature range 325—425°. An increase of 20° in temperature brings about a roughly two-fold increase in mobility. Greater frequency corresponds with increased mobility, an effect which is connected

with polarisation of the salt at the surface from which ions are being liberated. The mobilities of ions set free by other methods (volume ionisation) are of the order 10^{-2} , 10^{-3} , and the evidence points to charged complexes (cluster-theory) rather than to simple ions as the carriers in this work.

R. A. MORTON.

Ion-rays. G. C. SCHMIDT (Ann. Physik, 1927, [iv], 82, 664—682; cf. A., 1926, 877).—The emission of ion-rays is very sensitive to the presence of impurities. Specially purified lead chloride emits negative ions exclusively, whilst silver chloride, silver iodide, and cadmium iodide emit only positive ions at moderate temperatures. The emission falls off with time, except at higher temperatures. Near the m. p. it is constant. The presence of impurities frequently causes the appearance of a maximum in the time-emission curve, although the occurrence of an emission increasing with time does not necessarily denote impurities. The falling off in the emission of a pure salt is due neither to polarisation of the electrode or of the salt nor to the formation of complexes as a result of sudden cooling. The conductivity of very quickly-cooled salts is greater than that of slowly-cooled salts. The change, although small, is real, and it is therefore inferred that the change in emission of ions is due to a surface effect akin to photo-electric fatigue and passivity.

R. A. MORTON.

Separation of molecular streams in magnetic fields. A. LEU (Z. Physik, 1927, 41, 551—562).—Improvements are described in the technique of Gerlach and Stern. The principal error is thought to arise in the determination of the heterogeneous magnetic field. This measurement has been made by observing the magnetic moment of a bismuth wire in the field; the value so obtained for the susceptibility agrees within 3% of the accepted value, and no error greater than this arises in determining the magnetic moment in a molecular stream. Zinc and cadmium show no separation and have therefore no magnetic moment. A number of determinations have shown that the atoms of sodium and potassium are to be associated with one Bohr magneton (± 3 —4%) and those of thallium with one third of a Bohr magneton (± 4 %).

R. W. LUNT.

Magnetic separation in hydrogen streams. E. WREDE (Z. Physik, 1927, 41, 569—575).—A modification of the technique of Leu (cf. preceding abstract) has been adopted to determine the magnetic separation in a stream of unimolecular hydrogen. Tungstic oxide was found to be most sensitive as a target indicator, but molybdc oxide, silver nitrate, bismuth nitrate, and zinc chloride were also found to be satisfactory, particularly the last, although of slow reactivity. The separation observed corresponds with one Bohr magneton per hydrogen atom.

R. W. LUNT.

Electric double refraction in relation to the polarity and optical anisotropy of molecules. I. Gases and vapours. II. Liquids. C. V. RAMAN and K. S. KRISHNAN (Phil. Mag., 1927, [vii], 3, 713—723, 724—735).—I. An attempt is made to correlate, on the basis of Born's theory of electrical birefringence, the available data on the Kerr effect of gases and vapours with the optical anisotropy

determined from measurements of light scattering and with the polarity of the molecules as determined from measurements of their dielectric constants. With electrically polar molecules, the orienting action of an electrostatic field is found to be due chiefly to the couple exerted on the permanent electric doublet present and to be much larger than would be the case if the molecules were non-polar. With the aid of the simplifying assumptions of Gans (*Ann. Physik*, 1921, [iv], 45, 97) regarding the relationship between the constants of electrical and optical anisotropy, values of the Kerr constant have been calculated for several non-polar molecules from the factor of depolarisation of scattered light. These values are in good agreement with those observed. It is shown that in the case of polar molecules having an axis of optical symmetry, to which the permanent moment is parallel or is inclined at a known angle, it is possible to calculate the value of the moment from the Kerr constant and the depolarisation constant. Such calculations have been made for hydrogen chloride, methyl chloride, and ethyl chloride molecules. The value for the hydrogen chloride molecule is in exact agreement with that obtained by Zahn from dielectric constant measurements. Alternatively, if the value of the moment is known, its direction can be calculated from the same data, and the applicability of the method to simple benzene derivatives is indicated. The significance of the negative value of the Kerr effect in the case of di- and trichloromethane and the positive value in the case of monochloromethane is discussed, and is shown to be in agreement with Born's theory.

II. The work has been extended to an examination of the Kerr effect in liquids. As in the case of vapours, all the compounds exhibiting large Kerr effects are electrically polar. The influence of the polarity on the magnitude of the Kerr effect is greater in liquids than in vapours. In the case of non-polar molecules, the moments induced in the molecules by an external electrostatic field are sufficient to account for the observed double refraction. In the case of liquids where sufficient data are available, the observed Kerr constant is in numerical agreement with that calculated on the basis of Born's theory. The theory is supported also by the available measurements on the variation of the electrical birefringence of liquids with temperature.

A. E. MITCHELL.

Electric double refraction of benzopurpurin. T. WEREIDE (*Z. Physik*, 1927, 41, 857—863).—The electric double refraction of aqueous solutions of benzopurpurin (wt. concentration $5.9-95 \times 10^{-6}$) increases less rapidly than the concentration, and is diminished by high concentration of electrolytes.

R. W. LUNT.

Electrical anisotropy of crystalline liquids. M. JEZEVSKI (*Bull. Acad. Polonaise*, 1926, A, 263—271).—See this vol., 92.

Magnetic rotation of solutions of certain ferric salts. (MISS) C. E. RICHARDS and R. W. ROBERTS (*Phil. Mag.*, 1927, [vii], 3, 770—784).—As previous work (A., 1925, ii, 478) on the magnetic rotatory dispersion of certain solutions of nickel and cobalt had shown that in order to obtain effects character-

istic of the solute it was necessary to take into account the rotation due to the solvent, an extension has been made to solutions in which the paramagnetic rotation due to the ions in solution preponderates over the diamagnetic rotation of the solvent. With ferric sulphate solutions, whilst the rotation of the solution is positive, the effect due to the salt is distinctly negative. The rotatory dispersion curve indicates the presence of at least two absorption bands, one at 0.53μ and the other at 0.57μ . With ferric nitrate solutions, a similar result is obtained and an absorption band at 0.535μ is indicated. With ferric chloride solutions, the rotation changes from positive to negative with increasing iron content. In the solution of d 1.092, the rotatory dispersion curve suffers a marked change in the neighbourhood of 0.57μ . It is suggested that this is due to a partial dehydration of the ferric chloride molecule. All the indications are that ferric chloride and ferric sulphate solutions have the same magnetic absorption band. A solution of ferric ammonium chloride of d 1.091 gave a positive magnetic rotation and the rotatory dispersion curve gave indications of magnetic absorption bands at 0.57 and 0.53μ .

A. E. MITCHELL.

Connexion between chemical valency, electron grouping, and crystal structure. W. HUME-ROTHERY (*Phil. Mag.*, 1927, [vii], 3, 301—305).—Some of the conclusions of Grimm and Sommerfeld (A., 1926, 560) are criticised. Examples are quoted in which the same atomic configuration can be produced by more than one method of binding together of the atoms or by more than one electronic configuration. It is therefore held to be unjustifiable to argue that the fact that similar space-lattices are formed by different elements indicates similar electronic structure. It is also pointed out that the deduction from X-ray evidence that silicon and the compounds carbon silicide, boron nitride, aluminium nitride, and beryllium oxide are non-polar in the solid state, and that the atoms are held together in the solid in the same way as the atoms of carbon in the diamond lattice, should be received with caution.

A. S. RUSSELL.

Electronic nature of isomeric transformations. II. F. I. BEREZOVSKAYA (*Ukraine Chem. J.*, 1926, 2, 250—276; cf. A., 1926, 887).—The effect of magnetic fields on the structures of fumaric and maleic acids has been re-examined. The maximum change of maleic into fumaric acid occurred in a field of 4750—5150 units, when 12.75% of the total change took place in 7 hrs. Thereafter, as the field was increased, a small amount of maleic acid was formed. In a field of 7000 units, fumaric acid broke down analogously to oxalic acid, which is known to break down into carbon dioxide and formic acid when exposed to a strong magnetic field.

It is shown that methylfumaric acid is a stronger acid than fumaric acid, owing to the attraction of the carbon atom of the methyl group for the electrons of the carbon atom of the carboxyl group. Methylmaleic acid, in which the methyl group acts in the opposite sense, should be a weaker acid, and therefore have less mobile electrons. Hence in a magnetic field methylfumaric acid will be converted into methyl-

maleic acid. This also explains why dimethyl-fumaric acid does not exist. The effect of magnetic fields on alkylated maleic and fumaric acids will be examined.

E. ROTHSTEIN.

Electronic interpretation of the constitution of the boron hydrides and of compounds of boron, nitrogen, and hydrogen. M. ULMANN (Ber., 1927, 60, [B], 610—615; cf. Stock, A., 1926, 1218).—The position of boron in the periodic system renders equally possible the attainment of a stable electronic arrangement by the loss of three or the gain of five electrons. In the boron hydrides, the hydrogen atoms represent negative systems in the first case, in that each gains an electron, and positive systems in the second case, since each loses its single electron. In the former case, the hydrogen resembles that of the hydrides of the alkali and alkaline-earth metals, whereas in the latter case it is similar to that in the hydrides of elements on the right side of the periodic system. If it be assumed that gain and loss of electrons occur under similar energy conditions, it is possible to construct molecular models for boron hydrides and similar compounds from a uniform point of view. The hydride B_2H_6 contains a system of two boron atoms, one of which loses three electrons, whereas the other gains five. In each portion of the system, the stable, so-called "rare-gas" arrangement of electrons is present. The formula B_2H_6 can there-

fore be resolved into $BH_2 \cdot BH_4$ or $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{B}=\text{B}-\text{H} \\ | \\ \text{H} \end{array}$

and this is shown to be consistent with the chemical properties of the hydride. For the more complex compounds the following formulæ are developed on similar lines: $BH_2 \cdot BH_3 \cdot BH \cdot BH_4$, $BH_2 \cdot BH_3 \cdot BH \cdot BH_3 \cdot BH_2$, $BH_2 \cdot [BH_2 \cdot B]_2 \cdot BH_4$, and $BH_2 \cdot [BH_2 \cdot B]_3 \cdot BH_4$. For the compounds of boron, hydrogen, and nitrogen the structures $NH \cdot B \cdot NH \cdot B \cdot NH$ and $BH_2 \cdot NH \cdot BH \cdot NH \cdot B \cdot NH$ are proposed.

H. WREN.

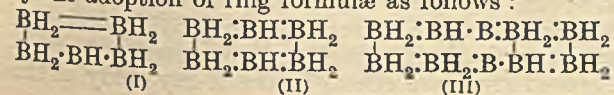
Constitution of boron [hydride] compounds.

J. A. CHRISTIANSEN (Z. anorg. Chem., 1927, 160, 395—403).—Stock ascribes to boron the valencies 3 and 4 in the various hydrides and their derivatives (A., 1926, 1218), but it is now shown that the behaviour of these compounds may be more satisfactorily explained on the assumption that boron has valencies of 3 and 5 and a co-ordination number of 4. On this basis, B_2H_6 would be formulated as $H_3B:BH_3$, and the ammonia compound either as the salt

$[H_2\overset{+}{B}:BH_2][\overset{-}{N}H_4]$ or as the dipolar compound

$[H_3B:NH_3]$, the former being the more probable in view of its analogy to the salt-like compound $B_2H_6Na_2$. The hydride B_4H_{10} may be written as $H_3B:BH_2 \cdot BH_2 \cdot BH_3$; on hydrolysis, this yields hydrogen and the acid $B_2H_6O_2$, the potassium salt of which is obtained by treating B_2H_6 with potassium hydroxide

and may be written as $[H_2(OH)\overset{+}{B}:\overset{-}{B}(OH)_2]K_2$. The comparatively great stability of hydrides with 5, 6, and 10 boron atoms is most satisfactorily explained by the adoption of ring formulæ as follows:



Formula (I) accounts for the fact that B_5H_9 combines with 4 mols. of ammonia to give $B_5H_9(NH_3)_4$, which with hydrogen chloride evolves 4 mols. of hydrogen rapidly and a further 3 mols. more slowly. The naphthalene formation of (III) is in agreement with its chemical properties and with its high m. p.

A. R. POWELL.

Sizes of ions and the structure of ionic crystals.

L. PAULING (J. Amer. Chem. Soc., 1927, 49, 765—790).—Theoretical. With the aid of an atomic model derived from Schrödinger's wave mechanics (Ann. Physik, 1926, [iv], 81, 109), radii are calculated for ions in a crystal having a small mutually-deforming force. The sum of the radii of two ions is equal to the interionic distance in a "normal" crystal composed of these ions with the sodium chloride structure, a "normal" crystal being one in which strong repulsion occurs only between adjacent anions and cations, and in which there is only so much deformation as is shown by the alkali halides. The calculated radii agree fairly well with the empirical values of Wasastjerna (A., 1923, ii, 593) and account satisfactorily for the experimental results both for "normal" crystals and for crystals in which the above additivity rule does not hold. Thus in some crystals (e.g., lithium chloride, magnesium sulphide) the interatomic distances depend on the anion radius only, since the anions are in mutual contact. Double repulsion (i.e., anion-anion as well as anion-cation) in sodium chloride, magnesium oxide, etc. crystals makes the anion-cation distances smaller than those observed. It is predicted that the fluorite structure is more stable than the rutile structure when the ratio of the cation radius to the anion radius exceeds 0.65, and *vice versa*. This has been verified experimentally. Similarly, the sodium chloride structure is more stable than the sphalerite structure when this ratio is greater than 0.33. This has been verified for certain beryllium compounds (e.g., the oxide and sulphide), which are to be considered, therefore, as ionic crystals. The aptness of such tetrahedral crystals to show deformation is attributed to a tendency of the anion to share an electron pair with each cation. Complex ions are considered very briefly.

S. K. TWEEDY.

Effective cross-section of the oriented hydrogen atom.

R. G. J. FRASER (Proc. Roy. Soc., 1927, A, 114, 212—221).—An apparatus is described for studying the normal hydrogen atom under conditions of space quantisation, and it is found that the effective collision area presented to the molecules of the resting gas (either hydrogen or argon) by the neutral hydrogen atoms in a beam of canal rays is unchanged by space quantisation. The hydrogen atom in the normal (1s) state is thus shown to be isotropic. This result is confirmed by Unsöld's analysis of the helium arc spectrum (A., 1926, 550), and receives a satisfactory interpretation on the basis of Schrödinger's wave mechanics.

L. L. BIRCUMSHAW.

Determination of the crystallite orientation [of metals] by the production of lines of slip. G. TAMMANN and H. H. MEYER (Z. anorg. Chem., 1927, 160, 347—354).—The method of maximum reflexion (A., 1925, ii, 1132) admits of the differentiation of three chief groups of crystallites on the surface of a

metal, the cubic, octahedral, and dodecahedral. By examining the lines of slip produced when the metal is subsequently subjected to deformation, it is possible to determine the exact orientation of these surface planes to the crystal. For example, with copper or iron, where slip takes place along an octahedral plane, the surface, if a cube plane, will show two systems of slip lines intersecting at an angle of 90° ; if an octahedral plane, three systems intersecting at 60° , and if a dodecahedral plane, three systems two of which intersect at 110° and the third bisects this angle. In any conglomerate of crystallites, all these three systems may develop together with a fourth, characteristic of cubic crystals, in which the lines are perpendicular to each other, but, owing to the orientation of the crystallites to the direction of rolling, no slip takes place along one or two of the slip planes in most of the crystals. The usual average is that 75% of the crystals show two systems of slip lines, 25% show three, and 0—0.2% show all four. Examples are given of the use of the method combined with the method of maximum reflexion in determining the orientation of the crystallites in cast copper ingots.

A. R. POWELL.

Tetragonal structure of carbon steel. N. SELJAKOV, J. KURDUMOV, and N. GOOTZOV (*Nature*, 1927, 119, 494).—Carbon steel quenching in water shows the body-centred, tetragonal structure. The numerical data indicate that the observed tetragonal structure of steel is a solid solution of carbon in the body-centred tetragonal lattice of metal atoms.

A. A. ELDRIDGE.

Constitution of mixed crystals. G. LUNDE (*Bull. Soc. chim.*, 1927, [iv], 41, 304—308).—From the results of the X-ray examination of certain mixtures (cf. Barth and Lunde, A., 1926, 114, 895), the general conclusion is reached that two compounds having different lattices of more or less compact formation can exhibit pronounced isodimorphism only if that compound formed from the smaller ions (atoms) crystallises in the more compact lattice. Exceptions to this rule are to be attributed to the reciprocal action of the electronic envelopes of the ions. A general consideration of the rule together with certain experimental results leads to the conclusion that in mixed crystals the constituents are perfectly mixed, but one of the constituents replaces the other in some arbitrary and irregular manner (cf. Vegard and Schjelderup, A., 1917, ii, 243).

S. K. TWEEDY.

Spatial systems of rhombic and monoclinic heptahydrates of sulphates of bivalent metals, and the series of mixed crystals
Mg(Zn)SO₄·7H₂O. H. G. K. WESTENBRINK (*Rec. trav. chim.*, 1927, 46, 105—123).—X-Ray investigation of MgSO₄·7H₂O showed that the space-lattice is of the simple rhombic type V_4 in Wyckoff's notation, and the substitution of CrO₄ for SO₄, or of Ni or Zn for Mg, has negligible effect on the dimensions of the elementary cell. The monoclinic modification of FeSO₄·7H₂O is of the type C_m^2 , and again the substitution of Co for Fe has little effect on the lattice. Of the three views on the nature of mixed crystals, the one that they consist of conglomerations of pure crystals of the two constituents is contrary to X-ray

and other evidence. Tammann's view that a mixed crystal is derived from a pure one by the replacement atom for atom of one type of atom by another, is also unlikely, for it necessitates the supposition that the value of n (i.e., the number of identical atoms distributed about a given atom) and also the dimensions of the elementary cell vary with the composition of the mixture. The best view is that the two types of atoms are distributed irregularly throughout the crystal, so that, in a given region, only those of one type are present, arranged according to their appropriate space-lattice. Thus the crystal possesses quasi-homogeneity only, but its action on X-rays will be identical with that of a lattice the dimensions of which are the mean of those of the constituents. Mixed crystal formation and compound formation can occur between the same constituents; with the system MgSO₄·7H₂O—ZnSO₄·7H₂O, however, the compounds Mg₂Zn(SO₄)₃·21H₂O and MgZn(SO₄)₂·14H₂O, as supposed by Hollmann (A., 1901, ii, 436), are not formed, for both the specific gravity and the refractive index of the mixed crystals vary continuously with composition, and, further, consideration of the lattices of the constituents and of the mixed crystals shows that such compounds are impossible. S. J. GREGG.

Effect of temperature on the crystal structure of calcite. C. Tsuboi (*Proc. Imp. Acad. Tokyo*, 1927, 3, 17—18).—A preliminary account is given of the effect of temperature in altering the mean relative positions of the atoms in a crystal of calcite. The value of the parameter, ϕ , defining the positions of the oxygen atoms at the ordinary temperature is 0.25, and this value decreases as the temperature is raised.

W. E. DOWNEY.

Crystal structure of hexamminecobaltic iodide
[Co(NH₃)₆]I₃. R. W. G. WYCKOFF and T. P. MCCUTCHEON (*Amer. J. Sci.*, 1927, [v], 13, 223—233).—From powder and Laue photographs of crystals of [Co(NH₃)₆]I₃, it appears that the correct structure is Co at 4b, I at 4c and 8e, N at 24a, with u —about 0.20. The length of the edge of the unit cube containing these four molecules is 10.88 Å.

C. J. SMITHELLS.

Crystal structure of selenides of beryllium, zinc, cadmium, and mercury, and determination of lattice constants. W. ZACHARIASEN (*Z. physikal. Chem.*, 1926, 124, 436—448).—The crystals of beryllium, zinc, and mercuric selenides are of the zinc-blende type, and the lengths of the edges of the elementary cubes in Å. are 5.129 ± 0.004 , 5.661 ± 0.003 , and 6.068 ± 0.004 , respectively. Cadmium selenide crystals are of the wurtzite type, and the lattice dimensions are $a=4.30 \pm 0.01$ and $c=7.01 \pm 0.02$. A method of determining the limits of error in determinations of lattice constants by Wyckoff's method is worked out.

R. CUTHILL.

Lattice-structure and electrical conductivity in the mixed-crystal series gold-copper, palladium-copper, and platinum-copper. C. H. JOHANSSON and J. O. LINDE (*Ann. Physik*, 1927, [iv], 82, 449—478; cf. A., 1926, 112).—The correlation between maxima in the conductivity-composition curves in mixed-crystal series and the appearance of superimposed structure effects in the X-ray study of the

alloys have been fully confirmed. Alternate heating and cooling hasten the appearance of regular orientation in the gold-copper series. In the palladium-copper system, alloys richer in palladium than 50 at.-% exhibit poor conductivity together with a face-centred cubic lattice free from superimposed structure effects. Tempered alloys containing up to about 25 at.-% of palladium are good conductors and show evidence of structure superimposed on the face-centred cubic lattice. Within the range 38—50 at.-%, the conductivity is high and the body-centred cubic lattice shows the superimposed structure. On the other hand, alloys quickly cooled from the m. p. show poor conductivity and ill-defined crystal structure. The absence of the body-centred lattice at concentrations higher in palladium than 50 at.-% is said to be due to the inability of palladium atoms to replace copper atoms in this lattice. Højendahl's views on electrical conductivity in alloys indicate that a lattice lacking in continuous lines or planes of similar atoms will exhibit poor conductivity, and the present work provides support for the idea. The system copper-platinum exhibits a face-centred cubic lattice with superimposed structure accompanied by high conductivity in the neighbourhood of 25 at.-% of platinum. In the region 40—50 at.-%, a trigonal phase appears with a maximum in the conductivity-composition curve at 1Cu:1Pt. From about 60 at.-%, the lattice is a face-centred cube with the conductivity decreasing as the proportion of platinum increases. The quickly-cooled alloys show no superimposed structure and the conductivity falls to a relatively low minimum in the region 50—70 at.-%. The trigonal phase is discussed in some detail.

R. A. MORTON.

X-Ray patterns of mullite and sillimanite. J. F. HYSLOP and H. P. ROOKSBY.—See B., 1927, 219.

X-Ray analysis of clays. L. B. STRUTINSKI.—See B., 1927, 219.

Analytical interpretation of the X-ray spectra of fatty acids and their mixtures. J. J. TRILLAT (Compt. rend., 1927, 184, 812—814; cf. A., 1926, 890).—Variations previously recorded in the X-ray spectra of pure fatty acids are due to the method of preparation of the specimen rather than to the presence of impurities. Orientation by fusion or evaporation of alcoholic solutions gives consistent results. The spectra of mixtures of two fatty acids consist usually of faint rays, and depend on the method of preparation of the specimen and on the proportion and difference in m. p. of the constituents. Separate spectra of the constituents are not obtained if the acids contain almost the same number of carbon atoms, except when traces of an impurity lower the m. p. of the mixture and promote their simultaneous orientation. With triglycerides, this has been used for detection of margarine in butter. The positions of the rays cannot be determined from the proportions of the constituents, and the use of thin lead sheets is preferable to that of glass for mounting in their qualitative determination.

J. GRANT.

X-Ray investigation of optically anomalous crystals of racemic potassium chlorosulphoacetate. W. G. BURGERS (Proc. Roy. Soc., 1927,

A, 114, 222—229).—Jaeger's view (A., 1925, ii, 948), that the apparently orthorhombic crystals of racemic potassium chlorosulphoacetate are really twins produced by almost perpendicular crossing of monoclinic lamellæ, has been tested by an X-ray investigation of the crystals. The crystals used were either the same as those employed by Jaeger or had been grown under similar conditions, *i.e.*, from aqueous solutions containing potassium bromide or chloride. A number of oscillation photographs about different crystallographic directions were taken, and the results indicated that the crystals are truly orthorhombic, and that the irregularities of their habit must be caused by a slight difference in orientation of successively crystallised layers. The dimensions of the unit cell, which contains eight groups $[\text{CHCl}(\text{SO}_3\text{K})\cdot\text{CO}_2\text{K}\cdot 1.5\text{H}_2\text{O}]$, are $a=8.58$, $b=8.60$, $c=23.76$ Å. The halvings correspond with the space-group Q^{14} , the underlying lattice being the simple orthorhombic lattice Γ_0 . It is probable that the optical anomalies of the investigated crystals can be explained by the presence of internal strains, and that the presence of alkali halides in the mother-liquor was, directly or indirectly, the cause of strained lamellar growth. L. L. BIRUMSHAW.

Space-lattice of *i*-erythritol. N. SCHÖNFELDT, K. HERRMANN, and O. HASSEL (Z. physikal. Chem., 1926, 124, 305—317; cf. Burgers, A., 1926, 339).—The X-ray diagram of *i*-erythritol shows that the unit cell is space-centred, has a volume of 1116.72×10^{-24} cm.³, and contains eight molecules. $\text{H}_2\text{C}\cdot\text{OH}$
 $\text{OH}\cdot\text{CH}$
 $\text{HC}\cdot\text{OH}$
 $\text{OH}\cdot\text{CH}_2$
(I.) The molecules are symmetrical with respect to a centre of inversion. Thus both the active and the *meso* forms have the space formula (I), but in the active form the $-\text{CH}_2\cdot\text{OH}$ groups lie in front of the plane of the paper, whilst in the *meso* form the lower one lies behind it. R. CUTHILL.

Structure of soil colloids. J. DUCLAUX (2me. Cons. Chim. Inst. Intern. Chim. Solvay, 1926, 91—123).—Both cellulose nitrate and cellulose films have the properties of a uniaxial crystal cut perpendicular to its axis; whatever be the conditions under which the film is formed, the birefringence remains constant. It is concluded that cellulose in a normal condition can be likened to a uniaxial crystal and that the biaxial varieties are oriented. Work on the birefringence and X-ray investigations of nematic soil colloids is discussed. CHEMICAL ABSTRACTS.

Recrystallisation centres in metals. A. E. VAN ARKEL and P. KOETS (Z. Physik, 1927, 41, 701—707).—It is shown that the number of crystals of γ -iron in mechanically deformed strips of steel is approximately proportional to the number of crystals of α -iron in the undeformed strips. R. W. LUNT.

Matthiessen's rule. W. GEISS and J. A. M. VAN LLEEMPT (Z. Physik, 1927, 41, 867—871).—The temperature coefficients of resistance of cold-wrought pure tungsten, molybdenum, nickel, and platinum have been compared with those of samples of the metals treated in various ways. Although the specific resistance of each group of samples varies considerably, Matthiessen's rule (Ann. Physik, 1864, 122, 47) that

the product of the specific resistance and the mean temperature coefficient of resistance is a constant has been verified for these metals. R. W. LUNT.

Electrical properties of some metallic compounds. H. ANDRÉ (Compt. rend., 1927, 184, 741—742).—Compounds of silver with sulphur or phosphorus will absorb a further quantity of these elements, in the fused state, at low temperatures. Their electrical resistances then decrease regularly with rise of temperature, particularly when sulphur is present, within limits which vary according to the sample. Direct current slowly displaces the silver, but alternating current at low temperatures has no apparent effect. J. GRANT.

Conduction of electricity by heavy metal sulphides. C. TUBANDT and M. HAEDICKE (Z. anorg. Chem., 1927, 160, 297—317).—At temperatures between 200° and 300°, compressed cylinders of black antimony trisulphide, lead sulphide, stannic sulphide, and molybdenum disulphide behave as purely metallic conductors. Cadmium sulphide is a non-conductor up to 250°, above which temperature it becomes a metallic conductor, its conductivity increasing rapidly with rise of temperature. Red antimony sulphide and yellow arsenic sulphide remain non-conductors below their transformation and m. p., respectively. Silver sulphide and cuprous sulphide are therefore the only electrolytic and mixed conductors (in the β -modifications) among the heavy metal sulphides. The double sulphides of silver with arsenic and antimony sulphides behave, like α silver sulphide, as purely electrolytic conductors in which the arsenic and antimony sulphides are inert constituents, only the silver ion migrating under the influence of the current. A. R. POWELL.

Dependence of surface tension on electric charge. O. RUFF, G. NIESE, and F. THOMAS (Ann. Physik, 1927, [iv], 82, 618—626).—The relation between the surface tension on a spherical droplet of a conducting material and the density of the electrical charge has been investigated. The equation $\sigma' = \sigma - \frac{4\pi r^2 \rho^2}{2\rho\pi}$ (ϵ is the density of the charge in e.s.u., σ is the normal surface tension, σ' that of the charged droplet, ρ the radius) is deduced and confirmed experimentally for mercury. R. A. MORTON.

Behaviour of drops and drop-electrodes in high electrical fields. O. RUFF, G. NIESE, and F. THOMAS (Ann. Physik, 1927, [iv], 82, 631—638).—The behaviour of drops of a variety of organic and inorganic materials in electric fields of high intensity has been investigated with respect to atomisation, brush discharge, phosphorescence induced when the particles fall into liquid air, viscosity, and surface tension. Atomisation occurs with a field of 20,000 volts in all the liquids tested except fused metallic elements and alloys. Liquids exhibiting low values for viscosity and surface tension are readily converted into sprays. The charge has only a small effect on the surface tension. The brush discharge observed at the orifice of the capillary is especially marked for glycerol, wax, fatty oils, phenanthrene, phenyl salicylate, and dextrin solution. The phosphorescence excited when the charged particles fall into liquid

air is very marked for diphenylamine, ethyl benzoate, gelatin solution, paraffin oil, and glycerol. The sodium and potassium eutectic exhibits a bright yellow glow as the droplets fall in an atmosphere of hydrogen at pressures below one atmosphere. R. A. MORTON.

Unipolarity of lead sulphide. H. LÜKE (Physikal. Z., 1927, 28, 213—221).—Thieme's observation (*ibid.*, 1916, 17, 615) that etched or roughened metals and crystalline alloys show unipolarity is denied. The compressed powder of crystalline lead sulphide behaves similarly to the crystal. Heating does not affect the unipolarity of large crystals, but increases the unipolarity of the compressed powder. Chemically-prepared lead sulphide shows no unipolarity, but heating at 150° or outgassing in a vacuum confers unipolarity on the resulting material. Heating at 600° causes the unipolarity to be reversed. The removal of moisture and gas from the compressed powder increases the unipolarity. W. E. DOWNEY.

Transverse thermo-electric effect in metal crystals. P. W. BRIDGMAN (Proc. Nat. Acad. Sci., 1927, 13, 46—50).

Magnetic properties of various substances. S. BERKMAN and H. ZOCHER (Z. physikal. Chem., 1926, 124, 318—326).—The magnetic susceptibilities of a number of dyes and metallic oxides and salts have been determined by measuring the force exerted upon them in a non-uniform magnetic field. R. CUTHILL.

Calculation of magnetic susceptibility of sodium chloride from data on intensities of X-ray reflexions. E. S. BIJLER (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 489—495).—A method of calculating the susceptibility of a diamagnetic atom from the electron distribution curve is described. The values calculated from available data for sodium chloride are rather larger than the experimental values, but the agreement is such as to justify the calculation of electron distribution from X-ray reflexion data. R. CUTHILL.

Measurement of resolving power of photographic materials. O. SANDVIK (J. Opt. Soc. Amer., 1927, 14, 169—177, and Z. wiss. Phot., 1927, 24, 336—347).—Resolving power, as determined by the parallel line method, decreases linearly with the logarithm of the ratio width of line/width of space. L. F. GILBERT.

Extinction coefficient measurements with diverging light. D. S. VILLARS (J. Opt. Soc. Amer., 1927, 14, 29—32).—The divergence of the light beam from a monochromator slit introduces less than 0.5% error in extinction coefficient measurements if the ratio of the total light transmitted rather than the ratio of the intensities is used in the calculations. The use, in photo-chemical work, of parallel light, produced at the expense of intensity, is therefore often unnecessary. L. F. GILBERT.

Preparation and optical properties of calcium hydroxide crystals. F. W. ASHTON and R. WILSON (Amer. J. Sci., 1927, [v], 13, 209—218).—Calcium hydroxide crystals obtained by various methods, which are described, show the same crystal

form and refractive indices. The crystals belong to the hexagonal system and occur as short hexagonal prisms or plates with perfect cleavage parallel to the (0001) face. The refractive indices are $\omega = 1.574 \pm 0.003$, $\epsilon = 1.545 \pm 0.003$ for sodium light. Birefracton is 0.029; $d_{20}^{20} = 2.230 \pm 0.005$; interference figure is uniaxial negative. The lattice constants are $a_0 = 3.579$, $c_0 = 5.028 \text{ \AA}$.; the unit cell contains one molecule. C. J. SMITHELLS.

Specific heats of a highly-cooled non-condensed phase. J. E. VERSCHAFFELT (Compt. rend., 1927, 184, 603—604).—The author disagrees with the assumptions of Perrakis (this vol., 101; de Kolosovski, *ibid.*, 301). J. GRANT.

Limiting value of latent heat of vaporisation at the absolute zero. J. J. VAN LAAR (J. Chim. phys., 1927, 24, 115—119).—The latent heat of vaporisation does not tend to zero at the absolute zero of temperature, as stated by de Kolosovski (A., 1926, 1198). The internal latent heat comprises two terms, the thermal energy and the potential energy; according to Nernst's heat theorem, the thermal energy may become zero at 0° Abs., but the potential energy, which is represented by a term of the form a/v , could only do so if the volume v of the liquid were to vanish. Onnes has shown experimentally that the latent heat of helium reaches a minimum at 1.5° Abs. and then increases with falling temperature, which is explained by the variation (with temperature) of the constants a and b of the equation of state; b increases with falling temperature, but a reaches a maximum at a very low temperature and then decreases, reaching a limiting value at 0° Abs. Contrary to de Kolosovski's assertion, Kirchoff's law for the variation of latent heat with temperature holds at very low temperatures. S. J. GREGG.

Thermal decomposition of nitrosyl chloride. H. A. TAYLOR and R. R. DENSLOW (J. Physical Chem., 1927, 31, 374—382; cf. Trautz and Gerwig, A., 1925, ii, 878).—The decomposition of nitrosyl chloride has been investigated between 700° and 900° by a dynamic method in which the rapidity of the reverse reaction was overcome by an increased rate of flow of the gas, by diluting with nitrogen. The effect of an increased surface (quartz) was negligible, and the temperature coefficient and energy of activation apparently have the values 1.025 and 6000 g.-cal., respectively. On the radiation theory, this energy of activation at the temperatures employed corresponds with a wave-length of 4.769 μ , which does not correspond with any known absorption band in the spectrum of nitrosyl chloride. L. S. THEOBALD.

Thermal conductivity of carbon dioxide. H. GREGORY and S. MARSHALL (Proc. Roy. Soc., 1927, A, 114, 354—366).—The discrepancies in the absolute values of the thermal conductivity of carbon dioxide, as determined by various observers either by the cooling-thermometer method or the hot-wire method, are probably due to the practice of attempting to eliminate convection losses by reducing the pressure. Such a procedure is justified only if the reduction of pressure is not carried beyond the point at which the mean free path of the molecules becomes comparable with the dimensions of the containing vessel. The

apparatus used in the present investigation is a modification of that described by Gregory and Archer (A., 1926, 231), using a vertical instead of a horizontal system of tubes, and taking every precaution to eliminate convective losses. Six series of readings were taken, corresponding with six wire temperatures varying from 8.908 to 25.147°, the thermostat temperature being maintained at 0°. By plotting the values of the absolute thermal conductivity against the corresponding mean gas temperatures, it is found by extrapolation that the value at 0° is 3.604×10^{-5} g.-cal. cm.⁻¹ sec.⁻¹ deg.⁻¹. The temperature coefficient of thermal conductivity in this region, deduced from the slope of the curve, is 0.0027. L. L. BIRCUMSHAW.

Heat conductivity of gases. S. WEBER (Ann. Physik, 1927, [iv], 82, 479—503).—Further refinements have been introduced into the improved Schleiermacher method. The new measurements result in a value of $573.8-574.2 \times 10^{-7}$ for the absolute heat conductivity of atmospheric air at 0°; the earlier value was 568.0×10^{-7} . For neon, the new value is 1104×10^{-7} , the old was 1089×10^{-7} ; for carbon dioxide, the corresponding values are 343.1×10^{-7} and 339.3×10^{-7} . The source of this discrepancy of about 1% has not been traced. R. A. MORTON.

Uncondensed systems at low temperatures. N. PERRAKIS (J. Chim. phys., 1927, 24, 169—172).—It is demonstrated thermodynamically that the molecular heat of any gas at a sufficiently low temperature becomes identical with that of a monatomic gas, thus confirming Eucken's data for the specific heat of hydrogen at low temperatures (A., 1912, ii, 232). H. F. GILLBE.

Density of water vapour. T. SHIRAI (Bull. Chem. Soc. Japan, 1927, 2, 37—40).—A sealed bulb containing a weighed quantity of water was broken by electrical heating, thus releasing its contents into the enlarged top of a barometer tube, on which the pressure was read. The mol. wt. of water so obtained never deviated by more than 0.3% from the theoretical value for unassociated water molecules, over the range 80—140°. S. J. GREGG.

Simple proof of the failure of Dalton's law for real gases. M. JAKOB (Z. Physik, 1927, 41, 737—738).—It is shown that Dalton's law of partial pressures does not apply to gases for which p_v is not constant with increasing p . W. E. DOWNEY.

Pressure effect on mixing gases. M. JAKOB (Z. Physik, 1927, 41, 739—742).—From the measurements of the isotherms of helium, neon, and helium-neon mixtures by Holborn and Otto (A., 1925, ii, 851), it is deducible that when helium and neon, both at the same pressure, are mixed, under constant volume and isothermal conditions, a comparatively large pressure alteration is to be expected.

W. E. DOWNEY.

Vapour pressure of liquid oxygen and nitrogen. B. F. DODGE and H. N. DAVIS (J. Amer. Chem. Soc., 1927, 49, 610—620).—The vapour pressure of oxygen is given by $\log_{10} p(\text{atm.}) = -372.808/T + 4.18939 - 0.0006195T$, or, less accurately, $\log_{10} p = -366.523/T + 4.06295$; that of nitrogen is given by $\log_{10} p = -316.824/T + 4.47582 - 0.0071701T + 2.940 \times 10^{-5}T^2$,

or $\log_{10} p = -304.494/T + 3.93352$. The simpler relations hold remarkably well over a very large pressure range up to the critical point. S. K. TWEEDY.

Vapour pressures of hydrogen cyanide. H. SNOZAKI, R. HARA, and S. MITSUKURI (Tech. Repts. Tôhoku Imp. Univ., 1927, 6, 157—167).—An accurate method of determining the vapour pressures of liquid and solid hydrogen cyanide is described. Vapour-pressure equations derived from measurements made between 187.09° and 319.30° Abs. have been calculated and the following constants deduced: m. p. $-13^\circ \pm 0.1^\circ$, heat of fusion 1942 g.-cal./mol., heat of sublimation at a number of temperatures including the value 8768 g.-cal./mol. at the m. p., heat of vaporisation at a number of temperatures including the value 6484 g.-cal./mol. at the b. p. 25.8°, the chemical constant 3.58. M. S. BURR.

Van der Waals' equation at the critical point. V. KIREJEV (Z. Elektrochem., 1927, 33, 91—94).—Theoretical. The ordinary solution of van der Waals' equation at the critical point leads to three values of the constant a in terms of the critical constants and, on substituting experimental critical data, these values are usually notably divergent. The value $a = 27R^2T_c^2/64p_c$ and the corresponding value $b = RT_c/8p_c$ give best agreement when substituted in van der Waals' equation at the critical point. Moreover, such values of a for various substances give values of $(p_c + k_c)v_c$, where $k_c = a/v_c^2$, which agree with the corresponding values of $T_c v_c (dp/dT)_c$ obtained from independent data for $(dp/dT)_c$ previously calculated (A., 1926, 1088). Hence, $k_c = 3\alpha^2 p_c$, where $\alpha = 3RT_c/8p_c v_c$; if α has its mean value, 1.42, for normal substances, $k_c = 6.1p_c$ instead of the usual relation $k_c = 3p_c$. The reduced equation of state then becomes: $[\pi + 3(\alpha/\phi)^2][3(\phi/\alpha) - 1] = 80$, which is converted into the usual reduced van der Waals equation when $\alpha = 1$.

H. J. T. ELLINGHAM.

Compressibility isotherms of hydrogen, nitrogen, and mixtures of these gases at 0° and pressures to 1000 atm. E. P. BARTLETT (J. Amer. Chem. Soc., 1927, 49, 687—701).—The observed compressibilities of hydrogen and nitrogen agree with those found by Verschoyle (A., 1926, 894); they are slightly lower (0.5—0.7%) than Amagat's values at low pressures, but for nitrogen agree closely with his values at high pressures (800—1000 atm.). The compressibility of a mixture of the gases is not a linear function of the composition. Empirical relationships are deduced. The normal density of hydrogen is 0.08982 g. per litre. S. K. TWEEDY.

Molecular association in the liquid state. K. M. STAKHORSKY (J. Chim. phys., 1927, 24, 204—208).—The degree of association of a number of liquids at various temperatures has been calculated from existing surface tension data, and is shown to decrease with increase of temperature and with increase of mol. wt. If the degree of association of water be calculated by the same method, an abnormally high value is obtained at low temperatures, owing to the anomalous variation of density with temperature in the neighbourhood of 4°.

H. F. GILLBE.

Molecular states of liquids. E. GAPONE (Ukraine Chem. J., 1926, 2, 321—329).—Various formulae for the calculation of the internal compression of liquids are given and it is concluded that the equation, $P(Mv)^{2/3}.T_c = 0.113$, where P is the internal compression, represents the facts best. It is found that the internal compression (112.3) of chlorobenzene is approximately equal to that of dimethylaniline (115.2), whence the above constant is calculated. It is concluded that there is no evidence for supposing that there is greater internal pressure in liquids the molecules of which are associated than in those the molecules of which are not.

E. ROTHSTEIN.

Measurement of surface tension. N. E. DORSEY (U.S. Bur. Standards Sci. Paper 540, 1926, 21, 563—595).—Seventeen of the more important methods of measuring surface tension are described, the most frequent sources of error considered, and methods whereby they may be avoided described in detail. The working equations applicable to each method are given, and a number of inaccuracies in the literature are pointed out.

H. F. GILLBE.

Surface tension of solids. N. K. ADAM (Phil. Mag., 1927, [vii], 3, 863—864).—It is shown that the assumption made by Antonov (A., 1926, 671), that the surface tension of a solid is the same as that of a liquid which neither rises nor falls in a capillary tube made of the solid, is incorrect and that the quantity responsible for the condition of equilibrium is the work of adhesion of the liquid to the solid. It is thought to be improbable that any relationship can exist between this quantity and the surface tension of a solid.

A. E. MITCHELL.

Variation of logarithmic decrement with amplitude and viscosity of certain metals. IV. G. SUBRAHMANYAM (Phil. Mag., 1927, [vii], 3, 854—857; cf. *ibid.*, 1926, [vii], 1, 1074).—Determinations of the viscosities of a number of metals from measurements of the logarithmic decrements of the amplitudes of vibration when wires are vibrating in states of maximum torsional elasticity, indicate that the coefficient of most metals is of the order 10^8 poises. This value is in agreement with that obtained by Iokibe and Sakai (*ibid.*, 1921, [vi], 42, 397), but is very different from those obtained by other observers.

A. E. MITCHELL.

Viscosity of ether at low temperatures. E. H. ARCHIBALD and W. URE (J.C.S., 1927, 610—614; cf. A., 1924, i, 493).—Measurements have been made of the viscosity of ethyl ether over a temperature range of 0° to -110° . The temperature coefficient of the viscosity increases rapidly, as the temperature falls, from 0.99 between 0° and -10° to 3.24 between -100° and -110° .

M. S. BURR.

Diffusion in solutions. E. ULLMANN (Z. Physik, 1927, 41, 301—317).—Furth's micro-method for the determination of the velocity of diffusion in solutions has been improved so that diffusion coefficients of coloured solution can be obtained within 6%. Measurements on solutions of neutral-red and trypanon-red show that the coefficient of diffusion varies with the concentration in agreement with Fick's law, the values given for infinite dilution being

4.2×10^{-6} and 3.5×10^{-6} . The size of the particles has been calculated from Einstein's equation (Ann. Physik, 1905, [iv], 17, 549—560). For potassium permanganate solution, Fick's law has been found to hold for concentrations up to 1 or 2%. The coefficient of diffusion for infinite dilution is 15.2×10^{-6} , in good agreement with the value 15.9×10^{-6} calculated from Nernst's diffusion equation. Data obtained for solutions of ferric saccharate are employed to derive an expression for diffusion in concentrated solutions, according to which it appears that the rate of diffusion is not proportional to the gradient of the concentration. The rate of diffusion is given within 10% by the first two terms of an exponential series in which the coefficients are themselves functions of the concentration.

R. W. LUNT.

Pressure of gaseous mixtures. J. E. LENNARD-JONES (Nature, 1927, 119, 459).—Published results show that the pressure of a gaseous mixture may be greater than that of either of its constituents, even when the molecular concentration and temperature are in all cases the same. Cohesive forces between molecules tend to diminish the pressure, whilst repulsive forces tend to increase it; the relationship of the effects depends on the temperature.

A. A. ELDRIDGE.

Properties of mixtures of acetone and isopropyl alcohol. G. S. PARKS and C. S. CHAFFEE (J. Physical Chem., 1927, 31, 439—447).—The behaviour of this system departs markedly from the ideal. Mixing is accompanied by absorption of heat, amounting to 387 g.-cal./g.-mol. in the case of the equimolar mixture. The heats of mixing were determined at 20°, and densities and refractive indices at 25°. An increase in volume, on the average 0.3%, accompanies the mixing. The vapour pressures observed at 25° and the partial pressures of the components of the various mixtures are larger than the values calculated from Raoult's law. The viscosities at 25°, measured in an Ostwald viscosimeter, show an average negative deviation of 34% from the values given by the cube-root equation of Kendall (A., 1920, ii, 670). The results indicate that pure isopropyl alcohol is associated to some extent, and that the addition of acetone causes dissociation of the associated molecules.

L. S. THEOBALD.

Significance of dielectric constant of a mixture. H. H. LOWRY (J. Franklin Inst., 1927, 203, 413—439).—A review of the literature showing that the dielectric constant of a mixture cannot in general be calculated from the data for the components.

R. A. MORTON.

Systems formed by certain inorganic compounds with liquid sulphur dioxide. H. T. BEACH and P. A. BOND (Proc. Iowa Acad. Sci., 1925, 32, 328—329).—An investigation of the solubility relationships of carbon, titanium, and tin tetrachlorides, tin tetrabromide, and tin tetraiodide with liquid sulphur dioxide.

CHEMICAL ABSTRACTS.

Formulae for the azeotropic constants for mixtures of alcohols and halogen compounds. M. LECAT (Compt. rend., 1927, 184, 816—818).—Formulae are given for the azeotropic lowering (A., 1926, 1199) in the case of mixtures of an alcohol

(methyl alcohol, ethyl alcohol, propyl alcohol, isobutylcarbinol, or glycol) with one of a number of organic halides. In general, the observed and calculated values agree for the mono- but not for the di-halogen derivatives. Trihalogen compounds agree with the formula, except in the case of methane derivatives, which evolve heat when mixed with ethyl alcohol. Carbon tetrachloride appears to be normal.

J. GRANT.

Partial molal volumes of water and salt in solutions of the alkali halides. V. K. LAMER and T. H. GRONWALL (J. Physical Chem., 1927, 31, 393—406).—A method for the calculation of the partial molal volumes of water, $\partial v/\partial n_0$, and of a salt, $\partial v/\partial n$, where n_0 and n are the number of mols. of water and salt, respectively, contained in a volume v of solution, from density determinations is described. Values for water and the alkali halides at 0°, 25°, and 50° have been calculated from the equations $\partial v/\partial n_0 = a_0 + a_2 m^2 + a_3 m^3 + a_4 m^4$ and $\partial v/\partial n = b_0 + b_1 m + b_2 m^2 + b_3 m^3$, where m is the molality, and a_0, b_0 , etc. are constants, which have been evaluated from the density data of Baxter and Wallace (A., 1916, ii, 219). These values are tabulated and discussed. The density data for potassium chloride at the above temperatures, and for rubidium chloride and caesium iodide at 0°, may be sufficiently in error to account for certain irregularities, but the values for the remaining chlorides are mutually consistent. The results, and especially the effect of temperature, are discussed in relation to the theory of Webb (A., 1926, 1208).

L. S. THEOBALD.

X-Ray study of alloys of lead and thallium. E. McMILLAN and L. PAULING (J. Amer. Chem. Soc., 1927, 49, 666—669).—X-Ray powder photographs of a series of lead-thallium alloys at the ordinary temperature show the presence of two solid solutions, one having the structure of lead and the other the low-temperature structure of thallium. There are no indications of the existence of the compound $PbTl_2$ (Lewkonja, A., 1907, ii, 261).

S. K. TWEEDY.

Solubilities and densities of saturated solutions of sodium and potassium halides at 25°. A. F. SCOTT and W. R. FRAZIER (J. Physical Chem., 1927, 31, 459—463; cf. Baxter and Wallace, A., 1916, ii, 220).—The densities at 25° and solubilities (g. salt/100 g. water) recorded are: sodium chloride, 1.19796, 26.406; bromide, 1.54181, 48.61; and iodide, 1.91901, 64.76; potassium chloride, 1.17786, 26.38; bromide, 1.37937, 40.57; and iodide, 1.72111 and 59.75.

L. S. THEOBALD.

Solubility. X. Solubility relations of stannic iodide. M. E. DORFMAN and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1927, 49, 729—737).—The solubility of stannic iodide between 10° and 40° in nine organic solvents and in sulphur at 104° and 130° is recorded. The specific volume of liquid stannic iodide between 145° and 275° is given by $v = 0.2368(1 + 0.00079t)$. The solubilities in these solvents and in iodine and methylene iodide agree well with the relative internal pressures of the substances, although there is no strict proportionality. Ideal solutions are obtained with sulphur and with iodine; the heat of fusion of stannic iodide is calculated to be 4000 g.-cal./mol.

S. K. TWEEDY.

Solubilities of metallic derivatives of nitrosophenylhydroxylamine. A. PINKUS and F. MARTIN (J. Chim. phys., 1927, 24, 83—102).—The application of potentiometric and conductivity methods is complicated by the tendency of the compounds to polymerise. An "indirect" colorimetric method is suggested as an alternative. Results obtained by the conductivity method for the ammonium and potassium salts are recorded. The values derived for λ_0 are 93.0 and 86.0, respectively. The mobility of the nitrosophenylhydroxylamine ion deduced from the potassium salt is 21.3 and from the ammonium salt 27.8, the divergence being explained by the instability of the ammonium salt. S. J. GREGG.

Solubilities of metallic derivatives of nitrosophenylhydroxylamine. II. A. PINKUS and F. MARTIN (J. Chim. phys., 1927, 24, 137—168).—The solubilities of the nitrosophenylhydroxylamine salts of the following metals have been determined at 18° by potentiometric, colorimetric, and conductivity methods (cf. preceding abstract); the results are in g.-mol./litre, and are the mean values of all the determinations made: silver, 1.4×10^{-3} ; mercurous, $< 6.6 \times 10^{-7}$; lead, 1.2×10^{-4} ; copper, 1.1×10^{-5} ; cadmium, 3.7×10^{-4} ; bismuth 4×10^{-5} ; antimonious, 4.5×10^{-5} ; stannous, 3.5×10^{-5} ; stannic, 2×10^{-5} ; iron, 3×10^{-7} ; aluminium, 3.4×10^{-5} ; nickel, 8.9×10^{-4} ; cobalt, 1.3×10^{-3} ; zinc, 4.9×10^{-4} . Arsenious, arsenic, and antimonious salts are not precipitated by cupferron. A scheme has been drawn up for a systematic examination of the employment of cupferron in gravimetric analysis. The electrochemical method of determining the solubilities of sparingly soluble substances has been modified so that it may be employed for compounds of unknown composition; comparison of the results obtained by this method and by the classical method indicates that whereas the precipitates formed by silver, copper, cadmium, and zinc are ionised normally in saturated aqueous solution, giving a cation of the metal and an anion of nitrosophenylhydroxylamine, the compounds of lead, nickel, and cobalt exist in solution largely as complexes.

The equivalent conductivities of aqueous solutions of cupferron and of its potassium derivative have been measured at 18°. The degree of ionisation of the salt and the mobility of the anion have been calculated at a number of concentrations between 0 and 0.1 g.-mol./litre. H. F. GILLBE.

Solubility. (Ternary systems of two salts in a volatile solvent.) C. TOURNEUX and (MLLE.) M. PERNOT (Bull. Soc. chim., 1927, [iv], 41, 397—400).—Experimental technique is described, including a rapid and accurate method for the removal of the solid phase by means of a centrifuge.

S. K. TWEEDY.

Adsorption of gases by glass walls. IV. Methyl chloride and oxygen. M. CRESPI (Anal. Fis. Quim., 1927, 25, 25—41; cf. Crespi and Moles, A., 1926, 1200).—The adsorption of methyl chloride by glass walls is given by $A = 0.25 \times 10^{-8} p^{3.5}$ or $0.38 \times 10^{-8} p^{3.5}$ per sq. cm. of surface, according as the glass is drawn into tubes or blown into bulbs. The corresponding values for oxygen are $0.043 \times 10^{-8} p^{2.3}$ and $0.065 \times 10^{-8} p^{2.3}$. G. W. ROBINSON.

Adsorption of water vapour by charcoal. A. S. COOLIDGE (J. Amer. Chem. Soc., 1927, 49, 708—721).—The adsorption isotherms of non-polar substances on charcoal are concave towards the log p axis, whereas those of polar substances are mostly convex. The explanation may lie in molecular association of the polar substance. Pure charcoal adsorbs only very small quantities of water, traces of inorganic impurities increasing the amount to a large extent. Similar results hold for ammonia. The hydrophobic nature of charcoal is offered as an explanation. For relative pressures (i.e., absorption pressure/vapour pressure of liquid) below 0.1, the adsorption of water vapour obeys Henry's law over a range -30° to 218° . Above this, the pressure increases less rapidly than the concentration until a constant relative pressure of 0.5 is attained. The adsorption reaches a maximum at the triple point. The heat of adsorption at the ordinary temperature is approximately equal to the latent heat of evaporation of liquid water; it increases slightly as the concentration increases. At higher temperatures, it is smaller at low concentrations and increases more rapidly with rising concentration. The partial molal heat capacity of adsorbed water at low concentration is 38 g.-cal./mol.

S. K. TWEEDY.

Absorption of hydrogen and carbon dioxide by pyrophoric iron, nickel, and cobalt. I. N. I. NIKITIN (J. Russ. Phys. Chem. Soc., 1926, 58, 1081—1094).—The absorption of hydrogen and carbon dioxide by finely-divided iron, cobalt, and nickel was investigated at various pressures and temperatures. The pyrophoric metals were obtained by the reduction of their carbonates with hydrogen at 520° for iron, and 350° for nickel and cobalt. At higher temperatures, the metal powders rapidly became crystalline, and lost much of their absorptive power. The addition of aluminium oxide raised the crystallisation temperature. Iron, which adsorbed hydrogen strongly at the temperature of liquid air, was inert between -80° and $+16^\circ$, and at higher temperatures absorbed the gas in increasing quantities. The low-temperature surface absorption obeyed Freundlich's expression, $a = kp^{1/n}$. Carbon dioxide was strongly absorbed, even at the ordinary temperature. On heating at 500° , absorption of the gas by the metal and inter-action took place. Nickel (which contained 9% of occluded gas impossible to remove) adsorbed hydrogen at low temperatures. A film of hydride is formed at the ordinary temperature, which begins to dissociate at 100° . The absorption of carbon dioxide was very slight at all temperatures. Cobalt and hydrogen gave variable results, whilst values with carbon dioxide were intermediate between those of iron and nickel. M. ZVEGINTZOV.

Absorption of gases by finely-divided metals. II. N. I. NIKITIN and W. I. SHARKOV (J. Russ. Phys. Chem. Soc., 1926, 58, 1095—1100; cf. preceding abstract).—The preparation and absorptive properties of finely-divided lead, copper, and silver were investigated. No results could be obtained with pyrophoric lead, prepared by the reduction of the carbonate, as it became crystalline below 300° . Copper did not absorb hydrogen at all, and carbon

dioxide only in small quantities at -80° . Silver, prepared by coagulation of Bredig's colloidal solution, adsorbed hydrogen and large quantities of carbon dioxide at low temperatures, but rapidly became crystalline at $150-200^{\circ}$.

Iron absorbed gaseous ammonia readily between -18° and 100° according to Freundlich's expression, but not at all at 500° . The absorptive power of cobalt is about one tenth that of iron, but persists up to 330° . Pyrophoric nickel could not be easily obtained, as it crystallised rapidly. Addition of precipitated aluminium oxide greatly increased its absorptive power, due, probably, to the specific adsorptive properties of the alumina.

M. ZVEGINZOV.

Chemical reactions and sorption phenomena.
 II. S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1926, 58, 983-993; cf. A., 1926, 571).—The application of the law of mass action to sorption phenomena is investigated. The selective sorption of acid radicals by basic gels, and *vice versa*, from neutral salt solutions is considered as a heterogeneous chemical reaction, which takes place inside the solid phase, after an initial surface adsorption. The active mass of the solid sorbent does not remain constant. Various expressions for the kinetics of sorption processes are compared, and the bimolecular formula: $dx/dt = k(a - \gamma x)^2$, where γ is a constant due to secondary processes, is investigated experimentally for the systems: alcoholic starch-alcoholic potassium hydroxide, wool-nitric acid, and wool-hydrochloric acid. The agreement is satisfactory. Regarding the phenomenon as a balanced reaction salt, $RA + \text{acid } HA' \rightleftharpoons RA' + HA$, an expression for the amounts of free RA' and HA produced is deduced and tested for the systems nitroalizarin-copper acetate; manganese dioxide gel-copper acetate, manganese dioxide-cupric chloride. The agreement is very close. The effect of temperature is also studied. The theoretical significance of these results is pointed out, and the necessity of considering absorption and adsorption as fundamentally different phenomena is emphasised.

M. ZVEGINZOV.

Adsorption in salt solutions by manganese dioxide and general deductions from this phenomenon. I, II, and III. M. GELOSO (Ann. Chim., 1926, [x], 6, 352-424; 7, 113-115).—The adsorption of salts from solution, more particularly by precipitated manganese dioxide, has been examined (cf. A., 1920, ii, 334; 1922, ii, 589; 1923, ii, 540; 1924, ii, 413). The variation in the properties of manganese dioxide precipitated under varying conditions was also studied. The main conclusions are summarised below. The composition of the manganese dioxide varies slightly but definitely with the conditions of precipitation. The precipitate is colloidal in nature, and is represented in general by the formula $80MnO_2 \cdot MnO$, the bivalent manganese oxide representing the "impurity" present in the colloid. This is more or less completely replaced by the adsorbed substance, the composition approaching more and more closely to the simple formula MnO_2 as the quantity of adsorbed substance is increased. A relatively smaller amount is displaced by iron than by nickel, but the total adsorption of the latter is

less. This variation in the composition of the adsorbent is, however, negligible in the study of the adsorption phenomenon itself. The latter is specific and characteristic of the salt solution employed, being relatively the more marked the more dilute the solution. In no case was evidence of a definite compound between the adsorbed substance and the adsorbent obtained, the adsorption increasing with increasing concentration of the soluble salt towards a maximum value, which corresponds with saturation of the solid phase. The same results are obtained with a previously precipitated specimen of manganese dioxide, but the total adsorption is less (about 0.6 in the case of iron). This is presumably due to the smaller surface area of the adsorbent owing to the presence of larger grains. The effect of concentration, temperature, and acidity on the adsorption is similar to the corresponding effects on the hydrolysis of salt solutions. It would therefore seem that the adsorption involves a preliminary hydrolysis, and the subsequent substitution of the "impurity" in the adsorbent by one of the products of hydrolysis. Thus increase of temperature increases the amount of adsorption, whilst an increase in the acidity of the medium decreases it, but the decrease is less when a strong acid, such as sulphuric acid, is replaced by a weak acid, such as acetic or formic acid. For the same adsorbent, the same increase in the molecular concentration of the solution corresponds with the same increase in the number of molecules adsorbed, independently of the nature of the substance adsorbed. This increase in adsorption with concentration decreases with rise of temperature, but at no temperature is the adsorption independent of the concentration of the soluble salt. Previous digestion of the adsorbent decreases its surface area, and hence its adsorptive power, the decrease at any particular temperature being greater the longer the period of pre-digestion (but never vanishing), whilst for equal periods of digestion the decrease is greater the higher the temperature employed. After adsorption, however, the surface is no longer modified by contact with the solution, whatever the temperature. In some cases, adsorption proceeds with a definite velocity, and probably obeys the general law for velocity of reactions in heterogeneous systems. The adsorption is probably reversible, tending to attain a dynamic equilibrium, which, however, is established too slowly for satisfactory experimental investigation.

The green solution obtained by the reduction, in acid solution, of potassium permanganate by arsenious acid (Geloso, A., 1921, ii, 115) is a colloidal solution of manganese dioxide of composition $nMnO_2 \cdot MnO$, where n is much greater than 2. On keeping or warming, an oxide of manganese is precipitated; the composition of this varies continuously according to the conditions of its formation. In neutral solution, precipitation occurs during titration; with insufficient acid a yellow solution (Mn_6O_{11}) instead of a green (Mn_3O_5) is obtained, and with a large excess of acid the solution becomes rose-coloured (Mn_2O_3). The precipitates are not regarded as definite chemical compounds, since a very slight alteration in the conditions alters their composition. Addition of increasing quantities of silver ions or manganous

sulphate increases the proportion of oxygen present in the precipitate, which, in the latter case, approximates very closely to the composition MnO_2 . Arsenic acid has a similar, but very much less marked effect, whilst potassium and nitrate ions are without action. A similar green solution is also obtained when concentrated sulphuric acid is added to a solution of potassium permanganate and an alkali arsenite (oxygen being evolved), but in this case both the liquid and the precipitated solid phases contain the same oxide, MnO_2 . In this colloidal state, the manganese dioxide possesses a large adsorptive power, the "impurity" being displaced by adsorbed salts in the same manner as previously observed for precipitated manganese dioxide (cf. above), but to a much greater extent. On the assumption that the adsorption is reversible, the heat of adsorption is calculated with the aid of the laws of displacement of equilibrium with temperature variation, and (except at the b. p.) the calculated value of K in the equation $\gamma = KC^m$ (Geloso, A., 1923, ii, 540) agrees closely with those obtained experimentally. An exact determination of manganese by a modification of Knorre's method is given (cf. A., 1922, ii, 398). J. W. BAKER.

Adsorption of ions by glass. H. DEVAUX and E. AUBEL (Compt. rend., 1927, 184, 601—603).—The adsorption of ions by glass was determined by washing a column of glass-wool with a solution containing the ion concerned, and afterwards washing with distilled water. Glass adsorbs cations (e.g., calcium, hydrogen, potassium, and quinine) reversibly, one ion being replaceable by another. Glass weakly decalcified by acids or by alkali metal salts will adsorb a single layer of calcium ions instantaneously. If the glass is strongly decalcified, penetration takes place into the glass corresponding with several layers of ions, and is a function of the time. Thus the glass behaves as a gel. J. GRANT.

Simultaneous adsorption of ions from solution. I. Adsorption of metal ions by hydrated manganese dioxide. M. MEHROTRA and K. C. SEN (J. Indian Chem. Soc., 1926, 3, 297—306).—The simultaneous adsorption of metallic ion pairs by hydrated manganese dioxide has been investigated for mixtures of barium and copper chlorides, barium and silver nitrates, barium and potassium nitrates, barium and aluminium nitrates, and silver and potassium nitrates. With the exception of silver, the adsorption of any metallic ion is decreased in presence of another adsorbable ion, but the sum of the adsorption of the two ions from a mixture is always greater than the adsorption of either of them alone. Adsorbed silver ion cannot be replaced by either potassium or barium ions, although the latter can be replaced by each other, and in general the greater the concentration of the replacing ion in solution the greater is the amount of adsorbed ion displaced. The cation is adsorbed to a greater extent from a salt which contains a highly adsorbable anion, the adsorption of barium from a mixture of its chloride and aluminium nitrate being greater than from pure barium chloride, and that of copper from a solution of copper chloride being increased in presence of sulphate. J. W. BAKER.

Adsorption by metallic hydroxides. I. Adsorption of arsenious acid by precipitated ferric hydroxide. K. C. SEN (J. Physical Chem., 1927, 31, 419—429; cf. Boswell and Dickson, A., 1919, ii, 49).—The ferric hydroxide used was precipitated at approximately 25° from 2*N*-ferric chloride by excess of dilute ammonia, washed by decantation, and dialysed until free from chloride. Potassium chloride, which, in common with ammonium chloride, was found to have no effect on the adsorption by ferric hydroxide, was added to prevent peptisation. The adsorption of arsenious acid in varying concentrations by a fixed quantity of hydroxide was then measured. Ageing of the latter for 4 months resulted in a 50% decrease in adsorption (cf. Boswell and Dickson, *loc. cit.*). Equilibrium is reached in 3 hrs., and increased contact of the solute with adsorbent has no effect on the adsorption. The generalisation of Mecklenburg (A., 1913, ii, 676) has also been studied. Sodium arsenite is strongly adsorbed by ferric hydroxide, and the adsorption of sodium hydroxide is appreciable. When the total amount of solute remains constant, adsorption increases with the concentration of the solution, and when the concentration remains constant, it is proportional to the quantity of solute present.

L. S. THEOBALD.

Adsorption. XX. Adsorption of ions from mixtures of electrolytes by sols of ferric hydroxide and stannic acid, and ion-antagonism. S. GHOSH and N. R. DHAR (Kolloid-Z., 1927, 41, 223—229).—Quantitative experiments were carried out on the adsorption of anions by ferric hydroxide sols from mixtures of potassium sulphate with each of the following salts of potassium: bromate, iodate, oxalate, ferrocyanide, and chloride. Similar experiments were made with stannic acid sol in mixtures of potassium chloride and barium chloride, copper chloride and barium chloride, silver nitrate and copper sulphate. In general, the adsorption of a given electrolyte is repressed by the presence of another electrolyte, the degree depending on the relative adsorbability of the two ions and also on the adsorbent power of the colloid. The effect of the second electrolyte is most marked when the adsorbent power of the colloid is low. The adsorption of the sulphate ion by ferric hydroxide is increased in presence of hydrochloric acid or ferric chloride.

E. S. HEDGES.

Hydrolytic adsorption. II. Adsorption of electrolytes by barium sulphate and liberation of acids and alkalis in presence of neutral salts. J. N. MUKHERJEE and J. K. BASU (J. Indian Chem. Soc., 1926, 3, 371—388).—Detailed results of experiments previously summarised (Mukherjee, A., 1925, ii, 1149) are given. The amount of acidity developed in a neutral solution of potassium chloride in presence of well-washed barium sulphate depends both on the concentration and nature of the acid present during the precipitation of the sulphate. If the precipitation is carried out in absence of acid, the well-washed precipitate kept in contact with acid for 48 hrs., and again well washed, it is possible by sufficient washing to remove the adsorbed acid, so that no acidity develops on treatment with potassium chloride solu-

tion. The acidity developed is therefore due to the liberation of hydrogen ions by interaction between the adsorbed acid and the neutral salt. The development of alkalinity or acidity when, in the precipitation of barium sulphate, one of the solutions is in excess (*loc. cit.*) is confirmed by *E.M.F.* measurements, and the variation of p_{H} with time is investigated. By electro-osmotic measurements, it is shown that the barium sulphate precipitated in presence of excess of barium chloride is positively charged, whilst it is negatively charged when potassium sulphate solution is in excess during the precipitation. This negative charge is reversed in the presence of 0.0004*N*-barium chloride solution. The washed precipitate obtained by mixing equal volumes of *N*-solutions of potassium sulphate and barium chloride has a slight negative charge, but when the potassium sulphate is replaced by *N*-sulphuric acid the precipitate carries a definite positive charge. The theoretical bearing of the results is discussed.

J. W. BAKER.

Adsorption by a polar precipitate. III. Electro-osmotic experiments with silver iodide. J. MUKHERJEE and P. KUNDU (*J. Indian Chem. Soc.*, 1926, 3, 335—341).—The adsorption of ions from solutions of silver, potassium, barium, calcium, and aluminium nitrates, and of potassium chloride, sulphate, bromide, and iodide by carefully purified silver iodide (cf. Taylor and Beekley, *A.*, 1925, ii, 855) has been studied by electro-osmotic measurements. The silver iodide carries a negative charge in contact with water. The order of adsorption of the cations is $\text{Ag} > \text{Al} > (\text{Ba}, \text{Ca}) > \text{K}$, silver reversing the charge on the precipitate. Unexpectedly, the iodide ion is only weakly adsorbed. The order of adsorption of the other anions is $\text{Br}' > \text{NO}_3' > \text{Cl}' > \text{SO}_4''$.

J. W. BAKER.

Adsorption. I. Explanation of adaptability phenomenon. V. N. KRESTINSKAIA (*J. Russ. Phys. Chem. Soc.*, 1926, 58, 998—1017).—An investigation of the observations of Bayliss and Freundlich on the phenomenon of adaptability. Both reversible and irreversible adsorption reactions were investigated. In the reversible systems, charcoal-aqueous bromine and charcoal-acetic acid, the total adsorption was independent of whether the charcoal was added at once or in successive small quantities separated by time intervals. In the irreversible systems: charcoal-crystal-violet solution, benzoic acid-charcoal, many days were required for the attainment of equilibrium, and consequently the parallel experiments were not strictly comparable. A new method was devised, based on the principle of "action impulse," *i.e.*, the product of the active mass of the reactants into the time of action, which gave sets of results which could be compared. The phenomenon of adaptability was not observed in these circumstances, and must be ascribed to the fact that the systems in which it appeared were not in equilibrium.

M. ZVEGINTZOV.

Surface tensions of water-alcohol mixtures. P. BRUN (*Compt. rend.*, 1927, 184, 685—687).—Comparative studies of the surface tensions of mixtures of water, ethyl alcohol, and an alcohol com-

pletely, partly, or non-miscible (propyl, *isobutyl*, and *isoamyl* alcohols, respectively) have been made. Triangular diagrams, analogous to those for the densities and refractive indices (*A.*, 1926, 683), have been constructed, from which the composition of the mixtures may be determined. In no case does the simple mixture law hold for the surface tensions.

J. GRANT.

Surface tension and viscosity of solutions of the hydroxides of potassium, sodium, lithium, thallium, and barium, and of sodium carbonate solution. O. FAUST (*Z. anorg. Chem.*, 1927, 160, 373—376).—The surface tension, viscosity, and specific gravity of solutions of the hydroxides of the alkali metals, barium and thallium, and of sodium carbonate have been determined at 20° for concentrations varying from 0.1 to 6*N*. In all cases, except thallous hydroxide, the viscosity increases rapidly and the surface tension slowly with the concentration; this effect is most marked with sodium hydroxide and least noticeable with potassium hydroxide. The viscosity of solutions of thallium hydroxide decreases with rise in concentration, probably owing to the lower state of hydration of the ions.

A. R. POWELL.

Cell mitosis. W. D. BANCROFT and C. GURCHOT (*J. Physical Chem.*, 1927, 31, 430—438).—When the surface tension of a drop of liquid is lowered locally at two opposite points, the drop tends to divide equatorially, along the line of the relatively highest surface tension.

L. S. THEOBALD.

Dielectric constants of dilute solutions of electrolytes. H. SACK (*Physikal. Z.*, 1927, 28, 199—210; cf. *A.*, 1926, 456).—The dielectric constants of certain aqueous solutions of electrolytes have been determined by the Nernst "bridge" method for concentrations of the order 0.00017—0.0013*M*. The expression $D_1 = D_0(1 - \alpha c)$ reproduces the experimental values (D_1 and D_0 are the dielectric constants of solution and solvent, respectively, c is the molar concentration, and α is a constant depending on the solute). The following values for α were obtained: sodium chloride, 7.1 ± 1.2 ; potassium chloride, 6.9 ± 1.0 ; lithium chloride, 7.4 ± 1.4 ; barium chloride, 16.5 ± 2.8 ; magnesium sulphate, 17.3 ± 2.7 ; copper sulphate, 19.0 ± 2.3 ; lanthanum nitrate, 24.2 ± 3.4 ; lanthanum chloride, 26.5 ± 3.3 .

On the basis of the dipole theory of the dielectric constant of aqueous solutions, the author's expression $D = D_0(1 - 3.0c)$, which is applicable only to uni-univalent salts, has been extended to multivalent ions. If d_1 is the drop in the dielectric constant of water due to the presence of a univalent ion, and d_z is that due to an ion of valency z , $d_z = d_1 \sqrt{z^3}$. This expression gives, in conjunction with a value of 3.3 for d_1 , a complete account of the experimental data, within the limits of error. The mathematical basis for the views expressed is discussed.

R. A. MORTON.

Rotatory dispersion, in the ultra-violet, of aqueous solutions of tartaric acid containing boric acid. R. DESCAMPS (*Compt. rend.*, 1927, 184, 876—878).—Earlier experiments (this vol., 307) have been continued using widely different molecular pro-

portions of boric and tartaric acids. Where definite conclusions can be reached, the rotatory dispersion curves all belong to the anomalous complex type. The results are explained by the presence of at least two constituents of opposite optical activities and different dispersions.
J. GRANT.

Anomalies of Raoult's cryoscopic law. A. JOURNIAUX (Bull. Soc. chim., 1927, [iv], 41, 308—313).—The abnormal mol. wt. obtained for metals in metallic solvents by cryoscopic methods (A., 1926, 116), as compared with those obtained by other methods, are shown to give the correct values when multiplied by the "coefficient of equivalence" of the solute with respect to the solvent (Guillet, A., 1906, ii, 357). If, from the point of view of structure and mechanical properties, 1% of tin in an alloy is equivalent to 2% of zinc, then the coefficient of equivalence of tin with respect to zinc is 2. The correction is inapplicable when allotropic changes occur (e.g., in the thallium-tin system).

S. K. TWEEDY.

Preparation of sols by reduction with tobacco liquor. A. JANEK (Kolloid-Z., 1927, 41, 242—243).—A filtered, aqueous extract of a cigar produces colloidal gold on boiling with a dilute solution of gold chloride, the product being red, violet, or blue, according to the amount of tobacco liquor used. A similar experiment, using silver nitrate, gives a brown colloidal solution of silver.
E. S. HEDGES.

Colloidal zinc. W. ENGELHARDT (Kolloid-Z., 1927, 41, 234—242).—An apparatus is described for the preparation of colloidal zinc in hot water by an electro-dispersion method, the influence of temperature, applied voltage, and duration of experiment on the stability of the product being investigated. Attempts to stabilise the product by previous addition of protective colloids were unsuccessful. The colloidal zinc, especially in hot solutions, is rapidly transformed into zinc oxide. The total zinc content of the sol was measured by adding 0.1*N*-sulphuric acid and titrating the excess with sodium hydroxide, and the content of free zinc by adding 0.1*N*-iodine and titrating the excess with sodium thiosulphate, or by analysis of the gaseous products of dispersion, or by measurement of the hydrogen produced on addition of acid to the colloid. The properties of colloidal zinc are described as regards colour, coagulation, viscosity, addition of electrolytes, and protection by other colloids. The system may be regarded as colloidal zinc in which the particles are protected by a sheath of zinc oxide.
E. S. HEDGES.

Preparation and properties of colloidal and monoclinic sulphur in organic liquids. I. D. GARARD and (MISS) F. M. COLT (J. Amer. Chem. Soc., 1927, 49, 630—636).—Sulphur sols were prepared by passing hydrogen sulphide and sulphur dioxide into organic liquids, the dense precipitate being removed by filtration. The sulphur concentration obtained in benzene (taken as a typical liquid) is practically independent of the purity of the latter, the order of introduction of the gases, and the method of stirring. The deep yellow benzene sols contain 1.4—1.8% of sulphur and are almost unaffected by electrolytes;

their high stability is probably not due to the protective action of acids or water. The sulphur dialyses through animal and cellulose acetate membranes more slowly than dissolved sulphur. Evaporation and freezing of the sol yield amorphous sulphur (?*S*_μ), and the solubility of crystalline sulphur in the sol is the same as in pure benzene. The sols in ethyl alcohol and glycerol are very unstable, the filtrate in the former case depositing all the sulphur as monoclinic crystals within 2 days. These crystals, some of which were remarkably stable, were also obtained from alcoholic ammonium polysulphide solutions.

S. K. TWEEDY.

Electrolytic preparation of colloidal silver halides. T. WEREIDE (Z. Physik, 1927, 41, 864—866).—Colloidal silver halides are produced when dilute solutions of hydrochloric, hydrobromic, and hydriodic acids are electrolysed between silver electrodes by alternating current of frequency 50 cycles per sec. The freshly-produced micelles have an abnormal mobility of 450×10^{-5} cm. sec.⁻¹/volt cm.⁻¹, which is reduced to the normal value for colloid particles by the addition of agar-agar.

R. W. LUNT.

Modification of the electric sign of colloids at will. A. BOUTARIO and (MLLE.) G. PERREAU (Compt. rend., 1927, 184, 814—816).—Two zones exist in the flocculation of colloidal solutions by multivalent electrolytes (this vol., 309). The signs of positive and negative colloids are reversed by the action of electrolytes with multivalent anions and cations, respectively, when the concentrations are such that flocculation does not occur.
J. GRANT.

Non-existence of the amorphous state. P. P. VON WEIMARN and T. HAGWARA (Koll.-Chem. Beih., 1927, 23, 400—427; cf. A., 1926, 338).—It is shown how von Weimarn's theory has led to the view that not only crystals, but all forms of matter possess a vectorial structure. The influence of the degree of dispersion of the structural elements of a substance on the vectorial character and the dependence of the degree of stability on the dimensions of the individual structural elements which occur in aggregates in the practically unoriented condition are considered. A summary is given of the conclusions reached from von Weimarn's theory which have been confirmed by the investigation of disperse systems in polarised light, and by X-ray examination. The views of Haber (A., 1922, ii, 553), relative to the conditions which give rise to crystalline or amorphous precipitates or sols, are criticised.
L. L. BIRUMSHAW.

Mechanical methods for dispersion of cellulose. P. P. VON WEIMARN (Kolloid-Z., 1927, 41, 258—260).—The author's method for the production of cellulose sols by means of the "dispersoid mill" is described. Nordlund's method for the dispersion of liquids (A., 1920, ii, 376) was applied to cellulose, using a concentration of 0.02—0.08 millimol. of sodium citrate per litre as the dispersion agent. Ultra-microscopic particles of cellulose were also observed in distilled water which had been vigorously shaken with filter-paper and kept, but the yield of colloid obtained by this method is too low to make it of practical use.
E. S. HEDGES.

Influence of polymerisation on the Röntgen diagram. I. Polymerisation and amorphous Röntgen spectra. J. R. KATZ (Z. physikal. Chem., 1927, 125, 321—330).—The types of Röntgen spectra given by polymerised substances such as caoutchouc, proteins, and polysaccharides are discussed. From Keesom's work on liquids composed of small molecules (Proc. K. Akad. Wetensch. Amsterdam, 1922, 31, 87), it would be expected that the diameter of the chief amorphous ring would decrease sharply when the molecules aggregate to form a polymerised molecule. The Röntgen diagrams have been determined for styrene and *m*-styrene, isoprene and caoutchouc, acrylic acid and polymerised acrylic acid, dicyclopentadiene and dicyclopentadiene-caoutchouc, and tung oil. The results show that in no case is there any appreciable difference between the diameters of the chief rings given by the polymerised and unpolymerised molecules. H. F. GILLBE.

Colloidal phenomena in dye solutions. W. C. HOLMES (J. Amer. Chem. Soc., 1927, 49, 790—791).—Springly soluble rosaniline phenoxide, $C_{20}H_{20}N_3 \cdot OPh$, prepared by the fusion of rosaniline base with phenol, readily forms aqueous colloidal solutions. Dilution of such solutions is accompanied by a deepening of the colour, owing to the dissociation of the solute molecules; after a time, association occurs and the colour fades. Dilute alcoholic solutions are fairly stable. Spectrophotometric measurements are recorded. S. K. TWEEDY.

Spontaneous structure formation in vanadium pentoxide sols. H. ZOCHER and K. JACOBSON (Kolloid-Z., 1927, 41, 220—222).—An introductory paper to experiments which show that some sols separate spontaneously into two phases, one isotropic and dilute and the other anisotropic and concentrated. E. S. HEDGES.

Spontaneous structure formation and thixotropy in fresh vanadium pentoxide sols. J. JOCHIMS (Kolloid-Z., 1927, 41, 215—220).—A drop of 1—2% vanadium pentoxide sol was examined under the ultramicroscope during strong illumination, and the formation of radially disposed, angular, rod-like particles was observed, the process being accompanied by increase in viscosity. This change is due to heat radiation rather than to light, since the effect is not observed when the heat rays are filtered out. The same change is brought about by the addition of small quantities of sodium chloride, calcium chloride, or potassium sulphate, whilst higher concentrations of the electrolyte cause the formation of a thixotropic gel. E. S. HEDGES.

Formation of hailstones and cause of the polymorphic behaviour of ice. K. C. BERZ (Kolloid-Z., 1927, 41, 196—200).—Attention is directed to the similarity in structure between hailstones and gallstones, oolites, etc., particularly in regard to their formation in concentric shells, and it is suggested that the water passes into a colloidal state during the formation of hail. The known physical properties of solid water under different conditions of temperature and pressure are considered in the light of molecular association, and it is thought likely that a

colloidal solution of polymerised molecules is produced in unassociated water molecules acting as the dispersion medium. E. S. HEDGES.

Continuity of electrical structure of colloid particles, ions, electrons, and sub-electrons. S. N. RAY (Kolloid-Z., 1927, 41, 193—195).—Theoretical. The ratio e/a , where e is the maximum charge on a particle irradiated by ultra-violet light and a the diameter of the particle, is a constant for a given colloidal substance. Consideration of the increase in charge of a particle resulting from the increase of the diameter by an element of length leads to a new "atomic" view of electricity differing from the electronic view. The cataphoretic motion of the particles is considered in this light. E. S. HEDGES.

Theory of the colloid reactions of the cerebrospinal fluid in reference to clinical practice. W. SCHMITT (Kolloid-Z., 1927, 41, 261—271).—A review of the colloid reactions of the cerebrospinal fluid. E. S. HEDGES.

Cerebrospinal fluid. A. STEIGMANN (Kolloid-Z., 1927, 41, 276—277).—In connexion with the work of Epstein and Rubinstein (this vol., 274) on the part of the cerebrospinal fluid precipitable by gold, the author points out that, in the inhibitive action of physiologically important substances on the reduction of silver sodium thiosulphate by hyposulphite, only cystine has an appreciable effect. It also appears to be necessary for the nitrogen to remain trivalent through the absence of acids. E. S. HEDGES.

Protected silver hydrosols. J. VOIGT (Kolloid-Z., 1927, 41, 271—275).—Addition of water to "collargol" causes partial precipitation of the colloidal silver, whilst with the silver sol "dispargen," complete precipitation occurs. The precipitated silver is peptised by the addition of small quantities of sodium chloride, and it is considered that small quantities of electrolytes are necessary for the stability of these sols. The minimal quantity of sodium chloride required to peptise completely the precipitate from diluted "dispargen" was determined. E. S. HEDGES.

Colour and sensitiveness to light of silver sols. E. WIEGEL (Z. wiss. Phot., 1927, 24, 316—325).—The slow change of colour of dextrin silver sols through orange, purple-red, and violet to blue is due to the presence of the sodium hydroxide used in their preparation. The time necessary for the coagulation to attain a given stage is greater the smaller the concentration of the sodium hydroxide originally present. Coagulation is also accelerated by the action of light, especially that of small wave-length. Spectrometric measurements in which the extinction coefficient is plotted against wave-length show well-defined maxima for the purple-red, violet, and blue sols, and the sols obtained by rapid coagulation show several absorption maxima, due to the irregularity of flocculation. Sols having an identical colour by transmitted light may be different with reflected light, according to the method of preparation; if produced by slow coagulation, they show only a turbidity, since the colloidal particles consist of smaller particles not in complete optical contact, whereas if obtained

by rapid coagulation they exhibit a metallic lustre, the particles being of a compact structure.

S. J. GREGG.

Constitution of arsenious sulphide sol in presence or absence of arsenious acid. S. G. CHAUDHURY and P. KUNDU (J. Indian Chem. Soc., 1926, 3, 345—348).—The atomic ratio of arsenic to sulphur in an arsenious sulphide sol in which arsenious acid is in excess is 1:1.46, whilst in another sol prepared by the action of an excess of hydrogen sulphide on arsenious acid, but in which both free arsenious acid and hydrogen sulphide are absent, the ratio is 1:2. The constitution of the former sol therefore corresponds with arsenic trisulphide and the latter either with $As_2S_3 \cdot As_2S_5$ or $As_2S_3 \cdot H_2S$, the latter being the more probable.

J. W. BAKER.

Complexity and micelles. Ferric hydroxide sol as a typical example of the colloidal state. G. MALFITANO and M. SIGAUD (J. Chim. phys., 1927, 24, 173—203).—An extensive investigation has been made of the properties of ferric hydroxide sol. The physico-chemical properties, studied chiefly from conductivity and osmotic pressure measurements, are shown to be those of electrolytic couples, with, however, a much greater tendency to association. Three types of flocculation are recognised: (1) When the solution is slightly opalescent, of a reddish-yellow colour, and does not show visible particles in the ultramicroscope, ultrafiltration effects no separation; (2) when the liquid is opaque, yellow-ochre in colour, but homogeneous to the eye, and shows distinct points of light in the ultramicroscope, ultrafiltration separates part of the colloid, which is said to be in the second stage of flocculation; the ultrafiltrate contains the colloid in the first stage of flocculation; (3) when the liquid commences to separate visibly into layers, ultrafiltration removes the whole of the colloid from solution, in what is termed the third stage of flocculation. The properties of the three forms of precipitate are: yellowish-red, and not sensibly reversible; dark red, and easily reversible; brick-red, and very resistant to the dissolving action of acids. Each precipitate is formed between certain limits of the ratio iron:chlorine, but is not necessarily of constant composition.

It is suggested that the precipitates are of the same type as Werner's co-ordination compounds; three forms are therefore theoretically possible: $\{[Fe(OH)_3]_6 \cdot Fe\}^{+++} Cl_3^-$; $\{[Fe(OH)_3]_3 \cdot FeCl\}^{++} Cl_2^-$; $\{[Fe(OH)_3] \cdot FeCl_2\}^+ Cl^-$.

A theory of micellary structure is built up from this point of view, and is adequately supported by a large amount of experimental evidence.

H. F. GILLBE.

Plant colloids. XVII. Peptisation of starch by ultra-violet light. M. SAMEO (Koll.-Chem. Beih., 1927, 23, 377—399).—On exposing thin layers of potato starch in presence of air to the rays of a quartz lamp, the starch becomes yellow and the odour of acetaldehyde is observed. The properties of solutions obtained by heating such starch with water under pressure indicate that considerable peptisation has occurred, together with a certain amount of oxidation and hydrolysis. The behaviour on electro-

dialysis depends on the length of exposure to ultra-violet light, the amount of "gel" being smaller the longer the time of exposure. The phosphorus remains largely in organic combination, and a simple organo-phosphoric acid can be isolated in the anode cell on electro-dialysis. The cleavage products separated by ultrafiltration, although possessing a lower optical rotation, show the typical iodine colorations of the amylo-compound. The mean molecular magnitudes of such compounds have been determined. Observations have also been made at 50° on starch which has been previously dried, or washed with hydrochloric acid and dried and exposed to ultra-violet light in a stream of dry nitrogen and in closed vessels in an atmosphere of nitrogen, whereby oxidation and hydrolysis are prevented. The solutions prepared under pressure from the exposed starch are sometimes cloudy and deposit a precipitate on centrifuging. Wheat starch is also peptised by ultra-violet light, and in this case the behaviour of the solution on electro-dialysis is the reverse of that of the unexposed starch. An explanation is offered for this. As with potato starch, a relatively simple organic acid containing phosphorus is found in the anode cell on electro-dialysis.

L. L. BIRCUMSHAW.

Complexity and micelles. G. MALFITANO and M. SIGAUD (J. Chim. phys., 1927, 24, 103—109).—Colloidal particles are formed by the union of complexes, which in turn are micellar, produced by the grouping of x mols. of a non-electrolyte M about one or more ions, so that the charge is concentrated at the centre of the particle; these complexes may capture more ions, in which case the newly-acquired charge will be resident in the periphery. A primary complex would thus be represented as $(M_x a)^{\pm b, r}$, and a secondary as $[(M_x a b)_r (M_x a)]^{\pm b, r}$. In flocculation, which consists in the union of complexes, growth proceeds mainly in geometrical progression, whilst in crystallisation, where atoms or molecules are added to much larger particles, it proceeds in arithmetical progression. The theory explains the three modifications of colloidal solution obtained by hydrolysing ferric chloride, since they are readily represented by $[Fe(FeO_3 H_3)_m]^{+++} Cl_3$, $[Fe(FeO_3 H_3)_m Cl]^{++} Cl_2$, and $[Fe(FeO_3 H_3)_m Cl_2]^+ Cl$. Moreover, the marked effect of the addition of anions of high valency in stabilising ferric chloride sol, contrasted with the negligible effect of cations, is also readily explained. S. J. GREGG.

Apparent viscosity of colloidal solutions. E. HATSCHKE (J. Physical Chem., 1927, 31, 383—392).—McBain's hypothesis of ramifying micellar aggregates (A., 1926, 351) is adversely criticised. There is no direct evidence of the existence of these aggregates in viscous sols. The ultramicroscope gives little information on the structure of these sols, but there is direct evidence that high viscosity and even gelation may be exhibited by a sol without aggregation or even mutual approach of the particles. Furthermore, sorption experiments can give no information on the degree of hydration in true or in colloidal solution and its variation with concentration. The amounts of liquid taken up by gelatin or rubber during swelling show that the volumes of the disperse phase postulated by Hatschek's formula are not impossible

or improbable. An examination of the behaviour of rubber in benzene, carbon tetrachloride, and in tetrachloroethane shows that rubber swells more in the chlorine-substituted derivatives, *i.e.*, in those solvents in which it exhibits higher viscosities. This is in strict accordance with the assumptions and formula of Hatschek. Finally, if the viscosity of a sol varies with the shear gradient, then single measurements at arbitrary and unknown shear gradients have no theoretical value.

L. S. THEOBALD.

Elasticity and some structural features of soap solutions. W. SEIFRIZ (Third Colloid Symposium Monograph, 1925, 285—295).—Elastic sodium stearate solution has rod-shaped particles, and curd masses crystallise from it; inelastic sodium stearate solution has spherical particles, and no curd crystallises. Sodium oleate is inelastic, and shows ultra-microscopic spherules. Ammonium oleate forms a highly elastic dilute solution, but concentrated solutions may be inelastic as sol, although elastic as gel.

CHEMICAL ABSTRACTS.

Viscosity and flow-elasticity of starch paste. H. FREUNDLICH and H. NITZE (Kolloid-Z., 1927, 41, 206—215).—The viscosity and flow-elasticity of starch paste rise rapidly with increasing concentration, and the high values are due mainly to the amylopectin in the outer sheath of the starch grain. As long as this retains its original membranous structure, the elastic properties do not appear, for a solution of the amylopectin prepared by warming is viscous, but inelastic. Addition of potassium thiocyanate to starch solutions produces a marked decrease in viscosity, and particularly in elasticity, which disappears altogether in a *2N*-solution. Potassium chloride and potassium sulphate exert a similar effect, except that at higher concentrations the viscosity and elasticity rise once more. Ultramicroscopical observation shows that in solutions of potassium thiocyanate the membranes of the starch grains rapidly disappear. It is believed that amylopectin and amylose are peptised and subsequently broken down, with decrease in viscosity and elasticity.

E. S. HEDGES.

Viscosity and hydration. II. Ageing and synæresis. S. LIEPATOV (Kolloid-Z., 1927, 41, 200—206).—A sol of geranin-*G* exhibits "structure"-viscosity, and thus the particles cannot be regarded as independent spheres. Application of Hatschek's formula leads to a value for the density of the substance which is not in keeping with its true density, indicating that the particles are heavily hydrated. Measurements of the increase in viscosity and the change in volume of sols kept for 4 hrs. indicates that continuous hydration of the particles occurs, and this is believed to be the cause of the increased stability of emulsoid colloids with age. On the other hand, the decrease in stability and in viscosity of suspensoid sols with age is attributed to aggregation of the primary particles. With emulsoid colloids, the particles increase in size until the force of attraction between them is sufficient to give the rigidity of a gel. The liquid still separating the particles may then withdraw, accounting for the phenomenon of synæresis. Synæresis was not observed in gels of geranin-*G* more concentrated than 3%. E. S. HEDGES.

Velocity of coagulation of colloids by salts in the presence of a peptiser. K. JABŁOZYŃSKI, G. KAWENOKI, and J. KAWENOKI (Rocz. Chem., 1926, 6, 861—868).—The relative rates of coagulation of ferric hydroxide sols, peptised by ferric chloride, are, for equivalent quantities of potassium iodide, bromide, nitrate, and chloride, in the ratio 1 : 7.92 : 72.9 : 169, whilst potassium thiocyanate and acetate coagulate immediately, although, according to Schulze (A., 1883, 295) and Hardy (A., 1900, ii, 396), the effects produced by these univalent anions should be equal. The differences are attributed to chemical reaction between the ferric chloride and the added salt. This effect is well marked with the chlorides, and much less so with the iodide. In the case of thiocyanate and acetate, double decomposition occurs and iron is removed from solution. It is thus evident that the precipitating power of these anions is closely connected with their ability to combine with ferric chloride.

For chlorides of the alkali and alkaline-earth metals, the rates of coagulation give the following series: $\text{Li} > \text{Na} > \text{K}, \text{NH}_4 < \text{Rb} < \text{Cs}$; and $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$. Whereas the adsorption of cations increases with increasing atomic weight, this stabilising factor is opposed by the tendency towards the formation of double salts.

R. TRUSZKOWSKI.

Volume changes in the formation of rubber sols. I. W. A. GIBBONS and E. HAZELL (J. Amer. Chem. Soc., 1927, 49, 620—630).—The formation of rubber sols in xylene is accompanied by a small volume change, usually (above 30°) a contraction, which is greatest at high temperatures and low concentrations. This is in agreement with the known density change of rubber near 30°. The condition of the rubber (milling etc.) has no great influence on the volume change.

S. K. TWEEDY.

Electrolytic coagulation of colloids. IV. Electrometric and conductimetric titration of mastic sols. A. J. RABINOWITSCH and R. BURSTEIN (Biochem. Z., 1927, 182, 110—120).—The preparation of *a* and *b* mastic sols is described. The former is obtained by pouring water into an alcoholic solution of gum mastic, the latter by pouring the alcoholic solution into water. *a*-Sols when titrated with alkali give a conductivity curve with a sharp minimum, whilst *b*-sols show a continuous increase in conductivity with no minimum or break. The hydrogen-ion concentration of *a*-sols, but not of *b*-sols, determined by conductimetric and electrometric methods is the same. *b*-Sols filter very slowly. *a*-Sols are more acid than *b*-sols, and consist of smaller particles. Mastic sols, when coagulated by salt solutions, undergo no increase in acidity. Mastic sols are much weaker acids than arsenic trisulphide sols. Various cations replace the hydrogen ions of mastic sols in equivalent proportions. The Hardy-Schulze law is inapplicable to the process.

J. PRYDE.

Influence of dielectric constant of medium on rate of coagulation of an arsenious sulphide sol by electrolytes. J. MUKHERJEE, S. G. CHAUDHURY, and S. MUKHERJEE (J. Indian Chem. Soc., 1926, 3, 349—357).—The coagulating concentrations of hydrochloric and sulphuric acids, and of potassium, lithium,

barium, and aluminium chlorides on an arsenious sulphide sol in presence of varying concentrations of ethyl and methyl alcohols, acetic, propionic, oxalic, and formic acids have been determined. In most cases, the addition of ethyl alcohol stabilises the sol. With aluminium chloride, the coagulating concentration diminishes with increasing concentration of the added substance, but when oxalic acid is added, it first increases and then diminishes. With barium chloride, the coagulating concentration is unchanged with formic acid, decreases with increasing concentration of methyl alcohol, and increases in all other cases. The authors believe that the main effect of the added substance is to lower the dielectric constant of the medium, and, in agreement with the results of Kruyt and van Duin (A., 1914, ii, 182), find that the behaviour of the coagulating ion cannot be predicted from its valency. Weiser's explanation (A., 1925, ii, 108) is shown to be insufficient. J. W. BAKER.

Charge reversal by hydrogen and hydroxyl ions with insoluble organic acids and amines, and reversal of the charge of hydrated silica and copper oxide by solutions of salts. J. N. MUKHERJEE and M. P. V. IYER (J. Indian Chem. Soc., 1926, 3, 307—322; cf. Mukherjee, A., 1922, ii, 689).—The effect of hydrogen and hydroxyl ions and of neutral salts on various insoluble organic acids, amides, and esters, and on hydrated silica and copper oxide has been determined by electro-osmotic measurements. Benzoic and *m*-aminobenzoic acids are positively charged in contact with their solutions in pure water, cinnamic, salicylic, boric, and phenylglycine-*o*-carboxylic acids are negatively charged. Hydrochloric acid causes a marked increase in the positive charge or decrease in the negative charge, and in the case of boric and the amino-acids, actually causes a reversal in sign. With the exception of amino-acids, which show a preferential adsorption of hydrogen ions, addition of alkali causes an increase in the negative charge, whilst neutral salts have very little effect. The insoluble organic acids, therefore, show a strong, and generally preferential adsorption of the constituent ions, and also adsorb hydrogen and hydroxyl ions in the dehydrated state, their effect being in all probability to neutralise the hydroxyl and hydrogen ions, formed by the dissociation of the fixed water molecules, in the primary layer. Both salol and *p*-nitroaniline are negatively charged in contact with pure water and show a preferential adsorption of hydroxyl ions. Both aniline hydrochloride and aluminium chloride cause reversal of the charge in hydrated silica. With the latter salt, there is an increase in the negative charge at low concentration, then a decrease, and finally reversal as the concentration is increased. Sulphate ions reverse the charge on hydrated copper oxide, but no reversal is observed with chlorides and nitrates. Neutral electrolytes increase the positive charge on copper hydroxide, the effect being independent of the nature of the cation.

J. W. BAKER.

Peptisation of metathoria. G. R. LEVI and A. REINA (Atti R. Accad. Lincei, 1927, [vi], 5, 174—180).—From X-ray observations made according to a modified form of the Debye-Scherrer method it

would seem that the space-lattice of metathoria is unchanged after peptisation. R. W. LUNT.

Sensitisation of sols by small amounts of other colloids. S. GHOSH and N. R. DHAR (Kolloid-Z., 1927, 41, 229—234).—The sensitisation of positively-charged colloids, such as ferric hydroxide, chromic hydroxide, aluminium hydroxide, and certain colouring matters by the negatively-charged colloids gelatin, albumin, and tannin is due to a neutralisation of the charge. On the other hand, the sensitisation of the negatively-charged colloids, arsenious sulphide, antimony sulphide, molybdenum pentoxide, silicic acid, silver, gold, and gum arabic by the same agents is due to repression of hydrolysis of the sols through the presence of small amounts of hydrogen ions in the gelatin, albumin, etc. E. S. HEDGES.

Sensitising of hydrophobe colloids by proteins. N. N. ANDREJEV (Biochem. Z., 1927, 182, 65—71).—Native proteins contain protein anions only, which at certain concentrations produce a coagulation of positively-charged sols. At lower concentrations, the protein anions sensitise the colloids to the action of neutral salts, whilst at higher concentrations the protein anions confer protection on the colloids. Native proteins produce no flocculation or sensitisation of negatively-charged colloids, but may exercise a protective action, as in the case of positive sols. Acidified protein solutions do, however, in certain concentrations, cause flocculation of negative sols.

J. PRYDE.

Decomposition of salt solutions by "galvano-colloidal" metal hydroxides. K. RUEGG (Kolloid-Z., 1927, 41, 275—276).—When a paste of aluminium hydroxide, or similar colloid, is placed in a solution of certain metallic salts, adsorption of either acid or base occurs, leaving the solution with excess of alkali or acid. This effect is considered in relation to the softening of water and the corrosion of metals in neutral salt solutions. In the latter case, it is supposed that the colloidal skin of hydroxide first formed adsorbs the basic constituent of the salt, leaving the acid to attack the metal further. E. S. HEDGES.

Imbibition of gelatin dried as a gel and as a sol. R. A. GORTNER and W. F. HOFFMAN (J. Physical Chem., 1927, 31, 464—466; cf. A., 1923, i, 965; Sheppard and Elliott, A., 1922, i, 387).—The imbibition of water by gelatin dried as a gel and as a sol has been studied. The initial rate of imbibition is generally greater in the gelatins prepared from the sols, but the amount imbibed is always greater in those prepared from the gels. The behaviour of the latter reflects, to a considerable degree, their previous history, and the differences in behaviour between the sol and the gel preparations are attributed partly to the persistence of a gel structure.

L. S. THEOBALD.

Differences in the heat of reaction between artificial and soil gels of silica, alumina, and iron with hydroxides. G. J. BOUYOUKOS (Soil Sci., 1927, 23, 243—247).—When soils, soil colloids, or artificial gels of silica, or the hydrated oxides of iron and aluminium are treated with potassium hydroxide or sodium hydroxide, heat of reaction apart from heat of wetting is developed. More heat is developed

with artificial gels than with soils or soil colloids. It is probable that the soil gels are not in the same condition as those prepared artificially.

G. W. ROBINSON.

Diffusion of aqueous sodium silicate solutions across semipermeable membranes. P. B. GANGLY (J. Physical Chem., 1927, 31, 407—416).—The diffusion of aqueous solutions of sodium silicate across membranes of parchment and of collodion has been studied. After equilibrium is reached, the concentration of silica in the original silicate compartment is usually greater than that in the water compartment. The distribution depends largely on the original ratio $\text{SiO}_2 : \text{Na}_2\text{O}$ of the solutions. Solutions up to the ratio 3:1 show but small variations in concentration during diffusion, indicating that the non-diffusible matter is small in these cases. Beyond this ratio, the amount of non-diffusible matter increases rapidly. The amount of sodium left in the silicate compartments also increases, and is greater than the quantity of sodium in the water compartment. This is taken to indicate that the colloidal matter at the higher ratios is present as molecular aggregates or ionic complexes containing sodium and silica. Measurements of osmotic pressure after equilibrium has been reached show that the colloidal matter increases with an increase in the ratio of SiO_2 to Na_2O (cf. Harman, this vol., 415), and p_{π} measurements show that hydrolysis plays no great part in the distribution processes.

L. S. THEOBALD.

Cation and anion exchange at the surface of permutite. H. JENNY (Koll.-Chem. Beih., 1927, 23, 428—472).—The ionic exchange between lithium, sodium, potassium, ammonium, magnesium, calcium, barium, and aluminium permutites and solutions of a number of chlorides of uni- and bi-valent metals has been investigated. The constants $1/p$ and K in Wiegner's modification of Freundlich's adsorption isotherm, $y = K[c/(a-c)]^{1/p}$ (where y = the exchanged quantity on 1 g. of permutite, a = the concentration of the added solution, and c = the concentration at equilibrium) have been calculated. The equivalence of the exchange was confirmed by experiments with potassium permutite and sodium chloride. The power of exchange of an ion increases with increasing atomic weight, and the exchange constants are directly proportional to the ionic volumes. The connexion with the hydration effect is discussed. In the case of univalent ions, the course of exchange from liquid to solid phase and from solid to liquid phase proceeds normally. With increasing hydration, the exchange from liquid to solid decreases, whilst that from solid to liquid increases. Hydrogen occupies an anomalous position. At low concentrations, bivalent ions have a greater power of exchange than the corresponding hydrated univalent ions, but at higher concentrations the power of exchange is less. The bivalent ions are more strongly adsorbed by the permutite than the univalent. The lyotropic series is not reversed with bivalent ions, as is the case with univalent. The anomalies shown by bivalent ions are ascribed to insoluble hydroxide formation with the hydroxyl ions of the Helmholtz inner layer.

L. L. BIRCUMSHAW.

Thermal dissociation of iodine and bromine. T. DE VRIES and W. H. RODEBUSH (J. Amer. Chem. Soc., 1927, 49, 656—666).—The thermal dissociation of iodine and bromine has been measured between 300° and 1300° Abs. (approx.) by an adaptation of Knudsen's vapour-pressure method (A., 1909, ii, 385). The equilibrium constant for $\text{I}_2 \rightarrow 2\text{I}$ is $\log_{10} p_{\text{I}}^2/p_{\text{I}_2} = -6840/T + \log_{10} T + 1.121$. The entropy of monatomic iodine at 298° Abs. and 1 atm. is 40.5; this is in agreement with the value predicted by the Tetrode equation (40.4), but is considered to be too low. The heat of dissociation of iodine is 31,600 g.-cal. (calc.). The results for bromine are less satisfactory. The equilibrium constant is $\log p_{\text{Br}}^2/p_{\text{Br}_2} = -9000/T + 3.695$, the calculated heat of dissociation being 41,200 g.-cal. The entropy of monatomic bromine at 298° Abs. and 1 atm. is 38.2, the Tetrode equation predicting 39.0.

S. K. TWEEDY.

Theory of concentrated solutions. III. E. WILKE and W. MARTIN (Z. physikal. Chem., 1927, 125, 420—430).—Measurements have been made of the *E.M.F.* of cells of the type $\text{Br}_2|0.1N\text{-HBr}|3N\text{-KCl}|N\text{-HBr}| \text{Br}_2$, with the object of testing the authors' theory of highly concentrated solutions (cf. A., 1926, 906).

H. F. GILLBE.

Dilution law for strong electrolytes. B. SZYSZKOWSKI (Bull. Acad. Polonaise, 1926, A, 325—346).—Molecular conductivity can be expressed as a function of concentration by $1 - a = 1 - \lambda/\lambda_0 = 0.5(\nu - 1)[\beta c^{1/2} - 2\gamma c + 3\delta c^{3/2} \dots]$, in which a is the conductivity coefficient ($a = \lambda/\lambda_0$), ν the number of ions into which the electrolyte dissociates, c the concentration in moles per litre, and β , γ , and δ are constants. By using a sufficient number of terms in the serial expansion, a dilution law for strong electrolytes at any concentration can be obtained. For uni-univalent salts over the range 0.1—0.0001M, $1 - \lambda/\lambda_0 = 1/2 \cdot \beta c^{1/2} - \gamma c + 3/2 \cdot \delta c^{3/2}$ is in agreement with experiment. Kohlrausch's data for 16 suitable salts were used for the calculation of the constants λ_0 , β , γ , and δ . The relationships found provide independent support for the Debye-Hückel theory, and require that λ_0 , β , γ , and δ should be considered as characteristic chemical constants of salt solutions. The ionic mobilities of a number of univalent ions are computed, and the values compared with those of Kohlrausch and of Debye. By an application of the Debye-Hückel theory, the mean ionic radii have been calculated for the 16 salts considered.

R. A. MORTON.

Formation of complexes between cadmium and alkali halides. F. BOURION and E. ROUYER (Compt. rend., 1927, 184, 598—600).—Ebullioscopic determination of the equilibrium constants has shown that in the formation of salts of the type $\text{K}_2[\text{CdI}_4]$, $\text{K}_2[\text{CdCl}_4]$, and $\text{Na}_2[\text{CdCl}_4]$, the constants decrease with the atomic weights of the halogens and of the alkali metals (cf. A., 1923, ii, 534; 1926, 796).

J. GRANT.

Aqueous solutions of sodium silicates. V. Osmotic activity, lowering of vapour pressures and f. p. R. W. HARMAN (J. Physical Chem., 1927, 31, 355—373; cf. A., 1925, ii, 1065; 1926, 478, 796, 907).—Measurements have been made at 25° by a

dynamic method of the lowering of the vapour pressure of sodium silicate solutions of the ratio $\text{Na}_2\text{O} : \text{SiO}_2 = 1 : 1$ and $1 : 2$ over the concentration range 0.1 — $2.5N_w$, and the lowering of the f. p. by the ordinary Beckmann method has been found for the ratios $2 : 1$, $1 : 1$, $1 : 2$, $1 : 3$, and $1 : 4$ over concentrations ranging from 0.01 to $2.0N_w$. The results from the two sets of measurements are in fair agreement, and are expressed, in both cases, in terms of the ionic and activity theories. The osmotic activity in the case of the ratios $2 : 1$ and $1 : 1$, and to a lesser extent $1 : 2$, is high, especially in dilute solutions, but in concentrated solutions the ratios $1 : 3$ and $1 : 4$ show an abnormally low osmotic activity, which, however, is unexpectedly high in dilute solutions. It is suggested that the ratio $1 : 1$ represents the metasilicate, Na_2SiO_3 , which hydrolyses and ionises, giving rise to sodium, hydroxyl, and SiO_3'' ions and crystalloidal silicic acid. The ratio $1 : 2$ represents the salt NaHSiO_3 , behaving in a manner similar to the metasilicate, and giving, in addition, the ion HSiO_3' . The ratios $1 : 3$ and $1 : 4$ suggest the existence of complex aggregates in concentrated solution and of ionic micelles of the composition $[m\text{SiO}_3, n\text{SiO}_2, aq]^m$, where $(m+n)/m$ equals the ratio $\text{Na}_2\text{O} : \text{SiO}_2$ (cf. Ganguly, this vol., 415). L. S. THEOBALD.

Influence of an "indifferent" gas on the concentration and activity of a vapour in equilibrium with a condensed phase or phases. II. I. R. MCHAFFIE (Phil. Mag., 1927, [vii], 3, 497—510; cf. A., 1926, 355).—The concentration of water vapour, in equilibrium with liquid water in presence of air up to a pressure of 100 atm., has been measured at 25° . The presence of filters in the high-pressure portion of the apparatus has been found to influence the results to a marked extent. The probable influence of such filters is discussed. The calculated activity coefficients are in good agreement with those derived from the results of Pollitzer and Strebel (A., 1925, ii, 104). The results are compared with those obtained previously for the system sodium sulphate-water (A., 1926, 355). A. E. MITCHELL.

Dissociation pressures of calcium, strontium, and barium carbonates. W. DUTOIT (J. Chim. phys., 1927, 24, 110—114).—The pressure was measured by a dynamic method, the carbonate being placed in a tube heated in a long furnace, and the carbon dioxide swept out by a slow stream of nitrogen and weighed in an absorption vessel. The results for calcium carbonate, covering the range 707 — 885° , agree closely with those of previous workers obtained by the static method using a manometer. Measurements were also made on strontium carbonate at temperatures between 950° and 1175° , and on barium carbonate over a small range. S. J. GREGG.

Influence of salts on the solubility of water in phenol. R. CERNATESCU and E. PAPAFLI (Z. physikal. Chem., 1927, 125, 331—340, and Ann. Sci. Univ. Jassy, 1927, 14, 285—301).—The solubility was determined by measuring the temperature at which a solution of water in phenol, saturated at 18° , became turbid as the solution was cooled, after the addition of a known quantity of the salt in question. The solubilities of the alkali halides in phenol, saturated

with water at 18° , are found to be in the same order as that of the metals in the periodic table, as is also their power of reducing the solubility of water in phenol. For a constant ratio of phenol to water, the Rothmund equation $(\eta - \eta_0)/\eta = K$ (A., ii, 1900, 467) is found to hold for the alkali halides over a wide range of concentrations. For the alkali iodides, K is proportional to the true radius of the positive ion, as calculated by Born. H. F. GILLBE.

Solubility influences. IV. Salting-out of aniline from aqueous solutions. S. GLASSTONE, (MISS) J. BRIDGMAN, and W. R. P. HODGSON (J.C.S., 1927, 635—640).—A continuation of previous work (cf. A., 1926, 18; this vol., 14). The solubility of aniline has been determined at 25° and 50° in aqueous solutions of various salts. From the data for salts insoluble in aniline, "hydration numbers" for both cations and anions have been determined on the assumption that the number for the iodide ion is zero. The hydration numbers of the anions are very similar to those previously obtained (*loc. cit.*) by the salting-out of ethyl acetate, but the results for some of the cations are abnormal. This may be due to hydrolysis of the salts, or may be connected in some way with the basic nature of the aniline. Experiments on the salting-out power of mixtures confirm the previous conclusion, that this is equal to the sum of the salting-out powers of the constituents, provided allowance be made for the electrical interaction of the ions.

M. S. BURR.

Solubility of calcium salts. I. Solubility of calcium carbonate in salt solutions and biological fluids. A. B. HASTINGS, C. D. MURRAY, and J. SENDROY, jun. II. **Solubility of tricalcium phosphate in salt solutions and biological fluids.** III. **Solubility of calcium carbonate and tricalcium phosphate under various conditions.** J. SENDROY, jun., and A. B. HASTINGS (J. Biol. Chem., 1927, 71, 723—781, 783—796, 797—846).—I. A formula for the solubility of calcium carbonate in solutions of known hydrogen-ion concentration and carbon dioxide tension has been derived. The influence of the hydrogen-ion concentration and of the presence of other salts on the solubility product has been studied. In the presence of dissolved phosphate, there is a tendency to form supersaturated solutions. The solubility of calcium carbonate in solutions of sodium citrate varies with the concentration of citrate and with the hydrogen-ion concentration. It is concluded that a slightly dissociated calcium citrate compound is formed. When solutions of citrate saturated with calcium carbonate are shaken with solid calcium phosphate, the calcium content decreases. From analyses of serum, it would appear that the solubility product for calcium carbonate is $10^{-6.40}$, compared with $10^{-7.40}$ in salt solutions of similar ionic strength. Calcium carbonate does not dissolve in serum from which much of the calcium has been removed by oxalate, nor does it precipitate from serum the calcium concentration of which has been augmented by the addition of calcium chloride even in presence of solid calcium carbonate, but after inorganic phosphate has been removed the equilibrium appears to be reversible with respect to

calcium salts. The solubility of calcium carbonate in serum of various concentrations and in exudates has been studied. Although it was not possible to demonstrate that the serum of parathyroidectomised dogs was less able than normal serum to retain calcium in solution, it was found that the parathyroid hormone, when added to solutions of inorganic salts, did actually tend to prevent the precipitation of calcium carbonate.

II. The following equations are derived for the dissociation constants of phosphoric acid: $pK_1' = 2.11 - 0.5\sqrt{\mu}$, $pK_2' = 7.15 - 1.25\sqrt{\mu}$, and $pK_3' = 12.66 - 2.25\sqrt{\mu}$, where μ is the ionic concentration. Values are obtained for the solubility product of calcium phosphate. When serum is shaken with calcium phosphate, the calcium content decreases without a corresponding diminution in the phosphate ions, and it is suggested that calcium carbonate is precipitated, although no precipitation of calcium takes place when the serum is shaken with calcium carbonate.

III. From the solubilities of calcium carbonate and of calcium phosphate in salt solutions of various hydrogen-ion concentrations, expressions have been obtained for the solubility products in terms of the total ionic concentration and also for the activity coefficients of these two salts as well as of the calcium ion. The results have been compared with similar data obtained from experiments in which the calcium content of serum was determined under various conditions, and in particular the rate at which calcium is lost when the serum is shaken with calcium phosphate and calcium carbonate has been ascertained. The effect of alteration of the serum concentration and of the presence of red blood cells on the solubility of these salts has been determined. These results are best explained by the assumption of the existence of some slightly dissociated calcium complex.

W. O. KERMAK.

Co-existing liquid and vapour phases of solutions of oxygen and nitrogen. B. F. DODGE and A. K. DUNBAR (J. Amer. Chem. Soc., 1927, 49, 591—610).—The liquid-vapour phase equilibria for binary mixtures of oxygen and nitrogen have been examined, the pressure and the composition of the phases being tabulated from 90° to 125° Abs. The interpolated results for 1 atm. differ considerably from those obtained by Baly (A., 1900, ii, 589).

S. K. TWEEDY.

Application of phase rule to calculation of liquid and vapour compositions in binary systems. Deviations from Raoult's law for hydrocarbon mixtures. G. CALINGAERT and L. B. HITCHCOCK (J. Amer. Chem. Soc., 1927, 49, 750—765).—The isothermal p - v graph for the vapour in equilibrium with a homogeneous binary liquid mixture yields a family of curves, each curve corresponding with a given composition of the liquid. Such systems are completely defined by two independent variables, e.g., p and T . If two systems are known for which p and T are the same, x and y , the molar fractions of constituent A in the liquid and vapour phases, respectively, will also be the same, and for each system $L_A x + V_A y = C_A$, where L_A and V_A represent the molar quantity of A in the two phases,

and C_A the total quantity of A in the system. V_A is obtained with the aid of the appropriate p - v curves, p and T being the same for each system; L is calculated from $C_A + C_B = L + V$, and so x and y may be determined without involving analysis of the phases present. Vapour pressure-composition data for 25° are tabulated for systems of butane with pentane, heptane, benzene, and "straw-oil," and also for the pentane-heptane system. The respective deviations of the total pressure at 20 mol.-% of the lighter constituent are 4, 0, 64, -2.6, and 7. Except for the butane-heptane system, which obeys Raoult's law even although the relative internal pressures are not the same, the results agree very well with Hildebrand's views. A critical review of previously published relevant data is given. S. K. TWEEDY.

Freezing points. III. The syncrystallisation rule of Bruni. J. TIMMERMANS (Bull. Soc. chim. Belg., 1927, 36, 179—190; cf. Viseur, this vol., 312).—Using methyl alcohol as solvent, the solubility curves at 20° for various salt-pairs have been investigated in an attempt to determine the miscibilities of *cis*- and *trans*-isomerides with one another and with the corresponding saturated compounds, and the following results obtained: sodium maleate and fumarate, immiscible; sodium succinate and maleate, systems rich in succinate form mixed crystals; sodium succinate and fumarate, apparently immiscible; potassium maleate and fumarate, possibly limited miscibility; potassium succinate and maleate, mixed crystals with gap from 0 to 30% maleate; potassium succinate and fumarate, unbroken series of mixed crystals. Measurements of the f. p. gave the following results: *cis*- and *trans*-acetylene dichloride, ethylene chloride and *cis*-acetylene dichloride, ethylene bromide and *cis*-acetylene dichloride, acetylene tetrachloride and *cis*-acetylene dichloride, acetylene tetrachloride and *trans*-acetylene dichloride, no mixed crystals; ethylene chloride and *trans*-acetylene dichloride, ethylene bromide and *trans*-acetylene dichloride, mixed crystals. Summarising the present data and those of Viseur (*loc. cit.*), it may be said that, in general, the *trans*-compound has a more marked tendency to form mixed crystals with the corresponding saturated compound than has the *cis* isomeride. It would hence appear that in the solid state similar atom groups in the saturated compounds are placed at antipodes, the molecule having a structure approximating to that of the corresponding *trans* unsaturated compound.

Ethylene dibromide and dichloride form an unbroken series of mixed crystals, a fact in harmony with their behaviour towards the two isomeric acetylene dichlorides. J. S. CARTER.

Double salts in the series of isomorphous mixed crystals of magnesium and zinc sulphate, and the occurrence of chemical compounds in the solid state. H. G. K. WESTENBRINK (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1374—1384).—X-Ray examination shows that $MgSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$ form a continuous series of mixed crystals. Compounds such as those described by Hollmann (A., 1901, ii, 436) are not formed.

M. S. BURR.

Solid solutions of calcium and sodium silicates. A. GINSBERG and C. NIKOYCSIEN (Nachr. geochem. Sekt. Ver. Metall. Chem., 1926, 35—38).—The system $\text{Na}_2\text{SiO}_3\text{--CaSiO}_3$ yields the compound $2\text{Na}_2\text{SiO}_3\cdot 3\text{CaSiO}_3$, m. p. 1255°; minimal m. p. occur at 1042° and 1230°.

CHEMICAL ABSTRACTS.

Equilibrium between molten metals and salts. C. TUBANDT and E. MÜNZING (Z. anorg. Chem., 1927, 160, 323—332).—The equilibria $\text{Pb} + 2\text{AgCl} \rightleftharpoons 2\text{Ag} + \text{PbCl}_2$ have been investigated between 500° and 1000°, and found to be in agreement with Lorenz' modification of the mass action law (A., 1924, ii, 484, 761). The silver content of the metal phase decreases linearly with rise in temperature, but is only slightly influenced by the addition of sodium or potassium chlorides, thus indicating that, in the molten state, silver chloride exists as Ag_2Cl_2 . Similar results were obtained in studying the equilibria $\text{Cu} + \text{AgCl} \rightleftharpoons \text{Ag} + \text{CuCl}$.

A. R. POWELL.

Binary alloys of lead with up to 2.2% of lithium. J. CZOCHRALSKI and E. RASSOW (Z. Metallk., 1927, 19, 111—112).—The saturated solid solution of lithium in lead contains from 0.04 to 0.09% Li, according to the temperature. With more lithium, a eutectic of lead and the compound Pb_3Li_2 is formed, which contains 0.65% Li and melts at 230°. The compound melts at 470° and contains 2.15% Li. All alloys containing less lithium than this are stable in the air, but those containing more lithium rapidly disintegrate. On allowing the alloy containing 5% Li to cool, liquid drops with a glistening metallic lustre are expressed from the interior of the ingot at 200°.

A. R. POWELL.

Binary system cobalt-tungsten. W. GEISS and J. A. M. VAN LIEMPT (Z. Metallk., 1927, 19, 113—114).—The temperature coefficient of electrical resistance of bars of cobalt-tungsten alloys, made by sintering intimate mixtures of the powdered metals with a current equal to 95% of that required to melt the alloy, have been measured and the results plotted against the composition. The figures obtained show that the two metals do not form a continuous series of mixed crystals. The curve falls abruptly with the addition of a very small quantity of cobalt to tungsten to a minimum at 5% Co, rises slightly to a maximum with 10% Co, falls again to a second, flat minimum at 30—55% Co, then rises sharply again to the value for pure cobalt.

A. R. POWELL.

Ternary systems. IV. Potassium carbonate, sodium carbonate, and water. A. E. HILL and F. W. MILLER, jun. (J. Amer. Chem. Soc., 1927, 49, 669—686).—No hydrated double carbonate is formed in the above system between 20° and 50°, but a continuous series of hydrated solid solutions exists, $(\text{K}_2, \text{Na}_2)\text{CO}_3\cdot 6\text{H}_2\text{O}$, in which the atomic ratio of potassium to sodium varies from 1:0.88 to 1:2.07. Above 25.12° and within limited concentrations, a stable anhydrous double carbonate $\text{K}_2\text{CO}_3\cdot\text{Na}_2\text{CO}_3$ is formed. Four quintuple points exist, each involving three solid phases. The lowest hydrate of potassium carbonate is $\text{K}_2\text{CO}_3\cdot 1.5\text{H}_2\text{O}$, stable at the ordinary temperature; below -6.2°, the stable hydrate is $\text{K}_2\text{CO}_3\cdot 6\text{H}_2\text{O}$.

S. K. TWEEDY.

System copper-tin-antimony. W. BONSAACK (Z. Metallk., 1927, 19, 107—110).—The ternary system copper-tin-antimony at 20° may be divided into eight regions, characterised by three constituents crystallising in the following order: (i) $\text{Cu}_3\text{Sn} + \text{CuSn}$, SbSn , ternary eutectic or pure tin; (ii) Cu_3Sn , CuSn , SbSn ; (iii) Cu_3Sn , Sb_3Sn_2 , SbSn ; (iv) Cu_3Sn , Cu_2Sb , Sb_3Sn_2 ; (v) Cu_3Sn , Cu_4Sn , Cu_2Sb ; (vi) Cu_2Sb , antimony, Sb_3Sn_2 ; (vii) copper, Cu_4Sn , Cu_2Sb ; (viii) Cu_4Sn , Cu_2Sb , Cu_3Sb . Thus in bearing metals which contain a large proportion of tin, no antimony-copper compound is stable at the ordinary temperature. All the above quasi-ternary systems exhibit peritectic reactions at higher temperatures, with corresponding instability and sensitivity to change on repeated melting. For the recovery of tin from old bearing metal by the liquation process, a temperature of 229° gives the most satisfactory results, the runnings then consisting of the ternary eutectic, which contains only relatively small quantities of copper and antimony.

A. R. POWELL.

Equilibria in systems in which the phases are separated by a semipermeable membrane. XVIII. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 1292—1302).—Theoretical. The influence of pressure on osmotic systems is considered.

M. S. BURR.

Kinetic theory of Eötvös' law. M. SATO (Sci. Rep. Tohoku Imp. Univ., 1926, 15, 805—817).—The physical meaning of surface tension is examined from the point of view of the kinetic theory. If λ is the surface energy per unit area and σ the surface tension, the relation between them is $\lambda = \sigma - T \cdot d\sigma/dT$. If a thin liquid film is stretched on a wire frame with forces holding the wires balanced against surface tension, the physical meaning of the above equation is that σ is the force on the wire, $-T \cdot d\sigma/dT$ the force due to the molecular impacts on the wire, and λ the cohesive force among the molecules in the film. Since the molecular impacts increase with temperature, the surface tension diminishes, but λ is independent of temperature. Since the thinnest film obtained by stretching is bimolecular, the surface layer is probably unimolecular, and the molecules in the surface are regularly oriented. If two molecules are in the first and second layers of the surface, respectively, and Z_0 is the mean distance between their centres, the physical meaning of Eötvös' law is that ϵ_0/Z_0 is constant for most liquids, ϵ_0 being the mean gap between the circumferences of the two molecules. The values of the molecular cohesion calculated on the above assumption are in fair agreement with those given by van der Waals' equation.

W. HUME-ROTHERY.

Change in activity of molten lead chloride on dilution with potassium chloride. J. H. HILDEBRAND and G. C. RUBLE (J. Amer. Chem. Soc., 1927, 49, 722—729).—Activity coefficients have been calculated from *E.M.F.* measurements at 500—600° of cells of the type $\text{Pb}|\text{fused PbCl}_2 + \text{KCl}(c)|\text{Cl}_2$, where *c*, the molar fraction of potassium chloride, is 0.0—0.4. The results are interpreted on the assumption that certain complexes which separate as solids (Lorenz and Ruckstuhl, A., 1907, ii, 152) also exist in a

partly ionised state in the lead chloride solution. The free energy change corresponding with the decomposition potential of fused lead chloride is $-58,700$ g.-cal. at 498° , in agreement with Gerke's value at 25° (A., 1922, ii, 682). S. K. TWEEDY.

F. p. and activity coefficients of aqueous barium nitrate, sodium sulphate, and sulphuric acid. M. RANDALL and G. N. SCOTT (J. Amer. Chem. Soc., 1927, 49, 647—656).—With an improved form of the Randall and Vanselow apparatus (A., 1925, ii, 33), the f. p. of the above dilute solutions were determined. The calculated activity coefficients suggest that sodium sulphate is a strong electrolyte, barium nitrate distinctly weaker, and sulphuric acid moderately strong. S. K. TWEEDY.

Activity of chlorine at various partial pressures. N. KAMEYAMA, H. YAMAMOTO, and S. OKA (Proc. Imp. Acad. Tokyo, 1927, 3, 41—43).—The *E.M.F.* at 25° of the cell $\text{Hg}|\text{Hg}_2\text{Cl}_2$, saturated $\text{KCl}|\text{PtCl}_2$, with chlorine at various concentrations has been measured. The cell behaves normally with respect to the change of partial pressure of chlorine above a partial pressure of 0.240 atm. W. E. DOWNEY.

Thermodynamics of non-isothermal systems. W. H. RODEBUSH (J. Amer. Chem. Soc., 1927, 49, 792—794).—The equilibrium condition assumed by Eastman (A., 1926, 797) is incomplete. Gibbs' equilibrium criteria are applied to the case of an ideal gas in a temperature gradient. Contrary to Eastman's statement, the reversible Soret effect is not necessarily zero. The difficulty in defining osmotic temperature might be surmounted by considering equilibrium to be established through the vapour phase (cf. following abstract). S. K. TWEEDY.

Thermodynamics of non-isothermal systems. E. D. EASTMAN (J. Amer. Chem. Soc., 1927, 49, 794—795).—The equilibrium condition previously used is considered to be sufficient, and when applied to an ideal gas yields the same result as that obtained by Rodebush (preceding abstract). The reversible Soret effect is not necessarily zero, although it is considered to be so in perfect solutions. Rodebush's suggestion regarding the definition of osmotic temperature is criticised. S. K. TWEEDY.

Calculation of affinity from entropy considerations. G. BOZZA and G. DEVOTO (Atti R. Accad. Lincei, 1927, [vi], 5, 180—186).—A mathematical note, preliminary to experimental work shortly to be published in which expressions for affinity and fugacity are derived from the Planck form of Nernst's hypothesis without making use of the Clausius-Clapeyron equation. R. W. LUNT.

Physico-chemical processes as the effects of the sum total of elementary adiabatic reactions. N. W. TANTZOV (J. Russ. Phys. Chem. Soc., 1926, 58, 947—956).—Theoretical. The thermodynamic nature of physico-chemical processes is considered from the point of view of chemical kinetics. The motion of molecules in systems not in equilibrium results in momentary adiabatic expansions and contractions of the elementary molecular volume. Changes of phase are considered from such a point of view. The

formation and persistence of nuclei during crystallisation from supercooled liquids occur more readily if the heat of the resulting contraction is small and the temperature of dissociation of the nucleus large, i.e., dQ/T or the change in entropy is small. Only those molecules coalesce, to form stable nuclei, and may be termed "active" molecules, which possess energy between certain limits. In metastable systems, where several phases may be formed, the nature of the nuclei which are formed is determined by the above energy considerations, and not by the law of chance. For crystallisation an optimum temperature exists, when the average kinetic energy of the molecules is equal to that of the "active" molecules which form the nuclei. The considerations are extended to chemical reactions. In consecutive reactions, the first, which is the easiest, must have the smallest entropy change. The Marcelin-Rice conception of the "critical increment" $d \log K/dT = \epsilon/RT^2$ in a decomposition reaction is shown to follow necessarily from the adiabatic nature of the individual molecular reactions. M. ZVEGINTZOV.

Heat of dissolution of sparingly soluble electrolytes. I. Heat of precipitation as a function of the concentration. [Silver chloride.] E. LANGE and R. M. FUOSS (Z. physikal. Chem., 1927, 125, 431—441; 126, 304).—Previous methods of determining the heat of dissolution of sparingly soluble electrolytes have assumed that it is of equal magnitude and of opposite sign to the heat of precipitation. It is shown that this is not strictly true, but that the heats of dilution of the solutions employed should be taken into account; the error involved by the omission may amount to several hundred g.-cal. A calorimetric method is described for determining the heat of precipitation of silver chloride from a solution of silver nitrate by potassium chloride solution, together with an account of tests made to ensure that the heat value is not subject to errors owing to adsorption from the solution by the precipitate or to variations in the crystal form of the silver chloride. The heat of precipitation of silver chloride at three concentrations is given, and by extrapolation of the heat-concentration curve to zero concentration, the true heat of dissolution is found to be -15.98 kg.-cal./mol. H. F. GILLBE.

Twenty-five years of theoretical electrochemistry. W. D. BANCROFT (Trans. Amer. Electrochem. Soc., 1927, 51, 63—78).

Conductance in liquid hydrogen sulphide solutions. G. N. GUAM and J. A. WILKINSON (Proc. Iowa Acad. Sci., 1925, 32, 324—325).—Solutions of the halides of phosphorus, arsenic, and antimony in liquid hydrogen sulphide are electrical conductors, the conductivity largely increasing with the atomic weight of the element. Replacement of the hydroxyl group of acetic acid by the thiol or amido-group or by chlorine largely increases the conductivity, whereas replacement of the hydrogen of the radical by chlorine or the amido-group abolishes the conductivity. Ammonium chloride in hydrogen sulphide is a non-conductor, but replacement of hydrogen by a methyl or an ethyl group greatly increases the conductivity.

CHEMICAL ABSTRACTS.

Molecular conductivity of cadmium iodide in acetonitrile. F. K. V. КОСН (J.C.S., 1927, 647—650).—The conductivity was determined at 0° and 25° for the range $\nu=10-8000$. The temperature coefficients change from positive to negative and back to positive again as the solutions become more dilute. This suggests the existence of at least three molecular species in solution. Since λ_0 for the most dilute solution is only 49.98, whilst the conductivity of the iodine ion is 96, cadmium iodide cannot be regarded as completely dissociated even at high dilutions. The temperature coefficient tends, with increasing dilution, towards the value of the temperature coefficient of fluidity of acetonitrile.

M. S. BURR.

Influence of iodine on the conductivities of sodium, potassium, cadmium, and mercuric iodides in alcoholic and in acetone solutions. E. THÖNNESSEN (Z. Physik, 1927, 41, 810—827).—Using Kohlrausch's method, the change in conductivity on the addition of iodine has been measured in the temperature range 5—40° for the following solutions: cadmium iodide, potassium iodide, and mercuric iodide in methyl alcohol, potassium iodide and sodium iodide in acetone, and sodium iodide in amyl alcohol. The observed increase is more marked in dilute solutions of these salts, and is greatest for the iodides of cadmium and mercury. These results are discussed with reference to viscosity and complex-ion formation; it is concluded, in contradiction to the results of recent work on strong electrolytes, that none of these salts is completely dissociated in aqueous solution.

R. W. LUNT.

Thermodynamic theory of reversible electrodes. B. SZYSZKOWSKI (Bull. Acad. Polonaise, 1926, A, 313—323).—Using the Debye-Hückel equations, the equilibrium between an electrode and an electrolytic solution has been treated by general thermodynamic methods. The treatment is illustrated by the calculation of the equilibrium constant for the reaction in the Daniell cell.

R. A. MORTON.

Effect of intermediate solutions on diffusion potentials. C. DRUCKER (Z. physikal. Chem., 1927, 125, 394—400).—The efficacy of various liquids when used as intermediate solutions to eliminate the potential at a liquid-liquid junction has been determined by *E.M.F.* measurements against the calomel electrode. Potassium nitrate and mixtures of potassium and sodium nitrates eliminate the liquid-liquid potential incompletely in strongly acid solutions. In addition to the concentrated solutions of potassium chloride and ammonium nitrate which are in common use for this purpose, saturated solutions of sodium nitrate and of lithium acetate may be employed. It is suggested that the acid and acetate form a layer of neutral salt on the two sides of the acetate bridge and that the resulting *E.M.F.* is zero. The measurements made confirm this view.

H. F. GILLBE.

Electrokinetic potential of metals. A. COEHN and O. SCHAFMEISTER (Z. physikal. Chem., 1927, 125, 401—419).—The applicability of Stern's theory of electrokinetic potential (Z. Elektrochem., 1924, 30, 508) to the case of metals in contact with liquids has

been tested. A method is described for measuring the electrokinetic potential, independently of the thermodynamic; its validity has been demonstrated by measuring the potentials of a number of dielectrics for which the potential-concentration curves are known. Results are given for platinum, gold, silver, molybdenum, and tungsten, which all have a negative charge in pure water. In solutions of potassium, calcium, and aluminium chlorides, the charge decreases with increasing concentration of electrolyte, and changes sign at a concentration which is lower the higher the valency of the positive ion. The maxima and minima in the concentration-potential curve required by Stern's theory are apparent only for molybdenum and tungsten in aluminium chloride solution; in other cases, the concentrations at which the maxima and minima occur are probably below the range investigated. Analogous results are found for lead and zinc, which have a positive charge when in contact with pure water, in solutions of potassium chloride and ferricyanide. Copper and cadmium, which have an indefinite charge in water, are positively charged when in contact with potassium ferricyanide solution of low concentration, and negatively charged at higher concentrations.

The influence of the valency of the active ion is demonstrated clearly by the nature of the concentration-potential curves, and the results are in good agreement with the theory of Stern.

The electrokinetic potential is independent of the thermodynamic. Measurements of the latter for metals in contact with various liquids show that it is usually of opposite sign to the electrokinetic potential, that it is influenced by valency and concentration in a totally different manner, that there is no change of sign with increasing concentration, and no maxima or minima occur in the concentration curve. A brief discussion is given on the nature of the difference between the two types of potential, together with its bearing on colloid chemistry.

H. F. GILLBE.

***P.D.* between two liquid phases.** S. W. VOSNESSINSKI (J. Russ. Phys. Chem. Soc., 57, 475—486).—The *E.M.F.* of concentration cells containing electrolytes distributed between two liquid phases was investigated, in order to test the thermodynamic equation. Two types of cell were used: *N*-calomel electrode|aqueous solution of A|non-aqueous A|aqueous B|non-aqueous B|*N*-calomel electrode; and *N*-calomel electrode|aqueous A|non-aqueous A (C_1)|non-aqueous A (C_2)|aqueous A|*N*-calomel electrode. The electrolyte A was always potassium chloride, whilst B was potassium bromide, potassium iodide, potassium thiocyanate, lithium chloride, or hydrochloric acid. The non-aqueous phases were amyl alcohol and phenol. Assuming Nernst's formula, the liquid/liquid *P.D.* is given by: $\pi = RT/F \cdot \log_e \sqrt{ak/aa}$ for cells containing one electrolyte, for which *ak*, *aa* are the partition coefficients of the cation and anion. If the simple partition law holds, the *E.M.F.* of such cells is zero. For cells containing two electrolytes with a common ion, the *E.M.F.* is given by $E = RT/F \cdot \log_e C_i C_{III} / C_{II} C_{IV}$, where C_i , C_{II} , C_{III} , C_{IV} are the concentrations of that ion.

Potassium chloride in water and phenol gave no

E.M.F., whilst the same salt in water and amyl alcohol gave an *E.M.F.* which decreased with rise of concentration. A theoretical expression for the *E.M.F.* of this cell was deduced which agrees with the observations.

In cells with pairs of electrolytes, that electrolyte which had the greater solubility in a given phase charged that phase to the higher potential.

M. ZVEGINTZOV.

Standard calomel electrodes and their preparation. A. BRODSKI (Ukraine Chem. J., 1926, 2, 277—288).—The author finds that calomel electrodes prepared by the method of Ostwald and Luther are not constant and cannot be reproduced. When purified calomel is introduced in constant proportion into the cell solutions, calomel and mercurous bromide electrodes can be obtained which have a constant reproducible potential within 0.0001—0.0002 volt, whether in alcoholic or aqueous-alcoholic solutions.

E. ROTHSTEIN.

Production of ions from solutions of mercury salts in water. A. BRODSKI and G. CHERCHEVER (Ukraine Chem. J., 1926, 2, 289—310).—The *E.M.F.* of $\text{Hg}|\text{Hg}_2(\text{NO}_3)_2, \text{Hg}|\text{Hg}_2\text{Cl}_2, \text{KCl}$, and $\text{Hg}|\text{Hg}_2\text{Br}_2, \text{KBr}$ electrodes have been determined between 11° and 27° by a new method free from errors associated with previous determinations. The solubility products of mercurous chloride and mercurous bromide derived therefrom are satisfactorily constant. The solubility products of other mercurous salts have also been determined.

E. ROTHSTEIN.

Temperature coefficient of contact *E.M.F.* J. J. MCHENRY (Phil. Mag., 1927, [vii], 3, 857—863).—The contact *E.M.F.* between clean copper and zinc has been found to be a linear function of the temperature, and may be expressed in the form $E = q + T \cdot dE/dt$, where dE/dt is 0.002 volt per degree, and q is very small and may be either positive or negative, depending on the relative cleanliness of the metals. It is suggested that for absolutely clean metals the contact *E.M.F.* is proportional to the absolute temperature, i.e., that q should vanish. Measurements made with copper-aluminium and copper-tin cells confirm this.

A. E. MITCHELL.

Platini-platino-chloride electrode. New type of chlorine electrode. V. F. MILLER and H. TERREY (J.C.S., 1927, 605—610).—Measurements have been made on the *E.M.F.* of the following cell:

$\text{Hg}|\text{Hg}_2\text{Cl}_2, \text{NaCl}|\text{NaCl} + \text{Na}_2\text{PtCl}_6 + \text{Na}_2\text{PtCl}_4|\text{Pt}$, the reaction at the positive electrode being $\text{PtCl}_6^- + 2e^- \rightarrow \text{PtCl}_4 + 2\text{Cl}^-$. With a constant sodium chloride concentration, the *E.M.F.* of this electrode is given by $E = E_0 + (RT/2F) \log [a_i]/[a_o] \times [a_{\text{Cl}}]_2$, where a_i , a_o , and a_{Cl} are the activities of the chloroplatinate, the chloroplatinite, and the sodium chloride, respectively. E_0 , however, changes slightly with change in concentration of sodium chloride, and the complete relationship may be expressed by the empirical equation $E = (E_0 + C) + (RT/2F)(\beta - 2) \log a_{\text{Cl}} + (RT/2F) \log i/o$, where C and β are constants. From the temperature coefficient of the cell, the heat of formation of sodium chloroplatinate from the chloroplatinite and chlorine, calculated by means of the Gibbs-Helm-

holtz equation, is 40,880 g.-cal., as compared with 42,000 g.-cal. found by Thomsen by direct measurement.

M. S. BURR.

Potential of the quinhydrone electrode in reference to the hydrogen electrode. E. BILLMANN and A. L. JENSEN (Bull. Soc. chim., 1927, [iv], 41, 151—166).—The mode of preparation and the age of the quinhydrone have no essential influence on the electrode potential. Slight impurities in the quinhydrone have only a very small influence on the *E.M.F.* The best method of purification is to wash the specimen with the electrolyte to be used immediately before making up the electrode. Reproducible values for the *E.M.F.* of the cell composed of quinhydrone and hydrogen electrodes are obtained when the quinhydrone is 0.00016M and above. At 18°, the *E.M.F.* is 0.70439 volt when the electrolyte is 0.1N-hydrochloric acid and 0.70479 volt when it is 0.01N-acid, whilst its value is 0.70416 volt when the electrolyte is 0.01N-hydrochloric acid and 0.09N-potassium chloride. The variations in *E.M.F.* produced by the presence of small quantities (3%) of oxygen in the hydrogen are within the experimental error.

S. K. TWEEDY.

Variation of cell constant with concentration and molal conductivity of aqueous barium nitrate, sodium sulphate, and sulphuric acid. at 0°. M. RANDALL and G. N. SCOTT (J. Amer. Chem. Soc., 1927, 49, 636—647).—The ratios of the constants of two cells, made of "pyrex" glass and having platinised electrodes, varies with the concentration of the three electrolytes used, as observed by Parker (A., 1923, ii, 530, 722). The variation is smaller in the cell with the more widely-spaced electrodes, in agreement with Parker's adsorption theory. It is predicted that sodium sulphate is more suitable than potassium chloride for the standardisation of cells. Adsorption of electrolyte by the glass walls also has a perceptible influence. The accurate determination of conductivity entails the careful standardisation of procedure and the use of the same cell for measuring both the unknown and standard solutions. The conductivities of the above electrolytes (0.001—0.2M) are tabulated for 0°; a graphical-analytical method for extrapolating and interpolating conductivity curves is described.

S. K. TWEEDY.

Electrode potential of aluminium. P. DROSSBACH (Z. Elektrochem., 1927, 33, 114—117).—Theoretical. From the heat of the reaction $4\text{Al} + 3\text{O}_2 = 2\text{Al}_2\text{O}_3$, and the specific heats of the participants at various temperatures, the decrease of thermodynamic potential accompanying the process is calculated to be 706,700 g.-cal. at 20°, whence the *E.M.F.* of the cell, $\text{Al}|\text{Al}_2\text{O}_3|\text{O}_2$ is 2.565 volts. Taking the potential of the oxygen electrode as +1.231, the potential of the aluminium electrode is $\epsilon_{\text{Al}} = -1.33 \pm 0.01$ volt at 20°. The value obtained by Neumann and Richter (A., 1925, ii, 797) is criticised.

H. J. T. ELLINGHAM.

Decomposition potentials in non-aqueous solvents. S. C. BISWAS and S. BOSE (Z. physikal. Chem., 1927, 125, 442—451).—Current-voltage curves have been obtained for solutions of potassium iodide and bromide, lithium chloride, and hydrogen chloride

in pure methyl alcohol. The decomposition potentials are compared with those for aqueous solutions. The presence of water in a methyl alcohol solution of hydrogen chloride has a marked effect on the decomposition potential, which in pure methyl alcohol is at 0.41 volt; in the presence of 10% of water there is another break in the current-voltage curve at 1.0 volt, and with 30% of water a third at 1.3 volts. The second break is ascribed to the formation of a complex between the hydrogen chloride and the solvent, whilst the third corresponds with the decomposition potential of hydrogen chloride in aqueous solution. The presence of water in the solutions of potassium iodide and bromide has very little influence on the current-voltage curves, since the ions show little tendency to combine with the strongly associated molecules of methyl alcohol; neither are the conductivities altered appreciably. On the other hand, traces of water in the solutions of lithium chloride alter the form of the decomposition curve very considerably, probably because of the formation of lithium hydroxide and of complexes with the solvent. The decomposition potentials in pure methyl alcohol are: potassium iodide, 0.32 volt; potassium bromide, 0.68—0.71 volt; lithium chloride, 1.2 volts; and hydrogen chloride, 0.41 volt. These values lie below the corresponding figures for aqueous solutions, but follow the same sequence. H. F. GILLBE.

Electrolytic polarisation. VI. Electrodeposition potentials of alloys of zinc with iron, cobalt, and nickel. S. GLASSTONE (J.C.S., 1927, 641—647).—In the electrolysis of a solution containing a mixture of zinc and nickel or iron sulphates the cathodic potential at low current density has a value which corresponds with the separation of the pure iron group metal; as the current density increases, the potential rises rapidly at a certain point, and an alloy consisting mainly of zinc is formed. Solutions of cobalt and zinc exhibit the same phenomenon. The critical current density is in general smaller the lower the temperature, the greater the proportion of zinc in solution, and the lower the hydrogen-ion concentration. On diminishing the current density, the corresponding fall in potential takes place only at very low current densities. The deposition potential of the alloy rich in zinc decreases with increasing temperature, but is independent of the hydrogen-ion concentration. The results do not appear to be in accordance with the theories of previous investigators. The sudden increase of potential may be attributed to a decrease in the concentration of the iron group ion in the neighbourhood of the cathode, resulting in the deposition of an alloy richer in zinc to maintain the flow of current, and hence an increase in the hydrogen overvoltage causing still more zinc to be deposited. The persistence of the higher potential on reducing the current density is probably due to the retardation, by the presence of large amounts of zinc, of the change from the metastable to the stable form of the iron group metal.

M. S. BURR.

Electro-endosmosis and electrolytic water transport. H. C. HEPBURN (Proc. Physical Soc., 1927, 39, 99—107).—Liquid transport produced by

passing an electric current through aqueous solutions of copper sulphate divided perpendicular to the flow of electricity by a diaphragm of powdered glass is determined. With constant applied potential, it decreases regularly with the concentration up to 0.005*N*, but is not thereafter appreciably changed up to 0.5*N*. The charge on the diaphragm decreases to a negligible value with concentrations above 0.005*N*. With solutions above this concentration, the liquid transport per faraday is related to the dilution by a linear law, and decreases to zero at 1.0*N*. Above 0.005*N*, the current flowing through the diaphragm is due entirely to the motion of ions in the electrolyte. C. J. SMITHELLS.

"Anode effect." V. SCHISCHKIN (Z. Elektrochem., 1927, 33, 83—91).—The anode effect at carbon electrodes in molten sodium, barium, and calcium chlorides, cryolite, and solutions of alumina in molten cryolite has been examined with reference to the appearance of the anode and the voltage-current relations. With increasing current, the voltage rises very sharply to about 20—25 volts: the "sparking" visible at the anode is attributed to the glowing of particles of carbon on the unwetted anode surface. With further increase of current, the voltage-current curve is slightly less steep: the continued sparking is now attributed to tiny arcs at the points of contact of the carbon particles with the underlying conducting surface of the anode. At a certain voltage, varying from 40 to 60 with different electrolytes, the curve becomes very much less steep, and sparking ceases. Under these conditions, the current passes by continuous discharge of ions and electrons across the gas film on the electrode surface. Finally, with further increase of voltage and current, this silent discharge changes to an arc discharge and the voltage-current curve becomes irregular. It is considered that the occurrence of the anode effect, when not due to a layer of some insoluble substance, is due to the production of chlorine (or fluorine) over the whole anode surface, which causes a change in the physical condition of this surface. This change may be produced either by superficial disintegration of the electrode by the halogen or by the formation of carbon halides and their subsequent decomposition with deposition of finely-divided carbon. The molten salt remains isolated from the anode surface by a gas film on the porous layer of carbon. Oxides dissolved in the molten salt oppose the onset of the anode effect, since the oxygen produced from them causes combustion of this porous carbon layer. For solutions of alumina (*p*%) in cryolite, the critical current density, D_K , for the onset of the anode effect is given by $D_K = ap^{2.3}$, where *a* is a constant. This relation also applies to data for solutions of barium and strontium oxides in the corresponding molten chlorides obtained by Arndt and Probst (Z. Elektrochem., 1923, 29, 323).

H. J. T. ELLINGHAM.

Dependence of current efficiency on anodic current density in the preparation of ammonium persulphate. O. ESSIN and E. KRYLOW (Z. Elektrochem., 1927, 33, 107—111).—In the electrolysis of saturated solutions of ammonium sulphate at temperatures between 10° and 30°, the current effi-

ciency, η , of persulphate formation at the anode at any moment is given by: $\eta = 100\left\{\frac{(c_0 - 2c)}{(c_0 - c)} - K\right\}\%$, where c_0 is the number of g.-equivalents of ammonium sulphate per litre originally present, and c is the equivalent concentration of persulphate at the given moment. For current densities between 2 and 16 amp./cm.² $K = 0$ (cf. A., 1926, 804); at lower current densities, K has a value which represents the fraction of the discharged sulphate ions which give sulphuric acid and oxygen instead of persulphuric acid. At 1 amp./cm.² K is constant (0.064), but at lower current densities it has a higher initial value and increases during electrolysis. If, however, the anolyte is kept neutral by continued additions of ammonia, K remains constant at a given current density, and its dependence on current density can be deduced from the probability theory, assuming that sulphate ions must be discharged within a certain distance of each other in order that persulphate may be formed. When the anolyte is not kept neutral, K increases during electrolysis at low current densities owing to increasing concentration of sulphuric acid producing free persulphuric acid which hydrolyses into monopersulphuric acid (H_2SO_5) and sulphuric acid, the former being converted into sulphuric acid and oxygen at the anode. H. J. T. ELLINGHAM.

Electrochemical behaviour of chromium. III. Equilibrium potential Cr|Cr⁺⁺ in sulphate solutions. G. GRUBE and G. BREITINGER (Z. Elektrochem., 1927, 33, 112—114).—From measurements of the *E.M.F.* of cells of the type Cr|CrSO₄ solutions (various concentrations)|saturated KCl solution|normal calomel electrode, the potential of the electrode Cr|Cr⁺⁺ was obtained for concentrations of chromous sulphate from 0.033 to 1.142*N*, assuming liquid junction potentials to be negligible and the calomel *P.D.* to be +0.286. The potentials remained constant for 15—20 min., but eventually became more positive. Assuming the degree of dissociation of chromous sulphate to be equal to that of copper sulphate in a solution of the same concentration, several concordant values were obtained for the normal electrode potential Cr|Cr⁺⁺; the mean is $0^{\circ}E_h = -0.557 \pm 0.007$ volt. Since for the equilibrium Cr⁺⁺|Cr⁺⁺⁺, $0^{\circ}E_h = -0.412 \pm 0.002$ volt (A., 1926, 687), Luther's rule gives for Cr|Cr⁺⁺⁺, $0^{\circ}E_h = -0.509$ volt.

H. J. T. ELLINGHAM.

Passivity. H. EGGERT (Z. Elektrochem., 1927, 33, 94—102).—If in one state (active) a metal dissolves spontaneously or anodically with a low valency in a particular solution, but in another state does not dissolve, or dissolves with a higher valency, the latter is a passive state. Electrode potential is not regarded as a true criterion for distinguishing active and passive states (cf. Schmidt, A., 1923, ii, 732). In a special apparatus a metal can be scraped in an atmosphere of any desired gas, and without removal from this atmosphere can be dipped into an electrolyte and its potential measured against a standard mercurous sulphate electrode. If iron, nickel, or chromium is scraped in nitrogen or hydrogen and then dipped into an aqueous electrolyte, it exhibits an active potential which gradually becomes somewhat more negative. If, however, oxygen is introduced, the potentials

become rapidly more positive. Scraping in oxygen reduces the potential slightly, but it soon recovers its noble value. Similar results are obtained when using non-aqueous electrolytes, e.g., methyl alcohol or even pyridine. Again, in solutions of lithium chloride in methyl alcohol, nickel and iron dissolve anodically according to Faraday's law; chromium dissolves as chromate. In methyl alcohol solutions of silver nitrate, iron and nickel do not dissolve anodically, but chromium dissolves slightly. The behaviour in pyridine solutions is complicated by the impossibility of removing the last traces of water from the pyridine. Part of the current is carried by the ions of water, and anodes of iron or nickel become oxidised. Moreover, in pyridine solutions of lithium chloride, the cathode becomes coated with a badly-conducting film (probably lithium hydroxide derived from the trace of water present). Nevertheless, it is shown that in pyridine solutions of lithium chloride, iron and nickel are active, whilst in solutions of silver nitrate, they are passive. Chromium dissolves in these solutions probably as chromate. Thus the anodic behaviour of iron, nickel, and chromium in non-aqueous electrolytes is similar to that in aqueous electrolytes. Experiments were also made to discover whether chromium which has been activated by scratching or by heating in perfectly dry hydrogen or nitrogen would retain its activity indefinitely when kept in these gases. This was found to be the case when using electrolytic chromium and gases quite free from oxygen (cf. Schmidt, *loc. cit.*). On exposure to air, however, the metal soon became passive. It was also shown that passive chromium is not activated by exposure to hydrogen or nitrogen unless it is scratched or heated. H. J. T. ELLINGHAM.

Becquerel effect. I. LIFSCHITZ (Chem. Weekblad, 1927, 24, 143—147).—The changes in potential of an electrode immersed in an electrolyte on exposure to specific radiations are reviewed and discussed. The results of Svensson have been examined and confirmed. The data so far available are insufficient for any comprehensive hypothesis. S. I. LEVY.

Electrodialysis in biochemistry. C. DHÉRE (Kolloid-Z., 1927, 41, 243—258).—The literature relevant to the application of electrodialysis to biochemical problems is reviewed and an account (with photographic illustrations of apparatus) given of the author's practical methods of electrodialysis. In reference to the purification of colloids, the author's experiments show not only that electrolyte impurities are removed more rapidly by application of an electric field, but also that the last traces of electrolyte can be readily eliminated, although these are retained strongly by the colloid when subjected to ordinary dialysis. The conductivity of such highly purified gelatin has been measured, and is shown to be higher than that of equally purified serum-albumin; the gelatin has an acid reaction towards litmus and the particles carry a negative charge, although the rate of migration towards the anode is less than that of less highly purified gelatin. Electrodialysed gelatin exhibits strong opalescence at a concentration of 2—2.5% and is completely coagulated by heating at 100°. Electrodialysed calf-serum coagulates when

heated at 39°, but is not coagulated by immersion in liquid air.

E. S. HEDGES.

Velocity of physico-chemical reactions. G. VAN LERBERGHE (Bull. Acad. roy. Belg., 1926, [v], 12, 520—526).—Mathematical. Equations for the velocity of physico-chemical reactions are given in a generalised form accessible to experimental verification.

S. J. GREGG.

Initial stages of gaseous explosions. I. Flame speeds during the initial "uniform movement." II. **Supposed law of flame speeds.** W. A. BONE, R. P. FRASER, and D. A. WINTER. III. **Behaviour of an equimolecular methane-oxygen mixture when fired with sparks of varying intensities.** W. A. BONE, R. P. FRASER, and F. WITT (Proc. Roy. Soc., 1927, A, 114, 402—419, 420—441, 442—449).—I. The speed of initial uniform flame movement through stagnant mixtures of oxygen with hydrogen, ethylene, and acetylene, respectively, when ignited at 15—18° and atmospheric pressure at the open end of a tube of diameter 2.5 cm. (closed at the other end) has been determined, using either a photographic or an electrical method. The photographic method is described in detail, and is applicable to all the hydrocarbon-oxygen (or air) mixtures with initial flame speeds exceeding 1000 cm./sec. The probable experimental error is less than 2.5%. The electrical method may be used for measuring flame speeds up to 300 cm./sec., and in some cases up to 600 cm./sec., with fair accuracy. When used with the same mixture, the two methods give results agreeing within the limits of experimental error. With hydrogen-oxygen mixtures, the "range of inflammability" lay between 10 and 94% hydrogen content approximately. With any given mixture containing either between 10 and 55%, or between 75 and 94% of hydrogen, a fairly constant initial uniform flame speed was observed; but between 55 and 75% the initial uniform speed was found to differ in successive experiments. With ethylene-oxygen or acetylene-oxygen mixtures, initially propagating flame at speeds exceeding 4000 cm./sec., no initial uniform movement was observable, but the flame was in each case continuously accelerated from the first until detonation was set up. The range of inflammability of the acetylene-oxygen mixtures lay between 3.5 and 88% of acetylene, and of the ethylene-oxygen mixtures between 4.5 and 60% of ethylene. It was found possible under suitable conditions to have a slow "uniform flame movement" developed in an explosive medium after a period of continuous acceleration, showing that such "uniformity" is not necessarily restricted to the initial phase of flame movement.

II. The validity of Payman and Wheeler's "law of flame speeds" (cf. A., 1926, 689), claimed to be applicable to all conditions of flame propagation, has been tested experimentally from the point of view of the behaviour of complex mixtures of certain hydrocarbons, hydrogen, and oxygen containing an excess of combustible gases. The fact that on the explosion of the mixture $C_2H_4 + H_2 + O_2$ or the mixture $C_2H_2 + 2H_2 + O_2$ no carbon separates and no steam condenses on cooling (Bone and Drugman, J.C.S., 1906, 89, 669) is held to be incompatible with the

supposed law. Moreover, according to the law, whenever either of these mixtures is exploded, the oxygen must be divided between the two combustible gases concerned in such proportion as would give rise to two primary mixtures propagating flame with the same speed as the original complex mixture. This is not confirmed by experiment. A number of "blending tests" have been applied to complex oxygen mixtures (both fast and slow) and to one complex air mixture; one of the two primary mixtures was always a hydrogen-oxygen (air) mixture, and the other a hydrocarbon-oxygen (air) mixture, the hydrocarbon being acetylene, ethylene, or methane. In no case have the requirements of the "speed law" been fulfilled. Moreover, with each complex ethylene- or methane-hydrogen-oxygen (or air) mixture examined, it has been found that the effect of progressively increasing the proportion of the primary hydrogen-oxygen (air) mixture in the various blendings in any given series is to lower the observed flame speed progressively, until a point is reached when the resulting complex mixture no longer propagates flame. This result is in direct contradiction to the "law."

III. A photographic study has been made of the behaviour of an equimolecular methane-oxygen mixture when ignited by sparks of varying character and intensity passed between electrodes fixed half-way along a horizontal glass tube, both ends being closed in one series of experiments, open in another. A series of observations was also made in which the same gaseous mixture was ignited at, or near, the open end of a horizontal glass tube of which the other end was closed. The phenomena observed are described, and a number of photographs reproduced. The photographs obtained in the first two series of observations suggest the possibility of (a) the occurrence, under ordinary sparking conditions, of a definite "induction period" of non-luminosity and no flame movement as a preliminary to the actual combustion; (b) an initial propagation through the medium of a feebly actinic "ghost-like flame" condition, involving only a very partial combination of the gases, and (c) the main combustion following later as the result of the superposing of a compression wave on a system which, during phase (b), has already become highly sensitive to chemical changes.

L. L. BIRCUMSHAW.

Ignition of gases. VI. Ignition by flames. Mixtures of the paraffins with air. N. S. WALLS and R. V. WHEELER.—See B., 1927, 243.

Gaseous explosions. Effect of fuel constitution on rate of rise of pressure. G. G. BROWN and G. B. WATKINS.—See B., 1927, 243.

Velocity of hydration of carbon dioxide in aqueous solution. A. EUCKEN and H. G. GRÜTZNER (Z. physikal. Chem., 1927, 125, 363—393).—The change with time of the conductivity of an aqueous solution of carbon dioxide immediately after dilution has been measured. The time-conductivity curve affords evidence of the change in the conductivity which may be ascribed to a slow hydration of the carbon dioxide. It is only possible by this method to assign an upper limiting value to the velocity co-

efficient. A more exact method in which the current flow through the solution is measured for different applied voltages gives for the velocity coefficient at 18°, 0.09; at 0°, 0.032.

The time change observed when an aqueous solution of carbon dioxide is neutralised with alkali is due to the instantaneous formation of carbonate, followed by a gradual combination with the excess of carbon dioxide to form hydrogen carbonate. By employing the velocity coefficient found for the hydration process, the rate of neutralisation may be calculated. The agreement between the observed and calculated values is good, but since the reaction is complete within about 1 min., inefficient stirring is liable to introduce large errors into the determinations.

H. F. GILLBE.

Decomposition of azomethane. A homogeneous, unimolecular reaction. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1927, 49, 912—916).—The isothermal decomposition at constant volume of azomethane at temperatures between 278.6° and 327.4° was studied in an apparatus similar to that used by Smith (A., 1925, ii, 876), the initial pressure being varied as much as 12-fold (3.62—43.46 cm.) and the glass surface 6.5-fold. The decomposition is homogeneous and unimolecular, although slight deviations occur at the lowest and highest initial pressures. The heat of activation is 51,200 g.-cal./mol. Photochemical decomposition proceeds in ultra-violet light, the rate being two thirds as great in a pyrex as in a quartz vessel, and the pressure becoming double on complete decomposition.

S. K. TWEEDY.

Hydrogen peroxide as an oxidising agent in acid solution. IV. W. H. HATCHER and G. W. HOLDEN. V. W. H. HATCHER, G. W. HOLDEN, and F. J. TOOLE. VI. W. H. HATCHER and G. W. HOLDEN. VII. W. H. HATCHER and F. J. TOOLE (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 395—398, 399—405, 407—413, 415—421; cf. A., 1926, 270).—IV. The reaction between hydrogen peroxide and formaldehyde in the molecular proportions of 1:1.1 has been followed at 25°, and is found to occur in accordance with the equation $2\text{H}\cdot\text{CHO} + \text{H}_2\text{O}_2 = 2\text{H}\cdot\text{CO}_2\text{H} + \text{H}_2$, a complex compound of the reactants probably being formed as an intermediate product. The unimolecular velocity coefficient diminishes continuously from the start in the manner characteristic of those oxidations with hydrogen peroxide in which the latter is decomposed catalytically.

V. The oxidation of glyoxal by hydrogen peroxide in aqueous solution at 25° is a unimolecular reaction, the mechanism probably being $2\text{CHO}\cdot\text{CHO} + \text{H}_2\text{O}_2 = 2\text{CHO}\cdot\text{CHO}\cdot\text{H}_2\text{O}_2$; $2\text{CHO}\cdot\text{CHO}\cdot\text{H}_2\text{O}_2 = 2\text{H}\cdot\text{CO}_2\text{H} + 2\text{H}\cdot\text{CHO}\cdot\text{H}_2\text{O}_2$; $2\text{H}\cdot\text{CHO}\cdot\text{H}_2\text{O}_2 = 2\text{H}\cdot\text{CO}_2\text{H} + \text{H}_2$. The process is accelerated by alkali and retarded by mineral acids. Glyoxal can conveniently be determined by titration with acid permanganate, or by treatment with hydrogen peroxide and titration with standard potassium hydroxide.

VI. The oxidation of acetic acid or glycollic acid by pure hydrogen peroxide at 100° occurs according to the unimolecular law, and probably involves the formation of per-acids as intermediate products

according to the scheme: (a) $\text{CH}_3\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}_2 = \text{CH}_3\cdot\text{CO}_3\text{H} + \text{H}_2\text{O}$; (b) $\text{CH}_3\cdot\text{CO}_3\text{H} = \text{CH}_2(\text{OH})\cdot\text{CO}_2\text{H}$; (c) $\text{CH}_2(\text{OH})\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}_2 = \text{CH}_2(\text{OH})\cdot\text{CO}_3\text{H} + \text{H}_2\text{O}$; (d) $\text{CH}_2(\text{OH})\cdot\text{CO}_3\text{H} = \text{CHO}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}$; (e) $\text{CHO}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}_2 = \text{CO}_2 + \text{H}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}$; (f) $\text{H}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}_2 = \text{H}\cdot\text{CO}_3\text{H} + \text{H}_2\text{O}$; (g) $\text{H}\cdot\text{CO}_3\text{H} = \text{H}_2\text{O} + \text{CO}_2$. Of these reactions, (b) and (d) are slow, and (e) and (g) are rapid. In no instance has formaldehyde been detected in the products of reaction, so that the formaldehyde reported by Dakin (A., 1908, i, 75) must have been due to a difference in the method of oxidation. Mineral acids retard the oxidation, whilst the sodium ion, and still more the potassium ion, decompose the hydrogen peroxide. Glycollic acid is much more resistant to oxidation than are formic, glyoxylic, and oxalic acids.

VII. The reaction between hydrogen peroxide and acetaldehyde at 61.5° to form acetic acid is slow, and the unimolecular velocity coefficient rises continuously from the commencement of the reaction, an effect which is ascribed to the formation of peracetic acid according to the equations $\text{CH}_3\cdot\text{CHO} + \text{H}_2\text{O}_2 = \text{CH}_3\cdot\text{CHO}\cdot\text{H}_2\text{O}_2$; $\text{CH}_3\cdot\text{CHO}\cdot\text{H}_2\text{O}_2 = \text{CH}_3\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}$; $\text{CH}_3\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}_2 = \text{CH}_3\cdot\text{CO}_3\text{H} + \text{H}_2\text{O}$. Lactic acid at 100° is also oxidised to carbon dioxide very slowly, perlactic acid probably being an intermediate product.

R. CUTHILL.

Decomposition and oxidation of dithionic acid.

D. M. YOST and R. POMEROY (J. Amer. Chem. Soc., 1927, 49, 703—707).—The rate of decomposition of dithionic acid in presence of hydrochloric and perchloric acids at 50° and 80°: $\text{S}_2\text{O}_6^{''} + \text{H}_2\text{O} = \text{SO}_4^{''} + \text{H}_2\text{SO}_3$, is proportional to the dithionate concentration and the total acid concentration, provided the latter does not exceed 0.6*N*. The rate increases more rapidly at higher concentrations, showing that the catalytic effect is due to hydrolysis. The rate of oxidation of dithionic acid is independent of the concentration and nature of the oxidising agents (iodate, bromate, and dichromate), and is the same as the rate of decomposition into sulphate and sulphite, showing that the first stage in oxidation is hydrolysis (Muller, A., 1911, ii, 266).

S. K. TWEEDY.

Effect of alkali on the oxidation of ferrous hydroxide by air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1927, 2, 40—44).—A standard stream of air was drawn through known mixtures of ferrous hydroxide and sodium hydroxide and the quantity of ferrous compound remaining after a given interval determined by treating with sulphuric acid and titrating with permanganate. If *v* c.c. of the latter are required at time *t* and *v*₀ at zero time, then $v = v_0 - kt$; *k* is a constant for a given concentration of alkali, but decreases as the latter increases. Hence the addition of alkali reduces the velocity of oxidation.

S. J. GREGG.

Transformations of iron in nature. I.

Theoretical. H. O. HALVORSON and R. L. STARKEY (J. Physical Chem., 1927, 31, 626—631).—Equations indicating the relationships between the activities of ferrous, ferric, and hydrogen ions and oxygen concentration are derived. Measurements of the amounts of ferrous and ferric ions in solution at various *p_H* values indicate that at *p_H* > 5 very small amounts of

ferrous iron will occur in solution under atmospheric conditions and that even smaller amounts of ferric iron are soluble.
L. S. THEOBALD.

Mutarotation and alkalinity of the medium. H. COLIN and (MLLE.) A. CHAUDUN (Compt. rend., 1927, 184, 749—751).—The rate of mutarotation of dextrose has been investigated in presence of ammonia and sodium hydroxide of concentrations ranging from $N/550$ to $N/6800$. Their effects become similar at concentrations below $N/5500$. In the case of lævulose, solutions of ammonia more dilute than $N/40,000$ have no effect.
J. GRANT.

Influence of stirring on velocity of reaction in heterogeneous systems. E. BEKIER and K. RODZIEWICZ (Rocz. Chem., 1926, 6, 869—880).—The velocity of dissolution of copper plates in solutions of iron alum is expressed by $K = (v/O\Delta t) \log_e c_1/c_2$, where O is the area of the plate, n the number of revolutions of the stirrer per min., and c_1 and c_2 are the initial and final concentrations of ferric salt over an interval of time Δt . K is a linear function of n and may be expressed by $K = a + bn$, where a is the value of K at which the y axis is cut by the curves obtained for the relation K/n , varying the volume of solution, the surface area of the plate, and the position and shape of the stirrer, and corresponds with the velocity constant of an unstirred solution. The value of a depends on conditions of stirring, and is not constant (cf. Klein, A., 1924, ii, 745).

R. TRUSZKOWSKI.

Velocity of reaction and energy of activation of halogen compounds. D. H. PEACOCK (J. Physical Chem., 1927, 31, 535—542).—A theoretical paper in which the alternating effect of substituents on the energy of activation is discussed. The effect of energy of activation in altering the ratios of velocities, and hence that of the products formed, at different temperatures is pointed out, and it is suggested that the alteration in this energy is a more fundamental expression than is velocity of reaction of the effect of substituents on reactivity. The effects of substituting one halogen for another on the velocity constant and on the energy of activation are compared in a number of reactions. Velocities of reaction are affected, not only by alterations in activation energy, but also by variations in the sensibility of the molecule and the stability of the activated state. The reactions discussed are examined with reference to the velocity equation of Dushman (A., 1921, ii, 315).

L. S. THEOBALD.

Complex homogeneous catalysis of hydrogen peroxide by sodium molybdate. E. SPITALSKY and A. FUNCK (Z. physikal. Chem., 1927, 126, 1—23).—A study of the catalytic decomposition of hydrogen peroxide by sodium molybdate in aqueous solution. The catalyst exists in an unstable and in a relatively stable catalytic state. The stable condition is attained when the unstable form is subjected to repeated treatment with hydrogen peroxide. In this case, the catalysis is quite regular and the shape of the reaction curve is independent of the initial concentration of hydrogen peroxide. In neutral solution, the reaction velocity rises gradually to a well-defined maximum, and ultimately becomes very

small as completion is approached. In dilute acid or alkali, the maximum disappears and the reaction velocity becomes sensibly constant over a wide range. The catalytic activity, with which the brown colour of the solution may be associated qualitatively, is greatest in dilute alkaline solutions. In strong acid or alkali, the catalysis ceases completely and the solution becomes colourless or nearly so. The results are discussed in terms of Spitalsky's theory of homogeneous catalysis (A., 1926, 1011), assuming the simultaneous formation of several catalytically active intermediate products with varying affinity constants and stabilities.
G. A. ELLIOTT.

Theory of the catalytic combustion of ammonia. M. BODENSTEIN.—See B., 1927, 217.

Catalytic oxidation of ammonia. III. L. ANDRUSSOV.—See B., 1927, 217.

Thermal decomposition of ammonia on the surface of a molybdenum wire. R. E. BURK (Proc. Nat. Acad. Sci., 1927, 13, 67—74).—The decomposition of ammonia on the surface of a heated molybdenum wire is apparently of zero order. The presence of hydrogen produces a slight accelerating effect, whilst that of nitrogen produces a marked retardation, the velocity after first decreasing with increasing concentration of nitrogen attaining a final limiting value. The film of nitrogen on the surface of the wire is very persistent and is not removed by pumping off in a vacuum. Wires, however, return to normal activity after performing one or more experiments with ammonia. Activated molecules only of nitrogen condense to form the poisoning film, which may consist of atomic nitrogen. Since the rate of reaction is not zero at nitrogen pressures which are so great that the surface is almost completely covered, the reaction must still proceed on parts of the surface which are not poisoned or, at a reduced rate, on a film of nitrogen. It is impossible to distinguish between the two possible mechanisms, since both yield theoretical kinetic expressions of the same type. At a given temperature and pressure of ammonia, the rate of reaction is represented by the equation reciprocal of half-life = $(k_3k_2/k_2 + k_1p) + k_4$, where k_1 , k_2 , k_3 , and k_4 are constants and p is the pressure of nitrogen. Experiments at various temperatures between 1097° and 1228° Abs. show that the logarithm of the half-life varies linearly with the reciprocal of the absolute temperature, the slope of the line corresponding with a heat of activation of 53,200 g.-cal. This is shown to be a true heat of activation. The present data are compared with those obtained with other catalysts (Hinshelwood and Burk, A., 1925, ii, 691).

J. S. CARTER.

Contact catalysis and the activation of gases by adsorption. H. S. TAYLOR and G. KISTIAKOVSKI (Z. physikal. Chem., 1927, 125, 341—362).—The activation of part of the adsorbed gas in hydrogenation reactions is ascribed to the action of the unsatisfied valencies of the outlying atoms on the solid surface. Earlier work on the ionisation potentials of adsorbed films of hydrogen and nitrogen on metallic surfaces is discussed and results are given which prove that the ionisations occurring at 11 and 13 volts are

due to nitrogen and hydrogen, respectively. A calorimetric method is described whereby measurements may be made of the heats of adsorption of small quantities of gas on catalytic surfaces. The curves showing the relation of the heat of adsorption to the degree of saturation of the surface are of different types for hydrogen adsorbed on active copper and on a copper surface poisoned with oxygen and for carbon monoxide adsorbed on active copper. The theory of catalytic surfaces, employed in conjunction with Langmuir's theory of adsorption, is capable of explaining these three types of curve, if it is assumed that only part of the surface atoms can activate the adsorbed gas molecules and that the activation is endothermic. The work of Schmidt and of Schwab and Pietsch is criticised, and it is suggested that the activation of hydrogen is due to atomic dissociation.

H. F. GILLBE.

Influence of the adsorptive power of the carrier on the catalytic activity of metal-carrier catalysts. T. SABALITSOHKA and W. MOSES (Ber., 1927, 60, [B], 786—804).—The catalytic hydrogenation of maleic and fumaric acids and sodium cinnamate has been examined in the presence of palladium deposited on blood, beech, fungus, bone, and sugar charcoal and on barium sulphate and kieselguhr. The adsorptive power of the catalysts towards hydrogen cannot be definitely determined. The sequence of adsorptive powers towards fumaric and maleic acids and sodium cinnamate is: blood > beech > fungus > bone > sugar charcoals > barium sulphate = kieselguhr. The activity of the catalysts obtained by loading different carriers with an equal amount of palladium depends to a greater or less extent on the carrier. With freshly-prepared materials, the activity towards all three unsaturated substances diminishes in the sequence blood > fungus > beech > bone > sugar charcoals > barium sulphate = kieselguhr = palladium without carrier. The activity is also dependent on the manner in which any given carrier is charged with a definite amount of metal; for example, sugar charcoal, barium sulphate, and kieselguhr catalysts, prepared from the hydroxide and subsequently preserved, have a greater activity than fresh catalysts prepared from the chloride. Ignition in a high vacuum and saturation with hydrogen diminishes the activity of all catalysts to an extent which increases with the number of such treatments; the catalyst is not re-activated by oxygen. The adsorptive power of the catalysts towards hydrogen depends on the type of carrier and is scarcely affected by the mode of charging with palladium; palladium-free carriers do not adsorb hydrogen measurably.

The activity of the palladised carriers depends greatly on the extent to which the palladium compound is adsorbed by the carrier previous to reduction. With carriers of low adsorptive power, more efficient catalysts are obtained by use of the readily adsorbable palladium hydroxide in place of the chloride, whereas with good adsorbents little difference is observed in the various products. The activity of palladised barium sulphate is dependent on the degree of division of the palladium. The catalytic activity is influenced in varying degree by the volume of the

liquid in which it is distributed during hydrogenation.

Separate determinations of the adsorptive powers of palladised catalysts toward hydrogen and the substances undergoing hydrogenation and of the catalytic activity of these catalysts under similar conditions indicate a proportionality between the three properties, but show that the catalytic activity does not depend directly on the magnitude of the adsorption. The important function of the carrier is the provision of a larger surface and favourable disposition of the catalysing metal by adsorption of the compound from which it is formed by reduction; it also secures a better distribution of the metal in the reaction mixture and preserves the fine division of the metal by hindering aggregation, which otherwise takes place readily.

H. WREN.

Products formed during the working of lead accumulators. II. L. MAZZA.—See B., 1927, 257.

Applications of passivity in electrolysis. O. DONY-HÉNAULT (Bull. Soc. chim. Belg., 1927, 36, 261—270).—Certain iron alloys, notably steels of the "stainless" type, become passive in contact with solutions containing chlorates, and to a less extent in contact with perchlorate solutions. Such alloys may be substituted for platinum for use as anodes in electrolytic processes involving high current densities and considerable local acidities (e.g., the decomposition of barium carbonate in the anode chamber of an electrolytic system containing chlorates). An iron-cobalt-copper alloy is rapidly attacked under these conditions. The passivity of lead is discussed and the importance of including overvoltage effects when considering the processes involved in the mechanism of the lead accumulator is emphasised.

J. S. CARTER.

Electrolysis of aqueous solutions of pure oxalic acid. E. DOUMER (Compt. rend., 1927, 184, 747—749).—The anodic products of the electrolysis of oxalic acid and its salts vary with the reaction. Electrolyses with various concentrations of pure oxalic acid and various current densities have shown that oxygen and carbon dioxide are produced at the anode, the former usually in the largest quantities and in amounts depending on the current density, but falling within certain limits (0.25 and 0.5 of the corresponding volume of voltametric hydrogen liberated). The results may be explained by the ionisation of 2 mols. of water for 1 mol. of oxalic acid. The oxalate ions partly decompose into carbon dioxide and partly react with the hydroxyl ions to produce oxygen.

J. GRANT.

Photo-decomposition of chlorine water and of aqueous hypochlorous acid solutions. II. A. J. ALLMAND, P. W. CUNLIFFE, and R. E. W. MADDISON (J.C.S., 1927, 655—669).—Measurements of the extinction coefficients are described for the range 365—436 μ for hypochlorous acid and chlorine water, both alone and also in presence of certain added strong electrolytes; the values of the extinction coefficient for chlorine in solution are very close to those for gaseous chlorine. From the amount of decomposition and the quantity of energy absorbed, the quantum efficiency at 365 μ for chlorine water is

calculated, and lies between 1.6 and 2.0; it varies very little with wave-length over the range 313—436 μ , but is greatly reduced by the addition of certain strong electrolytes, notably hydrochloric acid. A consideration of these results together with previous data (A., 1925, ii, 572) on the yield of chloric acid during decomposition, the volatility of chlorine in the different solutions, and the present extinction coefficient measurements leads to a theory of the mechanism of the reaction. This theory is found to be consistent with thermochemical data and with the observed order of reaction, and appears to permit of the separate determination of the efficiency of the primary and secondary photo-reactions.

S. J. GREGG.

Photochemical decomposition of hydrogen iodide. B. LEWIS (Nature, 1927, 119, 493).—Working at a pressure of hydrogen iodide of the order of 0.1 mm. of mercury, the quantum efficiency of the reaction is about two; Warburg's mechanism (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1918, 300) is thus experimentally substantiated. Hence a polar molecule may dissociate in a single elementary act.

A. A. ELDRIDGE.

Photochemistry of the alkali and alkaline-earth iodides. H. STOBBE and F. K. STEINBERGER (Z. anorg. Chem., 1927, 161, 21—45).—If alkaline solutions of potassium iodide in vessels of quartz or "uvio" glass are exposed to sunlight or the light from a mercury-vapour lamp, the alkalinity diminishes somewhat, probably due to the action of carbon dioxide from the air, and solutions which were originally only slightly alkaline contain after exposure hypoiodite and free iodine, whilst if the alkalinity is increased, iodate is formed as well, and in strongly alkaline solutions is the only product. It is therefore concluded that the photolysis involves the reactions: $2KI + O + H_2O = 2KOH + I_2$; $KI + I_2 = KI_3$; $2KOH + I_2 = KIO + KI + H_2O$; $3KIO = KIO_3 + 2KI$. With neutral iodide solutions, no free iodine is formed in absence of oxygen, and even when oxygen is present, no iodate, and only small amounts of hypoiodite, are formed in addition to free iodine. In presence of oxygen only, there is very little reaction, but if increasing amounts of carbon dioxide are introduced, the photolysis increases up to a maximum, beyond which it diminishes. Since other weak acids such as boric acid and *p*-nitrophenol also promote the reaction, it seems that carbon dioxide acts by increasing the hydrogen-ion concentration of the solution. In ordinary air, the formation of free iodine from neutral iodide solutions apparently is due mainly to the photolysis of hydrogen iodide, the above reactions occurring only to a small extent. When preserved in the dark, some solutions become yellow but remain neutral, whilst others remain colourless but become slightly alkaline. In the decomposed solutions, hydrogen ions, from carbonic acid, have brought about the reaction $2HI + O = H_2O + I_2$, whereas in the other solutions the alkali, presumably from the containing vessel, has removed the hydrogen ions, so the reaction $2KI + O + H_2O = 2KOH + I_2$ must be able to occur only in the light. The rate of decomposition of iodide solutions in the light increases with increase in the iodide concentration, but is not

directly related to it. If nuclei of iodine are already present at the outset, the velocity of reaction is greater at first than it is later, whilst if the nuclei are absent, the reverse is the case. In either case, the velocity after the initial stage becomes approximately constant for a considerable time. The photolysis of neutral iodide solutions to which the oxygen of the air has free access is a bimolecular reaction, but the velocity coefficient is dependent on the intensity and wave-length of the light and on the proportion of effective radiation absorbed, and increases with the time until so much tri-iodide is formed that all the active radiation is absorbed. Thus the behaviour of these solutions closely resembles that of hydrogen iodide solution (cf. Winther, A., 1920, ii, 427), as might be expected from the above. The wave-lengths most active in bringing about decomposition are in the ultra-violet, but the blue of the visible spectrum has also a slight effect. R. CUTHILL.

Photochemical decomposition of potassium persulphate. III. Effect of added electrolytes. J. L. R. MORGAN and R. H. CRIST (J. Amer. Chem. Soc., 1927, 49, 960—966).—There is no evidence of the existence of intermediate equilibria in the photochemical decomposition of potassium persulphate, such as occur in the thermal decomposition (Palme, A., 1920, ii, 685). The rate of decomposition is retarded by sulphuric acid, potassium sulphate, and potassium hydroxide; in no case can this retardation be due to an inner filter action. In each case, the velocity is a hyperbolic function of the amount of electrolyte added. The phenomena are discussed from the points of view of de-activation and of a kinetic salt effect. S. K. TWEDDY.

Alleged retardation of certain reactions by light. A. J. ALLMAND and R. E. W. MADDISON (J.C.S., 1927, 650—655).—Experiments were carried out on the oxidation of solutions of sodium sulphite when exposed to light of various wave-lengths and also in the dark. Curves correlating time of exposure and amount of oxidation showed no discontinuity even although successive portions of the curves applied to alternate dark and light periods, except in the case of ultra-violet light of very short wave-length. Thus light of ordinary wave-length has no effect on the rate of oxidation of sodium sulphite in solution.

S. J. GREGG.

Oxygen transmission by chlorophyll and the photochemical equivalent law. H. GAFFRON (Ber., 1927, 60, [B], 755—766; cf. Warburg and Negelein, A., 1922, i, 1097; 1923, ii, 718).—Under the influence of light, a solution of chlorophyll in acetone absorbs oxygen with gradual oxidation of the dye. In presence of a suitable acceptor, the absorption is accelerated and the chlorophyll suffers much less change. For this purpose, allylthiocarbamide is selected, which, in addition to complex compounds, yields sulphur dioxide and thence sulphur trioxide. The relationship between the volume of oxygen absorbed and the amount of light used shows that in this case Einstein's photochemical equivalent law is obeyed for a large range of the spectrum. There is no relationship between strength of absorption for light of differing wave-lengths and photochemical action,

provided that the absorption is complete. Confirmation is afforded to the observation of Warburg and Negelein (*loc. cit.*) that every quantum absorbed by the chlorophyll, independent of its energy, causes the same chemical action in the living plant. Variations in the concentration of dye and acceptor show that each is free in the solution; excess of dye hinders the photochemical change, which is promoted by the acceptor. The solvent is indifferent. The observations may be expressed quantitatively by the formula $\phi/\phi_0 = (C_A/C_F)\alpha K / ((C_A/C_F)\alpha K + 1)$, where ϕ and ϕ_0 are the observed and calculated photochemical activities, C_A and C_F the concentrations of acceptor and dye, and K is an empirical constant.

Similar behaviour is exhibited by hæmatoporphyrin and allylthiocarbamide dissolved in acetone.

H. WREN.

Special action of radiations from a mercury arc. E. ROUSSEAU (*Compt. rend.*, 1927, 184, 683—685; cf. Lecarme, *ibid.*, 1925, 181, 1079).—The photolytic effects of the mercury arc have been tested on a solution containing calcium monophosphate (10 g.), phosphoric acid (1 c.c.), and cherry-laurel water (Codex) (100 c.c.), the hydrogen cyanide remaining after various intervals of time being determined. The liquid was covered with a protecting layer of oil impermeable to ultra-violet rays. The effect must therefore be due to visible radiations in the green, red, or infra-red regions, or to an unknown photochemical radiation from the mercury arc analogous to that observed by Lecarme in ultra-violet solar radiations (*loc. cit.*).

J. GRANT.

Determination of the energies of reaction from a knowledge of the active radiations. R. AUDUBERT (*Compt. rend.*, 1927, 184, 881—883).—The Perrin-Lewis radiochemical theory has been verified by the determination of the initial frequencies (ν_0' and ν_0) of the light required to produce and reverse the reaction in the equation $Q = hN(\nu_0' - \nu_0)$, Q being the energy of reaction, h Planck's constant, and N Avogadro's number. The reaction studied was the oxidation and reduction, respectively, of ferrous and ferric salts ($\nu_0 = 3.5 \times 10^{14}$ and $\nu_0' = 2.0 \times 10^{14}$, respectively) by the same radiations, but with different intensities. The frequencies were determined electrometrically from the *E.M.F.* produced when a platinum electrode placed in an electrolyte is illuminated (*A.*, 1923, ii, 827), the potential increasing with the frequency for a particular intensity of radiation. The result has been confirmed by measurements of the affinity, and the oxidation of ferrous to ferric iron has been shown to be an endothermic reaction.

J. GRANT.

Existence of triatomic hydrogen. F. PANETH, E. KLEVER, and K. PETERS (*Z. Elektrochem.*, 1927, 33, 102—107).—Processes stated to yield triatomic hydrogen (cf. Wendt, *A.*, 1920, ii, 425; 1922, ii, 369; Grubb, *A.*, 1923, ii, 403; Venkataramaiah, *A.*, 1923, ii, 235; 1924, ii, 34) have been examined, but it is concluded that no evidence for the existence of this substance has been obtained. Hydrogen which has been passed through hot palladium or submitted to a silent discharge in an ozoniser does indeed blacken lead acetate paper after passage through a tube of

sulphur, but the effect is just the same if this sulphur tube is omitted. Hydrogen sulphide arises from traces of sulphur in the palladium or the glass, respectively. The phenomenon disappears if the palladium or the ozoniser is kept in use for some time and is not obtained if a quartz ozoniser is employed. Again, the supposed formation of ammonia by the action of pure nitrogen on hydrogen obtained by the action of acids on magnesium is disproved. Ammonia is obtained when pure hydrogen is substituted for nitrogen and arises from traces of nitride in the magnesium. The statement that when oxygen is exploded with excess of hydrogen the residual gas reduces permanganate or indigo could not be confirmed, in spite of wide variation of the experimental conditions. Hydrogen which had been subjected to α -rays from a mixture of thorium-*B* and thorium-*C* did not reduce sulphur, but using α -rays from polonium, a trace of hydrogen sulphide was detected. This is attributed, however, not to activation of the hydrogen, but to traces of finely-divided polonium being carried over on to the sulphur; sulphur and hydrogen are known to react under the direct influence of α -rays.

H. J. T. ELLINGHAM.

Conversion of hydrogen into helium. F. PANETH, K. PETERS, and P. GÜNTHER (*Ber.*, 1927, 60, [B], 808—809; cf. *A.*, 1926, 1077).—Possible sources of error in the previous experiments are indicated by the observations that asbestos evolves its helium content at a much lower temperature in hydrogen than in oxygen and that the arrangement of the apparatus may not exclude the penetration of helium from the atmosphere.

H. WREN.

Direct oxidation of lithium iodide. J. P. SIMMONS and C. F. PICKETT (*J. Amer. Chem. Soc.*, 1927, 49, 701—703).—Anhydrous lithium iodide decomposes at high temperatures in a stream of oxygen according to the equation $10\text{LiI} + 5\text{O}_2 = 2\text{Li}_2\text{O}_3 + 4\text{Li}_2\text{O} + 4\text{I}_2$.

S. K. TWEEDY.

Sodium hyponitrite. A. W. SCOTT (*J. Amer. Chem. Soc.*, 1927, 49, 986—987).—Sodium hyponitrite, which is not hygroscopic, is conveniently prepared as follows. To a saturated solution of 3.26 g. of hydroxylamine hydrochloride in anhydrous ethyl alcohol at -5° is added slightly more than the calculated amount of sodium dissolved in the least amount of alcohol. After filtering, 110 c.c. of anhydrous ether and 3.24 g. of sodium in the minimum amount of alcohol are added to the solution, which is then cooled to -5° and twice the calculated amount of either amyl or propyl nitrite added. After being kept at -5° for 1 hr., the sodium hyponitrite is collected, washed with alcohol, then with ether, and dried over sulphuric acid in a vacuum; the yield is 13.9%.

S. K. TWEEDY.

Dehydration of borax. M. A. RAKUSIN and D. A. BRODSKI.—See *B.*, 1927, 250.

Thermal dissociation of alkali fluoborates. J. H. DE BOER and J. A. M. VAN LIEMPT (*Rec. trav. chim.*, 1927, 46, 124—132).—The fluoborates of potassium (m. p. 530°), rubidium (m. p. 590°), and caesium (m. p. 550°) were prepared by precipitation of solutions of the corresponding chlorides by hydro-

fluoboric acid solution, and those of sodium and lithium by placing solid boron fluoride and the solid alkali fluoride together in an evacuated vessel. Since the proportion of substance dissociating is small, the ratio of potassium fluoride to boron trifluoride in the liquid phase is sensibly constant over the whole temperature range, and the system is therefore univariant. The results fit the following equations: for KBF_4 , $\log p(\text{mm. of mercury}) = -6317/T + 8.15$, whence the heat of reaction Q of the equation $\text{KBF}_4(\text{liquid}) = \text{KF}(\text{liquid}) + \text{BF}_3(\text{gas}) + Q$ g.-cal. is 28,900 g.-cal.; for RbBF_4 , $\log p = -5900/T + 7.45$, and $Q = 26,960$ g.-cal.; for CsBF_4 , $\log p = -5880/T + 7.35$, and $Q = 26,880$ g.-cal. By considering the formation of potassium fluoborate by the path $\text{KF} \rightarrow \text{K}' + \text{F}' + \text{U}_{\text{KF}}$, $\text{F}' + \text{BF}_3 \rightarrow \text{BF}_4' - \phi_{\text{BF}_4}$, the value of ϕ_{BF_4} is deduced and applied to calcium fluoborate, the heat of formation of which is thus shown to be negative, in accordance with the fact that calcium fluoride will not combine with boron fluoride. The refractive indices of saturated solutions of the salts were also measured and shown to be close to that of water.

S. J. GREGG.

Azidodithiocarbonic acid. III. Azidodithiocarbonates of lithium, sodium, rubidium, and caesium. A. W. BROWNE and A. F. AUDRIETH [with C. W. MASON] (J. Amer. Chem. Soc., 1927, 49, 917—925; cf. A., 1926, 39).—The crystalline *azidodithiocarbonates*, $\text{MS} \cdot \text{CS} \cdot \text{N}_3 \cdot x\text{H}_2\text{O}$, of lithium ($x=1$), sodium ($x=4, 2$, and 0), rubidium ($x=0$), and caesium ($x=0$) were prepared by the union of carbon disulphide with alkali azides (Browne and Hoel, A., 1922, ii, 848). The solubilities of the salts follow the order $\text{Li} > \text{Cs} > \text{Rb} > \text{Na}$; they are insoluble in carbon disulphide, chloroform, carbon tetrachloride, and benzene. They tend to decompose at the ordinary temperature: $\text{MS} \cdot \text{CSN}_3 = \text{MS} \cdot \text{CN} + \text{S} + \text{N}_2$. The violence of the explosion on detonation varies directly as the atomic weight of M, except that the lithium salt is more explosive than the sodium salts. The explosion liberates a gas with a sulphurous odour, leaving a viscous, yellow residue, probably a polymeride of thiocyanogen. Microscopical observations are recorded. The rubidium and caesium salts are very photosensitive; on alternate illumination and confinement in a dark space, "photolysis" occurs and the salt decomposes. The colour change on illumination is ascribed to free metal atoms held *in situ* in the crystal lattice, their valency electrons having been restored by some photo-process. It is suggested that the blue colour of Stassfurt halite may similarly be explained.

S. K. TWEEDY.

Reduction of copper oxide by gaseous reducing agents. W. G. PALMER (Trans. Amer. Electrochem. Soc., 1927, 51, 87—90).—See A., 1923, ii, 474.

H. J. T. ELLINGHAM.

Preparation of sodium aurothiosulphate. H. BROWN (J. Amer. Chem. Soc., 1927, 49, 953—959).—The following method is more rapid and economical than that described by McCluskey and Eichelberger (A., 1926, 255). A solution of 41.2 g. of hydrochloroauric acid in 75 c.c. of water is rendered faintly alkaline with 40% sodium hydroxide solution and a solution of 102 g. of sodium thiosulphate crystals in

200 c.c. of water is added. The mixture is mechanically stirred and 4*N*-nitric acid added dropwise until the red colour ceases to appear. When the mixture shows faint turbidity, it is filtered and precipitated with four times its volume of alcohol. The precipitate is redissolved in the minimum amount of water and, after filtration, reprecipitated. A further precipitation yields very pure sodium aurothiosulphate. The salt is dried over sulphuric acid in a vacuum and may be preserved in well-stoppered bottles in a refrigerator. It will keep at the ordinary temperature for 3 months if sealed in amber tubes under slightly reduced pressure.

S. K. TWEEDY.

Reducing properties of beryllium. Isolation of barium, magnesium, potassium, and aluminium. C. MATIGNON and (MLLE.) G. MARCHAL (Compt. rend., 1927, 184, 715—717).—On account of its high heat of oxidation, beryllium may be used to reduce certain metallic oxides. The oxide is well mixed with a slight excess of beryllium beyond the theoretical quantity required, pressed into a solid pastille, and heated in the electric furnace. Magnesium oxide and potassium hydroxide have been completely reduced by these means at 1280° and 700°, respectively. Barium and aluminium oxides are partly reduced to the corresponding metal at 1230° and 1280°, respectively, whilst lime forms a suboxide of calcium at 1230—1280°.

J. GRANT.

Preparation of beryllium chloride. C. MATIGNON and M. PIETTRE (Compt. rend., 1927, 184, 853—855).—Beryllia may be converted into beryllium chloride by the action of sulphur chloride at 700—800°, phosphorus trichloride at 850°, phosphorus perchloride, or carbon tetrachloride. Carbon tetrachloride at 800° for 1.25 hrs. gives a yield of 68—80%, the other reagents giving low yields, slow reactions, or impure products.

J. GRANT.

[Non-existence of] magnesium sulphate octahydrate. A. BENRATH and W. SOHRÖDER (Z. anorg. Chem., 1927, 161, 155—158).—Attempts to confirm the existence of the magnesium sulphate octahydrate reported by Takegami (A., 1921, ii, 698) have been unsuccessful.

R. CUTHILL.

Reactions of metals with solid salts on heating. B. GARRE (Z. anorg. Chem., 1927, 161, 108—112).—The heating curves of mixtures of various metallic oxides and carbonates with magnesium and aluminium, respectively, have been determined. The reactions with magnesium start more gradually and at a lower temperature than those with aluminium. With binary mixtures of zinc and tin with lead oxide or cupric oxide, or of cupric oxide with lead or nickel, the reaction commences below the m. p. of either component. If the heat of reaction is less than about 15 kg.-cal., the reaction is not complete below the m. p., so that a little above this temperature there is a second evolution of heat, and if the products of reaction still prevent complete decomposition there may be a third evolution of heat at a still higher temperature.

R. CUTHILL.

Potentiometrical study of the reaction between calcium ferrocyanide and solutions containing rubidium and caesium. C. DEL FRESNO and J. VÁZQUEZ (Anal. Fis. Quim., 1927, 25, 42—46, and

Z. Elektrochem., 1927, **33**, 149—150).—The potentiometric curves obtained by titrating 0.2*M*-solutions of calcium ferrocyanide against approximately 0.1*N*-solutions of rubidium chloride and caesium bromide, respectively, show discontinuities corresponding with the completion of the reaction $\text{Ca}_2\text{Fe}(\text{CN})_6 + 2\text{MX} = \text{CaX}_2 + \text{CaM}_2\text{Fe}(\text{CN})_6$, where $\text{M} = \text{Rb}$ or Cs and $\text{X} = \text{halogen}$. The agreement with the equation is not sufficiently good for the method to be used for quantitative determinations. G. W. ROBINSON.

Analysis and preparation of cadmium sulphides. P. HULOT (Bull. Soc. chim., 1927, [iv], **41**, 313—316).—Ten different cadmium sulphides have been prepared, mainly by the reaction of a solution obtained by boiling sulphur with sodium carbonate solution with solutions of cadmium salts under varying conditions, and by the action of sodium monosulphide solution on a suspension of cadmium carbonate. Specimens were also prepared in the dry way; they contained 71 to 73.9% of cadmium and 21.2 to 19.2% of sulphur, whereas those prepared in the wet way contained 67 to 69.1% of cadmium and 16.3 to 18.4% of sulphur. The presence of free sulphur was carefully avoided. The products were analysed by fusing with potassium nitrate, extracting the cooled melt with water, and weighing the residue as cadmium oxide, the sulphate being determined in the extract. S. K. TWEEDY.

Fractional precipitation of barium and radium chromates. L. M. HENDERSON and F. C. KRACEK (J. Amer. Chem. Soc., 1927, **49**, 738—749).—The separation of barium and radium by fractional precipitation of the chromates in 0.05—0.3*N* acid solutions is as efficient as the bromide method of separation. The method is advantageous when only small quantities of the barium-radium mixture are available, or when the solution containing the mixture is too dilute to be concentrated economically by the chloride method. S. K. TWEEDY.

Causes of the surface devitrification of glasses. K. TABATA.—See B., 1927, 219.

Reduction of metallic chlorides by hydrogen. A. B. BAGDASARIAN (Trans. Amer. Electrochem. Soc., 1927, **51**, 1—46).—Equilibria involved in the reduction of lead, zinc, and cuprous and ferrous chlorides by hydrogen at various temperatures below the b. p. of the chlorides or the corresponding metals have been studied by analysing the gases obtained by passing a slow stream of hydrogen over the chloride or of hydrogen chloride over the corresponding metal. In the latter case, the reaction is relatively slow and measurements were made at various rates of gas flow, the true equilibrium composition of the resulting gases being obtained by extrapolation to zero gas velocity. Under these conditions, values of the equilibrium constant, K , were in good agreement, irrespective of the side from which the equilibrium was approached. The curve correlating $\log K$ with $1/T$ is a straight line except for ferrous chloride, where two breaks are obtained, due probably to the transition points of metallic iron. The free energy equations for the reduction of lead, zinc, and cuprous chlorides by hydrogen have been calculated, and by

combining with existing data, the following quantities have been calculated: heats of formation of cuprous chloride (CuCl) and lead chloride, 31,280 and 85,145 g.-cal., respectively, at 25°; free energy of formation of cuprous chloride (CuCl), 28,435 g.-cal. at 25°; latent heats of fusion of cuprous chloride (CuCl) and zinc chloride, 2246 and 7380 g.-cal., respectively.

A process is suggested for the treatment of certain classes of complex ores and other metallurgical products, in which the material is chlorinated in the dry way with chlorine or hydrogen chloride at a suitable temperature and the metallic chlorides thus formed are reduced by hydrogen at elevated temperatures. Hydrogen and chlorine could be regenerated by electrolysis of the hydrogen chloride produced in the reduction process. H. J. T. ELLINGHAM.

Active nitrogen. II. Reactions with gases. E. J. B. WILLEY and E. K. RIDEAL (J.C.S., 1927, 669—679).—The value 43,000 g.-cal./g.-mol. previously given by the authors (A., 1926, 893) for the mean energy content of active nitrogen has been confirmed by a study of the reactions of the gas with other gases of varying critical increments. Hydrogen, carbon monoxide, carbon dioxide, and water vapour, with their critical increments above 55,000 g.-cal./g.-mol., had no effect on the after-glow. The characteristic luminosity of iodine (dissociation energy 34,500 g.-cal./g.-mol.) and of bromine (46,200) were easily excited, but that of chlorine (55,000) only very slightly. Hydrogen iodide was readily, hydrogen bromide less readily, and hydrogen chloride not at all decomposed by active nitrogen, the respective energies of decomposition being 45,700, 50,000, and 90,000 g.-cal./g.-mol. On the other hand, from a mixture of hydrogen and chlorine a considerable quantity of hydrogen chloride was formed, probably owing to the intermediate excitation of the chlorine molecules by second-type collisions. Nitric oxide, the critical increment of which is below 55,000 g.-cal., was readily decomposed into nitrogen and oxygen, whereas nitrous oxide, with its energy of activation 60,300 g.-cal./g.-mol., was unaffected. The slight reactions that occur with substances of higher critical increment than the mean 43,000 are due to a statistical distribution in the after-glow of three species of active molecules, some just above and others below the mean values. S. J. GREGG.

Compounds of nitrosyl chloride with inorganic chlorides. H. RHEINBOLDT and R. WASSERFUHR (Ber., 1927, **60**, [B], 732—737; cf. this vol., 229; Gall and Mengdehl, *ibid.*, 219).—The following additive compounds are obtained from nitrosyl chloride and the inorganic chloride dissolved in well-cooled carbon tetrachloride: SbCl_5NOCl , m. p. about 170° after darkening at about 150°; $\text{SnCl}_4\text{,}2\text{NOCl}$, m. p. about 188° after darkening at 100—110°, and becoming lighter at 150°; $\text{TiCl}_4\text{,}2\text{NOCl}$, which does not melt below 220°; $\text{PbCl}_4\text{,}2\text{NOCl}$. In absence of solvent, the following compounds are prepared: AlCl_3NOCl , m. p. 108—110° after softening at 90—100°, decomp. 140—150°; BiCl_3NOCl , m. p. 115—120° after softening at 80°, slight decomp. 150°; FeCl_3NOCl , m. p. 128° after softening at about 115°.

H. WREN.

Nitrosulphonic acid. F. RASCHIG (Ber., 1927, 60, [B], 616—620).—In reply to Manchot and others (this vol., 32), the author maintains his conception that "blue acid" contains the compound, $O:N(OH)\cdot SO_3H$. The following observations are cited in favour of this view. A solution of sodium nitrite in concentrated sulphuric acid in absence of air acquires under the action of mercury, copper, or silver an intense blue colour, which gradually fades; the colourless solution contains nitrous oxide. Nitrosulphonic acid forms with a solution of sulphur dioxide in sulphuric acid a blue solution from which nitric oxide is quantitatively evolved, $2NO_2\cdot SO_3H + SO_2 + 2H_2O = 2NO + 3H_2SO_4$. Nitric oxide is absorbed by copper sulphate dissolved in concentrated sulphuric acid in the molecular ratio 1:1 at atmospheric temperature and pressure; the conception that the dark blue solution contains the copper salt of nitrosulphonic acid is strengthened by the observation that hydroxylamine-sulphonic acid is oxidised by Caro's acid in presence of sulphuric acid and a trace of copper to a dark blue compound, whereas hydroxylamine is not similarly affected.

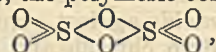
H. WREN.

Stabilised aqua regia. E. BRINER (Bull. Soc. chim. Belg., 1927, 36, 79—88).—When sealed tubes containing concentrated solutions of nitric and hydrochloric acids in the proportions usually used for the preparation of aqua regia are heated for a short time at 100° , or allowed to remain for several hrs. at the ordinary temperature, two conjugate solutions result. The heavier liquid phase, which has the characteristic colour of nitrosyl chloride, consists mainly of liquid chlorine and nitrosyl chloride formed as a result of the reaction $3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O$. This system is termed "stabilised aqua regia." Measurements of the vapour pressures of such systems show that within the limits of co-existence of two liquid phases the observed pressures (2.86 and 5.2 atm. at 0° and $20.5\text{--}21.0^\circ$, respectively) are dependent only on the temperature. Application of the phase rule leads to the conclusion that there are two independent components, nitric acid and hydrochloric acid. The thermal equation is $3HCl_{conc.} + HNO_{3conc.} \rightleftharpoons Cl_{2liq.} + NOCl_{liq.} + 2H_2O - 21.8 \text{ kg.-cal.}$ Measurements of the electrical conductivity at 0° and 20° of the aqueous phase after the establishment of equilibrium show that within the limits of co-existence of two liquid phases the specific conductivities at these two temperatures, 0.324 and 0.465 mho, respectively, are independent of the concentrations and proportions of the two acids. Mixtures of nitric and hydrobromic acids behave similarly, the vapour pressures of the univariant systems being, however, much smaller (0.25 and 0.50 atm. at 0° and 16° , respectively). Mixtures of nitric and hydriodic acid do not form a univariant system, the iodine formed as a result of the primary reaction being oxidised to iodic acid with production of nitric oxide.

J. S. CARTER.

Behaviour and constitution of monosulphuric and disulphuric anhydrides. VI. G. ODDO and A. SCONZO (Gazzetta, 1927, 57, 83—103; cf. this vol., 300, and following abstract).—On the supposition that monosulphuric anhydride (sulphur trioxide, α -form)

has the structure $S[:O]_3$, and the β -form, or disulphuric anhydride, the polymeric constitution,



the resemblance to the polymerisation of an aldehyde suggested that negative catalysts might stabilise the α -form. With small quantities of sulphur, tellurium, carbon tetrachloride, or phosphorus oxychloride, the α -form was preserved for months; other substances gave less satisfactory or negative results. A tendency to the formation of the translucent or colloidal form was observed.

The α -form does not combine with sulphuryl chloride or with chlorosulphonic acid; with chlorinating agents, the two forms show different behaviour. Thus with phosphorus pentachloride the α -form gave sulphur dioxide, chlorine, and phosphorus oxychloride, with some pyrosulphuryl chloride. With the β -form no sulphur dioxide or chlorine was evolved, pyrosulphuryl chloride alone being formed, $S_2O_6 + PCl_5 \rightarrow S_2O_5Cl_2 + POCl_3$. Sulphur monochloride with the α -form yielded sulphur dioxide and dichloride; with the β -form, no gas was evolved, the reaction being as before. The α -form reacted rapidly and the β -form slowly with carbon tetrachloride, giving carbonyl chloride and pyrosulphuryl chloride, for which the scheme $2SO_3 + CCl_4 \rightarrow [SO_2Cl\cdot O]_2 CCl_2 \rightarrow [SO_2Cl]_2 O + COCl_2$ is suggested; the velocity constant shows that the reaction is unimolecular.

These results are considered to prove the structures assigned above to the α - and β -forms of sulphur trioxide.

E. W. WIGNALL.

Sulphuric anhydrides and sulphuric [acids]. VII. G. ODDO (Gazzetta, 1927, 57, 104—116).—A summary of papers on sulphuric anhydrides (sulphur trioxides) (A., 1901, ii, 650; preceding abstract) and sulphuric acids (A., 1908, ii, 353; 1909, ii, 377, 792; 1910, ii, 1035; 1911, ii, 717; 1918, ii, 189, 352).

E. W. WIGNALL.

Colour of selenium dioxide. A. WELLER (Ber., 1927, 60, [B], 649).—Selenium dioxide is not an isolated example of a colourless substance which gives a coloured liquid and vapour (cf. Meyer and Langner, this vol., 220). Similar behaviour is exhibited by tellurium dioxide and tetrachloride.

H. WREN.

Colours of chromous, vanadous, and tervalent uranium ions. K. SOMEYA (Z. anorg. Chem., 1927, 161, 46—50).—Reduction of a uranyl chloride solution with zinc amalgam and hydrochloric acid yields a reddish-purple solution, which on dilution with water or dilute hydrochloric acid becomes dark green. Addition of potassium thiocyanate to this diluted solution deepens the colour and turns it somewhat brown, whilst concentrated hydrochloric acid restores the purple colour. It therefore seems probable that the purple colour is not due to tervalent uranium ions, but to undissociated salt molecules or to complex ions. The violet solution obtained by reducing an ammonium vanadate solution fades on dilution and is restored by potassium thiocyanate or concentrated hydrochloric acid, probably for the same reason. Reduction of a very dilute solution of potassium dichromate gives an almost colourless solution, the chromous ion probably being colourless, whilst

addition of thiocyanate produces the blue colour of more concentrated solutions. R. CUTHILL.

Preparation and composition of the crystalline phospho- and arseno-conjugated ceruleo-molybdates. G. DENIGÈS (Compt. rend., 1927, 184, 687—689).—The preparation from sodium molybdate and disodium phosphate of a molybdenyl phosphomolybdate, $[4(\text{MoO}_3) \cdot \text{MoO}_2]_2\text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$, sapphire-blue hexagonal plates, is described. The name phospho-conjugated ceruleo-molybdate is suggested for the compound, which is produced whenever the MoO_3 radical is reduced in presence of the phosphate ion. The corresponding arseno-compound is prepared analogously and has similar properties (cf. A., 1920, ii, 770). J. GRANT.

Occurrence of manganese homologues of atomic numbers 43, 61, and 75. W. PRANDTL (Ber., 1927, 60, [B], 621—623).—Repetition of the work of Noddack, Tacke, and Berg (A., 1925, ii, 939) fails to yield evidence of the existence of elements 43 and 75 in columbite. The presence of ekamanganese in platinum ores cannot be regarded as established. There is no evidence of the existence of element 61, and its presence in cerite earths (cf. Rolla and Fernandes, A., 1926, 1083; this vol., 9) is regarded as impossible. H. WREN.

Interaction of manganese salts and permanganates. II. Action of manganese chloride on permanganates. J. G. F. DRUCE (Chem. News, 1927, 134, 161—163; cf. this vol., 332).—When the residue of potassium chloride and manganese dioxide resulting from the reaction $2\text{KMnO}_4 + 2\text{MnCl}_2 = \text{Cl}_2 + 2\text{KCl} + 4\text{MnO}_2$, is treated with either concentrated sulphuric or hydrochloric acid, the extract from the final non-volatile residue yields an impure potassium manganichloride, K_2MnCl_5 . Attempts to prepare the salt K_2MnCl_6 were unsuccessful. M. S. BURR.

Reduction of iron ores by hydrogen. I. G. GALLO.—See B., 1927, 278.

Behaviour of iron pyrites with hydrogen. II. G. GALLO.—See B., 1927, 279.

New ferromagnetic ferric oxide. R. CHEVALIER (Compt. rend., 1927, 184, 674—676).—The production of ferromagnetic ferric oxide (Fe_2O_3) from the oxide Fe_3O_4 depends on the conditions of the oxidation by hydrogen peroxide in presence of ferrous sulphate and sodium hydroxide. The specific moment of the product increases with the amount of the excess of sodium hydroxide present. The optimum temperature is 45—50°, and above this the magnetisation decreases rapidly, the ferric oxide being unstable, and contaminated with magnetite or free ferrous oxide at 100°. Such magnetic oxides show no hysteresis, as in the case of those prepared by dry oxidation of magnetite at 400° (Malaguti). The latter, however, are more stable at high temperatures. The ferromagnetism is attributed to a micellar structure rather than to the presence of simple polymerised molecules. J. GRANT.

Higher oxygen compounds of the metals of the eighth periodic group. I. Iron. D. K. GORALEVITCH (J. Russ. Phys. Chem. Soc., 1926, 58,

1129—1158).—The preparation and properties of the salts of ferric acid are described. On fusing ferric oxide with potassium hydroxide and excess of potassium nitrate or, better, potassium chlorate, bright green *potassium perferrate* is obtained, which is more stable than potassium ferrate and can be purified by cautious sublimation. It decomposes very slowly when kept in air, explosively when warmed, on treatment with concentrated sulphuric acid, or on impact if mixed with sulphur, phosphorus, or charcoal.

It is quite stable in alkaline solutions, but acids readily decompose it, with evolution of oxygen and, in the case of hydrochloric acid, chlorine. Oxidising agents like chlorine and hydrogen peroxide give a deep red solution of potassium ferrate with evolution of oxygen. Neutral solutions of the perferrate give no reaction for ferric ions until, on the addition of acid, decomposition has commenced. Salts of the alkaline earths give white *precipitates* containing water of crystallisation. They are stable, non-explosive, and soluble in dilute acids, the solutions containing the unstable free ferric acid, since the green colour of potassium perferrate is obtained on addition of alkali. The *sodium* salt is also described. Analysis of the hydrated barium salt gave the formula $\text{BaFeO}_5 \cdot 7\text{H}_2\text{O}$.

The decomposition of the free ferric acid was also investigated. At low temperatures, traces of a very volatile, unstable *anhydride*, probably FeO_4 , were isolated, which was insoluble in water, but soluble with decomposition in dilute acids. The properties are compared with those of ruthenium and osmium tetroxides. M. ZVEGINZOV.

Chlorides and chloro-salts of rhodium. M. DELÉPINE (Bull. Soc. chim. Belg., 1927, 36, 108—118).—Rhodium trichloride has been prepared as the anhydrous salt and as the hydrate $\text{RhCl}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$. The following salts have been prepared and analysed: hexachlororhodiates: sodium, $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$; potassium, $\text{K}_3\text{RhCl}_6 \cdot \text{H}_2\text{O}$; lithium, $\text{Li}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$; sodium lithium, $\text{Na}_{1.5}\text{Li}_{1.5}\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$; rubidium, $\text{Rb}_3\text{RhCl}_6 \cdot \text{H}_2\text{O}$; ammonium, $(\text{NH}_4)_3\text{RhCl}_6 \cdot \text{H}_2\text{O}$; aquopentachlororhodiates: potassium, ammonium, caesium, *rubidium*, $\text{M}_2\text{Rh}(\text{H}_2\text{O})\text{Cl}_5$; silver hydroxypentachlororhodate, $\text{Ag}_3\text{Rh}(\text{OH})\text{Cl}_5$. J. S. CARTER.

Determination of small quantities of hydrogen in nitrogen as hydrogen chloride. G. HEYNE.—See B., 1927, 217.

Reagents for standardisation of acids. K. O. SCHMITT (Z. anal. Chem., 1927, 70, 321—340).—The loss in weight of analytical samples of sodium and potassium hydrogen carbonates at various temperatures is always greater than the theoretical. The tests of Lunge and of Sebelien for hydroxides in presence of large quantities of carbonates being found unsatisfactory, a new method of examination, based on titration of the hydrogen carbonate and of the resulting carbonate, taking into account the loss in weight, was employed; in this way, it was found that sodium carbonate, prepared by ignition of the hydrogen carbonate, contains both oxide and hydroxide. Potassium hydrogen carbonate of satisfactory purity (99.98—100.00%) may be obtained by recrystallisation; the saturated solution must be cooled

rapidly, with energetic stirring, a stream of carbon dioxide being continually passed through the mixture.

S. I. LEVY.

Neutral litmus paper as indicator. W. EKHard (Z. Spiritusind., 1927, 50, 70—71).—The end-point, which is dependent to some extent on the colour sense of the observer, should be regarded as the point at which the colour just begins to alter. Fresh paper should always be used. At the neutral point, the paper should be compared with a control moistened with conductivity water. The paper, which should be kept hermetically enclosed from gases and protected from direct sunlight, should be of a medium violet colour of unvarying intensity. C. RANKEN.

Reference electrode for potentiometric titrations. T. R. BALL (Ind. Eng. Chem., 1927, 19, 370).—As a substitute for a calomel electrode, an asbestos fibre is sealed into one end of a 5 mm. gauge glass tube, which is filled with 3*N*-sulphuric acid as electrolyte for oxidation-reductions in acid solution or with *N*-potassium chloride for acidimetric titrations. Connexion to the potentiometer is made by a platinum wire inserted in the electrode. Satisfactory results are obtained in oxidation-reduction and in precipitation determinations (such as zinc with potassium ferrocyanide or silver with sodium sulphide), but acidimetric titrations are less trustworthy.

L. M. CLARK.

Application of the electron tube to potentiometric titrations. J. W. WILLIAMS and T. A. WHITENACK (J. Physical Chem., 1927, 31, 519—524).—An apparatus for the general application of the electron tube ("valve") to potentiometric titrations is described. Results in agreement with the usual potentiometric and volumetric titrations were obtained in the oxidation of ferrous ammonium sulphate by potassium dichromate, in the reduction of permanganate, in the iodine-sodium thiosulphate reaction, and in the neutralisation of acetic acid by potassium hydroxide. In agreement with Kolthoff and Furman ("Potentiometric Titrations," 1926, 268), the potential break in the precipitation of zinc by potassium ferrocyanide occurs before the volumetric end-point is reached. L. S. THEOBALD.

Relation of titration acidity and p_H values [especially for mixtures of weak acids]. K. TAUFEL and C. WAGNER (Z. angew. Chem., 1927, 40, 133—141).—Curves showing the variation in p_H during neutralisation of different types of acids and mixtures thereof are given. With a mixture of hydrochloric and acetic acids for which the curve shows two discontinuities, one part shows the relation of p_H to the concentration of free hydrochloric acid, one part to that of free alkali, and the intermediate curve gives the relation of p_H to the concentration of dissociated and undissociated acetic acid during the elimination of hydrogen ions. Here $p_H = -\log K + \log [A'] - \log [HA]$. In this way, the curve can be analysed into its component curves, and the principle is developed for other cases. By a suitable choice of indicators, one acid can therefore often be titrated in the presence of others. In some cases, *e.g.*, the determination of hydrochloric and other acids in gastric juice, no marked discontinuity occurs in the curve,

and the correct value of p_H to take as the neutralisation point can then be fixed only by blank tests. If the acids present in the mixture are of the same order of dissociation, *e.g.*, lactic acid and acetic acid, the components are neutralised simultaneously and indirect methods of analysis are necessary, or the curves may be analysed mathematically. With complicated systems, the intermediate part of the curve may approach a straight line. The inclination of this line, *i.e.*, the rate of change in p_H within the limits of the zone, is of practical importance in brewing and other processes involving enzymes. It can be determined by pairs of titrations with suitable indicators. Other cases discussed are the variations of p_H in soils and the souring of wine. C. IRWIN.

Comparison of the accuracy of the titration of halides and thiocyanates by Fajans' method, the usual methods, and the potentiometric method. I. M. KOLTHOFF and L. H. VAN BERK (Z. anal. Chem., 1927, 70, 369—394).—The potentiometric titration of chloride, bromide, iodide, and thiocyanate in neutral solution gives results within 0.02% of the theoretical when a slight deficiency of 0.1*N*-silver nitrate solution is added and the titration finished with 0.01*N*-silver nitrate. At the end-point, the solution has a potential of -0.08 volt against the mercuric sulphate-0.5*M*-potassium sulphate electrode in the case of chlorides, -0.17 volt in the case of bromides, -0.22 volt with iodides, and -0.18 volt with thiocyanates. In acid solutions, this potential is more negative in every case, but neutral salts have no effect. From numerous potentiometric titrations, the solubility products of the various silver salts have been calculated as silver chloride 1.5×10^{-10} ; silver bromide 6.5×10^{-13} ; silver thiocyanate 1.2×10^{-12} , and silver iodide 9×10^{-17} . The titration of chloride or bromide by Mohr's method gives good results if allowance is made for the amount of indicator (potassium chromate) added; titration of iodide or thiocyanate by this method, however, gives results which are generally 1—2% too high. Volhard's method is satisfactory for bromide, iodide, and thiocyanate if the solution is well shaken during the titration of the excess silver with thiocyanate. Titration of chloride with silver nitrate, using fluorescein as indicator, and of bromide, iodide, and thiocyanate, using eosin as indicator (Fajans and Wolff, A., 1924, ii, 776), gives excellent results in neutral or acetic acid solutions, provided that no great quantity of a strong electrolyte is present. A. R. POWELL.

Günzburg's reaction for free hydrochloric acid. P. N. VAN ECK (Pharm. Weekblad, 1927, 64, 304—307).—The red coloration developed when a mixture of phloroglucinol and vanillin is brought into contact with hydrochloric acid is not a specific test for that acid; the same coloration is given by most mineral and many organic acids, and by various salts. S. I. LEVY.

Separation of hydrochloric from hydrobromic and hydriodic acids. G. G. LONGINESCU and (MLLE.) M. N. BĂDESCU (Bull. Sci. Acad. Roumaine, 1927, 10, 2—4).—See this vol., 124.

Determination of perchlorate in Chile saltpetre with nitron. A. VÜRTHEIM.—See B., 1927, 250.

Argentometric determination of iodide in presence of chloride with the help of the absorption indicators of Fajans. I. M. KOLTHOFF (*Z. anal. Chem.*, 1927, 70, 395—397; cf. Fajans and Wolff, A., 1924, ii, 776).—The determination of iodide in presence of chloride by Fajans' method is best carried out in presence of ammonium carbonate, using eosin as indicator; the solution becomes dark violet at the end-point. The results for iodide are accurate to 0.2—0.5% in the presence of up to 40 times the weight of chloride, but bromides interfere.

A. R. POWELL.

Iodometric analysis of peroxides. C. WAGNER.—See B., 1927, 249.

Coalescence of an unfilterable precipitate of barium sulphate. H. M. TRIMBLE (*J. Physical Chem.*, 1927, 31, 601—606).—The solution pressure of barium sulphate at approximately 100° ceases to be a function of particle size for particles larger than 2 μ in diameter. The coalescence of barium sulphate precipitates on digestion cannot be adequately explained as a growth of large from smaller particles, for long digestion at higher temperatures fails to bring this about in the case of particles of diameter greater than 2 μ , and the growth of large crystals themselves after digestion is inappreciable. Aggregates are formed by digestion without stirring, but not by digestion with stirring, in which case all the crystals present grow at the expense of any material separating from solution. The coalescence of precipitates is better explained by aggregation of particles followed by the cementation of individual particles in the aggregates by means of barium sulphate deposited either from the still supersaturated solution or from the solution of particles of diameter less than 2 μ .

L. S. THEOBALD.

Volumetric determination of sulphate in drinking water. A. BAHRDT.—See B., 1927, 238.

Preservation of standard solutions of sodium thiosulphate. I. YOSHIDA (*J. Chem. Soc. Japan*, 1927, 48, 26—27).—The alteration of 0.1*N*-sodium thiosulphate solution is only 1% after 10 months, with frequent exposure to air. For preservation, 0.05*M*-borax, 0.1*N*-disodium hydrogen phosphate, or carbon disulphide may be employed. Specially pure sodium thiosulphate and special distilled water need not be used.

K. KASHIMA.

Application of mixtures of ammonium halide and sulphate in quantitative analysis. L. MOSER and W. MAXYMOWICZ (*Ber.*, 1927, 60, [B], 646—649).—All salts of the alkali and alkaline-earth metals, of manganese, zinc, cadmium, lead, or (less advantageously) of cobalt and nickel which contain anions decomposable by hot halogen acids or sulphuric acid are quantitatively converted into sulphates when heated with a mixture of ammonium sulphate and ammonium halide. The effect can frequently be produced with ammonium sulphate alone, but much more slowly. The favourable action of the ammonium halide depends on the intermediate production of metallic halide which reacts with sulphur trioxide formed from the sulphate. The substance under investigation (0.1—0.4 g.) and 1—2 g. of a mixture of ammonium sulphate and ammonium chloride (1 : 3

by weight) is gently heated in a porcelain or silica crucible so that slow but recognisable volatilisation of the ammonium salts occurs, and the operation is repeated until the weight of the residue remains constant. The proportion by weight of ammonium bromide or iodide to sulphate must not exceed 1 and 0.75, respectively.

H. WREN.

Determination of traces of nitrogen peroxide in air. E. KOHN-ABREST.—See B., 1927, 251.

Gasometric determination of nitric oxide, with special reference to absorption by ferrous chloride. V. N. MORRIS (*J. Amer. Chem. Soc.*, 1927, 49, 979—985).—A simple gas burette is described in which the absorbing liquid is allowed to drop into the gas, a fresh surface of the liquid thus continually being exposed. The apparatus is successfully applied to the determination of nitric oxide, the most suitable absorbing agent being concentrated ferrous chloride solution.

S. K. TWEEDY.

Determination of phosphorus pentoxide as magnesium ammonium phosphate. W. M. MCNABB (*J. Amer. Chem. Soc.*, 1927, 49, 891—896).—The determination is carried out by a combination of the methods of Schmitz (A., 1925, ii, 67) and Brookman (*Repert. anal. Chem.*, 1882, 2, 297). The phosphate is precipitated (preferably, for accurate results, from monopotassium hydrogen phosphate solution) as magnesium ammonium phosphate, which is transferred to a tared crucible; particles clinging to the sides of the beaker are dissolved in warm dilute nitric acid and the solution added to the crucible. After rendering alkaline with ammonia (to prevent volatilisation of phosphorus pentoxide) the contents of the crucible are evaporated and ignited to constant weight.

S. K. TWEEDY.

Electrometric study of the precipitation of phosphates. H. T. S. BRITTON (*J.C.S.*, 1927, 614—630).—The dissociation constants $K_1=0.94 \times 10^{-2}$, $K_2=1.4 \times 10^{-7}$, and $K_3=2.7 \times 10^{-12}$ satisfy the hydrogen electrode titration curve of phosphoric acid by sodium hydroxide. The alkaline-earth hydroxides when added to phosphoric acid solution give rise to supersaturated solutions from which the monohydrogen phosphate separates only gradually, and on addition of more alkaline earth becomes converted into the normal phosphate. With lime-water, further addition over two equivalents actually causes an increase in the hydrogen-ion concentration, since the calcium hydroxide decomposes the supersaturated solution of dicalcium phosphate, precipitating both di- and tri-calcium phosphates. The presence of sucrose prevents this anomalous increase. Calculations from Bassett's data on the system $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ at 25° show that calcium phosphate is not precipitated from solutions more acid than p_{H} 5.5. Hydrogen electrode titrations with trisodium phosphate of salt solutions of zirconium, thorium, aluminium, beryllium, chromium, zinc, manganese, magnesium, and calcium show that in all cases except the last two, basic salts are formed. The redissolution of the aluminium phosphate in excess of the precipitant is due to the formation of sodium aluminate, the necessary alkali being supplied by the hydrolysis of the trisodium phosphate. The possibility of the

phosphate separation is due to the fact that in a solution buffered at p_H 5 (by acetic acid and sodium acetate) the phosphates and, in presence of a deficiency of phosphoric acid, the hydroxides, only of aluminium, chromium, and iron can be precipitated. The importance of p_H data with reference to phosphate soil fertilisers is discussed. S. J. GREGG.

Titration of hypophosphoric acid and its salts by means of permanganate. D. KÖSZEGI (Z. anal. Chem., 1927, 70, 347—349; cf. A., 1926, 702; Kolthoff, *ibid.*, 1018).—The examples of unsatisfactory agreement in the author's earlier paper cited by Kolthoff are due to typographical errors, and not to any want of accuracy in the method. S. I. LEVY.

Paper strips for the Gutzeit determination of arsenic. E. L. GREEN (Ind. Eng. Chem., 1927, 19, 424).—It is important that papers to be used in the Gutzeit test for arsenic approximate closely to a standard size. A device for use with a print trimming machine is described whereby such approximation can be attained. L. M. CLARK.

Micro-determination of carbon. Applications. M. NICLOUX (Compt. rend., 1927, 184, 890—892).—Sulphuric acid is added to a mixture of a solution of the substance to be analysed with potassium dichromate, silver chromate, and sodium sulphate contained in an evacuated vessel. On warming, carbon dioxide is evolved and is absorbed in potassium hydroxide solution and determined by titration. A degree of accuracy of 0.003 mg. has been obtained using solutions containing 2.0—2.5 mg. of a number of organic compounds. Quinoline-sulphonic acid alone resists complete oxidation. The method is useful in biochemical work. J. GRANT.

Rapid determination of silicon in steel and iron. J. VERFÜRTH.—See B., 1927, 255.

Determination of excess of alkali in hypochlorite solutions. A. WACHTER (J. Amer. Chem. Soc., 1927, 49, 791—792).—An aqueous suspension of nickelous hydroxide (5 g./litre) is added to the solution: $2Ni(OH)_2 + NaClO + H_2O = NaCl + 2Ni(OH)_3$. The mixture is heated and filtered, the filtrate being titrated with acid as usual. The method is inapplicable in presence of ammonium salts and also when the alkali is calcium hydroxide. S. K. TWEEDY.

Specific reagent for sodium. I. M. KOLTHOFF (Z. anal. Chem., 1927, 70, 397—400).—Zinc uranyl acetate gives a yellow, crystalline precipitate of the compound $(UO_2)_3ZnNa(CH_3CO_2)_9 \cdot 9H_2O$ with neutral solutions of sodium salts containing more than 50 mg. of sodium per litre. Acid solutions are preferably neutralised with zinc oxide before applying the test. The reagent is prepared by dissolving 10 g. of uranyl acetate and 30 g. of zinc acetate in 100 c.c. of water and adding 9 g. of 33% acetic acid. For the detection of traces of sodium in potassium salts, 2 c.c. of a 1% solution of the salt are mixed with 2 c.c. of the reagent and 2 c.c. of absolute alcohol; in the presence of sodium, a precipitate appears within 15 min. A. R. POWELL.

Determination of calcium in aluminium alloys. P. G. WARD.—See B., 1927, 282.

Schlagdenhaufen's reaction [for magnesium]. A. HAMY.—See B., 1927, 217.

New reactions of zinc, copper, and cadmium. R. MONTEQUI (Anal. Fis. Quím., 1927, 25, 52—76).—The reactions of salts of copper, zinc, and cadmium with alkali mercurithiocyanates are described. Photomicrographs are given of the complex copper zinc and cadmium zinc mercurithiocyanates formed. The theory of the reactions is discussed. G. W. ROBINSON.

Determination and separation of copper by means of 8-hydroxyquinoline. R. BERG (Z. anal. Chem., 1927, 70, 341—347; cf. J. pr. Chem., 1927, 115, 178).—Copper is precipitated quantitatively from a solution containing 5 g. of sodium acetate in 100 c.c. of 10% acetic acid by addition of a 2% alcoholic solution of 8-hydroxyquinoline; the results using a solution containing about 5 g. of sodium tartrate and 20 c.c. of 2*N*-sodium hydroxide per 100 c.c. (total) are also satisfactory. As the precipitate may be filtered, washed, and dissolved in dilute acids, and the copper determined quantitatively by the iodide method, the reagent permits of exact determination of copper in presence of ferric iron, bismuth, tin, arsenic, and antimony, which are not easily precipitated in the alkaline tartrate solution, and of zinc, which is precipitated with the copper, but does not interfere with the iodide titration. S. I. LEVY.

Separation of copper and mercury. J. KRAUSS (Z. angew. Chem., 1927, 40, 354—355).—The usual methods of separating copper and mercury are criticised, and a new method, based on that of Rivot, and depending on the precipitation of the copper as cuprous thiocyanate, is described. The solution (200 c.c.), containing approximately 0.15 g. each of the two metals, is treated with 50 c.c. of a solution of 53.5 g. of ammonium chloride and 3 g. of hydroxylamine sulphate per litre, and heated to boiling. The copper, now in the cuprous condition, is precipitated with 30 c.c. of 0.1*N*-ammonium thiocyanate, the solution allowed to cool with stirring, the precipitate collected, and dried at 105—110°. The filtrate containing the mercury is acidified with 25 c.c. of hydrochloric acid, d 1.126 (25%), and mixed with 10 c.c. of a solution containing 5 c.c. of bromine in 50 c.c. of sodium hydroxide solution (d 1.168—1.172). After removing the excess of bromine, the mercury is precipitated from the warm solution (50—70°) by passing in hydrogen sulphide. E. HOLMES.

Determination and separation of rare metals. VIII. **Determination of thallium as thallos chromate.** L. MOSER and A. BRUKL (Monatsh., 1926, 47, 709—725).—Thallium is best determined after reduction to a thallos salt by the following method (cf. Mach and Lepper, B., 1926, 390). The boiling ammoniacal solution is treated with 2% by weight of solid potassium chromate and kept for 12 hrs. The precipitate of thallos chromate is filtered on an asbestos mat, washed with 1% potassium chromate solution, then with 50% aqueous alcohol, and dried at 120°. A quantitative separation of lead and thallos salts may be effected by treating the acid solution with 20 c.c. of 33% sulphosalicylic

acid solution and excess of ammonium phosphate. After making alkaline with ammonia, the lead phosphate is collected and thallium determined as above in the filtrate. Manganous salts may be removed in the same way. In presence of sulphosalicylic acid, thallium may be precipitated from faintly alkaline solutions containing aluminium, ferric, or chromic salts. Thallium is separated from zinc, cadmium, nickel, or cobalt by precipitation as the chromate from solutions rendered strongly alkaline with ammonia. From the filtrate, zinc is best recovered as the phosphate, cadmium as the sulphide, nickel by means of dimethylglyoxime, and cobalt as hydroxide. In presence of silver, mercury, or copper, thallium is precipitated from a faintly alkaline solution containing potassium cyanide or, in the case of the first two, sodium thiosulphate. The filtrate is boiled with an excess of sodium thiosulphate, when silver, mercury, or copper sulphide separates. Bismuth in 0.1% solution is separated from thallium by precipitation as the phosphate, BiPO_4 , thallium being determined in the filtrate. The separation of arsenic and thallium has been previously described (*loc. cit.*), and the method is also applicable to antimony-thallium mixtures. Stannic salts may be removed by precipitation as oxide from a boiling, neutral 0.1–0.2% solution. Double precipitation is necessary in presence of large quantities of tin. Quadri-valent selenium does not interfere with the precipitation of thallium chromate from ammoniacal solutions.

H. E. F. NOTTON.

Colorimetric determination of iron. A. SAGAIATCHNI and M. RAVITCH (*J. Russ. Phys. Chem. Soc.*, 1926, 58, 1018–1022).—Methods for the determination of small quantities of iron in presence of other ions are summarised. The depth of the violet colour obtained by the addition of salicylic acid to slightly acid (0.01N), very dilute (<0.3%) solutions of ferric iron depends on the concentration of the ferric ion, which can be determined to within 2%. The solutions are compared with a standard the details of preparation of which are given.

The method can be used in presence of cations of the first three groups, sulphate, chloride, nitrate, acetate, moderate amounts of phosphate, and small quantities of organic matter. Free alkali or organic polybasic acids destroy the colour.

M. ZVEGINTZOV.

Precipitation of zirconium with picric acid. M. SPETER.—See B., 1927, 255.

Delicate colour test for antimony and tungsten. E. EEGRIWE (*Z. anal. Chem.*, 1927, 70, 400–403).—Addition of a solution of antimony pentachloride in hydrochloric acid to a solution of a dye of the xanthone group produces a violet to blue fluorescence in the previously red solution. The metal is separated as in the usual course of group analysis and the chloride solution oxidised to the quinquevalent state by boiling with sodium nitrite; a few drops of the solution added to 5 c.c. of a 0.05% solution of tetraethylrhodamine produce a blue to violet colour in transmitted light if only 0.005 mg. of antimony is present. Large quantities of stannic chloride and relatively small amounts of iron do not interfere. Similar reactions are given by solutions containing 0.01 mg.

of molybdenum, 0.007 mg. of bismuth, 0.015 mg. of thallium (as TlCl_3), or 0.0012 mg. of gold. Mercuric chloride also gives the coloration in a concentration of 1 mg. of mercury per c.c. To test for tungsten in a solution free from any of the above-named metals, hydrochloric acid is added so as to obtain a colloidal solution of tungstic acid. One drop of this solution containing only 0.005 mg. of tungsten will produce a perceptible violet tint with 5 c.c. of the reagent.

A. R. POWELL.

Grating-spectrometer (wave-length spectrochemical) of Loewe and Schumm for the spectrochemical investigation of natural pigments. O. SCHUMM (*Z. physiol. Chem.*, 1927, 164, 58–60).—An apparatus is described which gives a spectrum of which the red is much broader, and the blue and violet are much narrower, than in the prism spectrum. Absorption phenomena in the blue and violet are therefore clearer and more defined.

A. WORMALL.

Illuminator for use in metallographic microscopy. L. E. JEWELL (*J. Opt. Soc. Amer.*, 1927, 14, 159–167).—A modification is described of George's method (*Trans. Amer. Soc. Steel Treating*, 1923) of securing, with medium and high powers, in the photomicrography of opaque objects, an approach to the relief effects ordinarily obtained with oblique illumination at low magnifications.

L. F. GILBERT.

Graphic correction for the exposed thread for readings of mercury-in-glass thermometers. E. BERL and A. KULLMANN (*Ber.*, 1927, 60, [B], 815–817).—An arrangement is made whereby the correction can be ascertained graphically from the number of degrees in the exposed thread and the difference between the recorded temperature and the mean temperature of the exposed thread.

H. WREN.

Determination of m. p. E. BERL and A. KULLMANN (*Ber.*, 1927, 60, [B], 811–814).—The m. p. of a substance as observed in Thiele's apparatus depends on the position of the burner, thermometer, and capillary tube. These difficulties are avoided by the use of a cylindrical metal block in which two holes are bored for thermometers and two for capillary tubes. The block is heated by a small burner. The ends of the capillary tubes are visible through a tunnel drilled through the block; the ends of the tunnel can be covered with a strip of mica.

H. WREN.

Apparatus for determining the softening point of paraffin and other waxes, pitches, etc. H. HERBST.—See B., 1927, 244.

Glass water still. G. G. KRETCHMAR (*J. Opt. Soc. Amer.*, 1927, 14, 187–189).—A simple apparatus capable of distilling 700 c.c. of water per hr. is described. The heater is a 600-watt nickel-chromium wire element. The efficiency is about 85%.

L. F. GILBERT.

Laboratory fractionating columns. J. B. HILL and S. W. FERRIS (*Ind. Eng. Chem.*, 1927, 19, 379–382).—The efficiency of various types of fractionating column is investigated, comparison being established in such manner that the ability to produce contact between refluxing liquid and distilling vapour is the factor influencing efficiency. The columns are therm-

ally insulated, the vapour is distilled at a constant rate while a constant, controlled amount of reflux is fed back at the top of the column, a portion of the issuing vapour being removed for analysis. Of the long type of column, the Snyder floating-ball column is most efficient over a wide range of distillation rate; columns packed with glass tube or rod, iron chain, or Lessing rings show approximately equal efficiencies, whilst the Young rod and disc fractionator, except at low distillation rates, is the least efficient apparatus examined. Using a similar method, short columns of types in general service are found to depend largely on fractional condensation in the column, and not to the production of intimate contact between ascending vapour and descending condensate. L. M. CLARK.

Adapter. G. N. QUAM (Ind. Eng. Chem., 1927, 19, 425).—An adapter for use in alcohol distillation has a drying tube scaled on to the side and fits into the stopper of the receiving vessel, which can therefore be changed with minimum exposure of the anhydrous distillate. L. M. CLARK.

Distillation flasks. A. MÜLLER (Z. angew. Chem. [Chem. App. u. Maschinenw.], 1927, 40, 19).—Entrainment of liquid particles is prevented by extending the side tube slightly into the neck of the flask, the end of the extension being drawn out and bent downwards. The flask may have two necks, one carrying the side tube. For vacuum distillation, the side tube is widened to avoid any constriction. C. IRWIN.

Kjeldahl digestion apparatus. E. G. HASTINGS, E. B. FRED, and W. H. PETERSON (Ind. Eng. Chem., 1927, 19, 397).—A wide, horizontal lead fume pipe has a series of side tubes which carry adjustable lead stoppers, on to which is fitted the battery of Kjeldahl distillation flasks. Fumes from the digestion are carried away by the current of air produced by a leaden water injector in the fume pipe. No hood or suction fan is required. The apparatus is economical in the amount of acid used, and the time of digestion is less than that required in the usual hood method. L. M. CLARK.

Laboratory stirring apparatus. A. MÜLLER (Z. angew. Chem. [Chem. App. u. Maschinenw.], 1927, 40, 18).—The cover of the vessel has five equal ground-glass connexions which serve for a thistle funnel, the gas outlet, a thermometer, a Soxhlet condenser, and the stirrer. The latter is designed with a liquid seal to render it gas-tight. C. IRWIN.

Pipette. A. MÜLLER (Z. angew. Chem. [Chem. App. u. Maschinenw.], 1927, 40, 18).—At the upper end of the pipette is a bulb closed by a ground-glass stopper connected to a cock, a right-angle bend, and an expansion filled with a suitable absorbent. The latter is closed by a mouth-piece. One such attachment serves for a range of pipettes. C. IRWIN.

Apparatus for extraction by dialysis. P. W. DANCKWORT and E. PFAU (Arch. Pharm., 1927, 265, 65—68).—It is convenient to use dialysis for separating, e.g., soluble toxic compounds from such colloidal material as stomach contents. An apparatus for this purpose, in which the volume of solvent used is relatively small, is described and figured. The extrac-

tion is based on the Soxhlet principle. The collodion bag to contain the colloidal material is of any capacity up to about 2 litres, and is suspended in a specially constructed glass vessel, capable of being evacuated.

W. A. SILVESTER.

Apparatus for measuring the turbidity of opalescent glass. W. EWALD.—See B., 1927, 252.

Gauge for measurement of high vacua. R. E. BURK (J. Physical Chem., 1927, 31, 591—595).—A gauge combining the principles of the ordinary manometer, the McLeod gauge, and the quartz fibre manometer is described. The gauge can be easily made from pyrex glass, and can be baked out and calibrated *in situ* without a previous knowledge of its dimensions. Pressures from several decimetres to 1×10^{-7} mm. of mercury can be measured. A 2-way stop-cock of large bore which greatly accelerates evacuation is also described. L. S. THEOBALD.

Apparatus for circulating gases. H. N. STEPHENS (Ind. Eng. Chem., 1927, 19, 425).—A circulating capacity of 25—30 litres per hr. can be attained by the use of two 500 c.c. levelling bulbs and two reversed mercury traps. Mercury is raised into one of the bulbs by an aspirator and on admission of air through an automatic control falls into the second bulb. On the compression stroke, gas passes through one air trap and into the reaction chamber, and on the expansion stroke it flows back through the second air trap into the higher levelling bulb. L. M. CLARK.

Vacuum oven and thermoregulator. D. H. BRAUNS (J. Amer. Chem. Soc., 1927, 49, 985—986).—The oven consists of a long, wide pyrex tube, sealed at one end and flanged at the other in such a way that a tubulated desiccator lid can be fitted.

The initial adjustment of the mercury in a thermoregulator is facilitated by a reservoir sealed on to the stem of the regulator and communicating with the latter through a plug or stop-cock. The stem and capillary of the regulator are filled with mercury and the reservoir is attached to a water-pump. By manipulating the stop-cock, the mercury can readily be adjusted to any desired height within the capillary. S. K. TWEEDY.

Anhydrous barium perchlorate and mixed alkaline-earth perchlorates as dehydrating reagents. G. F. SMITH (Ind. Eng. Chem., 1927, 19, 411—414).—Barium perchlorate trihydrate on dehydration in a vacuum at 100—140° gives the anhydrous salt without fusion, and this equals sulphuric acid in drying efficiency. A mixture of barium perchlorate with up to 35% of magnesium perchlorate (A., 1922, ii, 850) can be dehydrated at 250° and 102 mm. pressure without fusing; the granules of such a mixture containing 26.5% of magnesium perchlorate in a drying column 15 cm. long and 2.5 cm. in diameter allow only 0.001 g. of water to remain unabsorbed when air 60% saturated with moisture is passed through for 5.5 hrs. at the rate of 53 litres per hr. L. M. CLARK.

Apparatus for removing the supernatant liquid from centrifuged precipitates. W. KRANE (Z. physiol. Chem., 1927, 164, 50—51).

Grüneisen's criteria for the capillary viscosimeter. N. E. DORSEY (J. Opt. Soc. Amer., 1927, 14, 45—53).—The manner of derivation of Grüneisen's criteria for use in designing capillary viscosimeters (Wiss. Abhandl. Physikal. Tech. Reichsanst., 1904, 4, 151) is unsatisfactory and the criteria themselves are erroneous. Other criteria, in accordance with Bond's observations (Proc. Physical Soc., 1921, 33, 225; 1922, 34, 139), are formulated.

L. F. GILBERT.

Laboratory emulsifier. R. C. SMITH (Rev. gén. Colloïd., 1927, 5, 412—414).—The apparatus consists of a vertical revolving axis to the end of which is fixed a brass tube with an orifice above the two end discs situated one above the other and joined by four curved blades covered with brass gauze. The liquid to be dispersed enters at the orifice and is passed through the gauze into the dispersion medium. When the dispersed phase is denser than the dispersion medium, the apparatus is reversed, the orifice is covered with gauze, and the two discs are made of equal diameter so that the liquid is sucked in by the revolving blades and passed out of the orifice. A band of brass on the side and bottom of the containing test-tube has the effect of keeping the denser liquid to the centre of the tube. The apparatus may be readily adapted for continuous emulsification.

D. G. HEWER.

Modification of Mohr's pinch-cock for burettes. L. MOSENDS (Z. anal. Chem., 1927, 70, 404—405).—The ordinary Mohr pinch-cock is provided with an adjustable screw so that the arms may be kept sufficiently apart to permit the liquid to flow from the burette drop by drop. A titration is started in this manner, then the cock is opened full to allow a steady stream of solution to run out, and finally, by releasing the cock again, the titration is finished by drops. A note by W. FRESSENIUS (*ibid.*, 405) states that this modification has been in use in his laboratory for 50 yrs., but has not previously been published.

A. R. POWELL.

Mercury and ammonia vapour an explosion hazard. C. VAN BRUNT (Science, 1927, 65, 63—64).—The circumstances of an accidental explosion indicate the possibility of the formation, during 10 yrs. at the ordinary temperature, of a mercuriammonium oxide from mercury in the safety-valve of a carboy containing concentrated ammonia solution.

CHEMICAL ABSTRACTS.

Interchangeable laboratory furniture. A. H. WHITE (Ind. Eng. Chem., 1927, 19, 404—405).—Standardised benches, balance cases, and apparatus cupboards are described. Benches are separate from the standardised plumbing arrangements for water, gas, or fume hoods and are removed bodily when the latter need attention.

L. M. CLARK.

Mineralogical Chemistry.

Measurements of the amount of ozone in the earth's atmosphere and its relation to other geophysical conditions. II. G. M. B. DOBSON, D. N. HARRISON, and J. LAWRENCE (Proc. Roy. Soc., 1927, A, 114, 521—541; cf. A., 1926, 493).—Simultaneous measurements of the amount of ozone in the earth's atmosphere have been made, by the method previously described (*loc. cit.*), at various places in N.-W. Europe. Exposures were made, where possible, three times daily. A determination of the monthly means of the ozone values at Oxford shows the dates of maximum and minimum to be April and October, respectively. This result is unexpected. The general annual variation is very similar over the two years investigated (1925 and 1926). The connexion between the amount of ozone and *H* (horizontal component of the earth's magnetic force) range is much more marked on days of high magnetic character, the days of low character showing little differentiation between the amounts of ozone corresponding with high and low *H* range. For 1925, the ozone values at Oxford tended to be higher on days of low rather than high sunspot number, but for 1926 the opposite effect was found. The most marked relation between the ozone content of the atmosphere and any geophysical quantity is found in the case of pressure distribution. Almost without exception, the ozone value is high in marked cyclonic systems and low in anticyclonic systems. The reasons for the connexion between the amount of ozone and the meteorological upper-air conditions are discussed.

L. L. BIRCUMSHAW.

Gold in sea-water. F. HABER (Z. angew. Chem., 1927, 40, 303—314).—Numerous analyses of sea-water from various parts of the world show that the average gold content of the South Atlantic, round latitude 48° S., is 0.008 mg. per m.³, with a highest single value of 0.044 mg. For the Bay of San Francisco, it is very little higher, in spite of the fact that these waters are fed by streams passing through a gold-bearing country. In a few cases, especially round the Newfoundland Bank, concentrations from 2.25 to 8.46 mg. per m.³ have been found. In Arctic regions the mean value is 0.04 to 0.047 mg., but a few samples of surface ice gave remarkably high values, in one case as much as 4.843 mg. per m.³ The concentrations of silver are of about the same order of magnitude, but vary between wider limits. Analytical methods for the determination of very small quantities of gold and silver are described.

M. S. BURR.

Origin of the earth's surface structure. J. JOLY and J. H. J. POOLE (Nature, 1927, 119, 524—525).

Highly penetrating radiation from the earth. L. N. BOGOLAVLENSKY and A. A. LOMAKIN (Nature, 1927, 119, 525).—The radiation, which is complex, appears to originate from radio-elements diffused in the soil.

A. A. ELDRIDGE.

Occurrence of platinum in Norwegian rocks and minerals. G. LUNDE (Z. anorg. Chem., 1927, 161, 1—20).—The amounts of platinum and silver in a number of Norwegian rocks and minerals have been

determined. For analysis, the material was fused with six times its weight of a mixture of equal parts of lead acetate, fusion mixture, and anhydrous borax, and the metallic bead cupelled. The bead of silver and platinum so obtained was measured micro-

scopically, then fused repeatedly with boric acid to remove the silver, and measured again.

R. CUTHILL.

Anhydrous silicas containing clays. Composition of ochres. A. P. BIGOT.—See B., 1927, 253.

Organic Chemistry.

Preparation of octane. H. F. LEWIS and G. R. YOHE (Proc. Iowa Acad. Sci., 1925, 32, 327—328).—Using butyl bromide (50 g.), sodium (10.5 g.), and ether (40 c.c.), a 73% yield of octane is obtained, with agitation, in 5 hrs.; without agitation, the yield is 44%. High yields can be obtained in less than 1 hr. by dropping butyl bromide on to sodium in a pyrex flask.

CHEMICAL ABSTRACTS.

Preparation of $\beta\epsilon$ -dimethylhexane. H. F. LEWIS and J. W. FLEMING (Proc. Iowa Acad. Sci., 1925, 32, 328).—Nearly quantitative yields of $\beta\epsilon$ -dimethylhexane are obtained by interaction of *isobutyl* bromide and sodium in a reflux apparatus in absence of a solvent.

CHEMICAL ABSTRACTS.

Preparation of hydrocarbons by reduction of organic substances. Use of carbon and carbon monoxide. J. CAMPARDOU (Compt. rend., 1927, 184, 828—830).—By the use of carbon monoxide in presence of wood charcoal as catalyst at 400—450°, yields up to the theoretical of vinyl or ethylenic hydrocarbons are obtained with organic compounds containing hydrogen and oxygen, alcohols and ethers affording vinyl hydrocarbons, whilst acids, ketones, and aldehydes yield olefines. The two reactions (1) $C+H_2O \rightarrow CO+2H_2$ and (2) $CO+H_2O \rightarrow CO_2+H_2$ thus appear general in organic chemistry. Reduction according to equation (2) is practically always exothermic and is independent of pressure, and is accordingly best conducted at the lower limit of the activity of the catalyst. Reduction according to equation (1) is often endothermic, and requires a relatively high temperature, limited by decomposition of the hydrocarbons. The conversion of phenol into benzene according to equation (1) absorbs 20 g.-cal., whereas reduction by equation (2) liberates 22.4 g.-cal. (cf. Stadnikov, A., 1926, 1110).

R. BRIGHTMAN.

Catalytic preparation of unsaturated hydrocarbons from carbon monoxide and hydrogen. C. R. HOOVER, M. J. DORCAS, W. D. LANGLEY, and H. G. MICKELSON (J. Amer. Chem. Soc., 1927, 49, 796—805).—When a mixture of equal parts of carbon monoxide and hydrogen is passed, together with a little oxygen, at 100°, over a nickel-palladium catalyst, supported on aluminium or pumice, at the rate of 1500—2000 c.c. per c.c. of catalyst per hr., the exit gas contains 1—3% of ethylene. The catalyst loses one half of its activity in 30 hrs. The following catalysts, in order of decreasing activity, also effected the production of ethylene: nickel-copper-palladium, iron-nickel-palladium, nickel-platinum, copper-cobalt-iron, copper-palladium, copper-cobalt-nickel, carbon-palladium, nickel-copper, and copper-cobalt.

The favourable effect of aluminium as a catalyst support is ascribed to the formation of traces of aluminium oxide. Catalysts prepared by precipitation with sodium or potassium carbonates appeared to be the most active. Cobalt, and possibly copper, were the only single-component catalysts by means of which unsaturated hydrocarbons could be obtained. The formation of acetylene or benzene could not be observed. Nickel-palladium and nickel-platinum catalysts, at 100°, yielded small amounts of nickel carbonyl. Nickel and nickel-palladium catalysts yield 20—25% of methane at about 250°, the activity of the catalysts being only slightly diminished after several days' use.

F. G. WILLSON.

Propylene derivatives. H. GOUDET and F. SCHENKER (Helv. Chim. Acta, 1927, 10, 132—140).—Catalytic reduction of *n*- and *iso*-propyl alcohols with anhydrous alumina at the optimum temperature, 460—470°, gives propylene in 89 and 98% yields, respectively, provided the catalyst is frequently renewed. When an equimolecular mixture of propylene and chlorine is passed slowly through an illuminated cooled tube and the product washed immediately with sodium carbonate solution, an 80% yield of $\alpha\beta$ -dichloropropane, n_D^{20} 1.4388, together with small amounts of $\alpha\beta\beta$ -trichloro- and $\alpha\alpha\beta\beta$ -tetrachloro-propane, is obtained. Treatment of the $\alpha\beta$ -dichloropropane with alcoholic potassium hydroxide solution under specified conditions gives a mixture of α - and β -chloropropylenes in 95% yield, which, on fractional distillation, gives 25—30% of the β -isomeride, n_D^{20} 1.404, the remainder being a mixture of constant b. p. (b. p. 30—32°) consisting mainly of the α -isomeride (cf. Reboul, A., 1879, 127). By the action of *m*-xylene on $\beta\beta$ -dichloropropane, β -chloropropylene, or a mixture of these in presence of aluminium chloride, a 25—27% yield of $\beta\beta$ -*di-m-xylol*propane, m. p. 174.5°, is obtained. This yields a *dinitro*-derivative, m. p. 256° (decomp.), when treated with ordinary nitric acid, a *tetranitro*-derivative, decomp. 295—300°, when nitrated with fuming nitric acid, and a *hexanitro*-derivative, decomp. 205°, when treated with a mixture of fuming nitric and sulphuric acids.

J. W. BAKER.

Polymerisation of the amylenes. J. F. NORRIS and J. M. JOUBERT (J. Amer. Chem. Soc., 1927, 49, 873—886).—The five isomeric amylenes were prepared by improved methods in pure condition, and their behaviour was studied with concentrations of sulphuric acid varying from 46% upwards. β -Methyl- Δ^{β} -butene and β -methyl- Δ^{α} -butene are the most readily polymerised, and the acid solutions obtained yield *tert*-amyl alcohol when saturated with am-

monium sulphate, and consequently contain no alkyl hydrogen sulphate. The solutions obtained when Δ^{α} -pentene and Δ^{β} -pentene were used gave *sec.*-amyl alcohol only after dilution and hydrolysis. γ -Methyl- Δ^{α} -butene is the only amylene which is polymerised without first dissolving in the acid used. The formation of the diamylenes appears to be the result of the dehydration of the amyl alcohol in solution, or of that formed as the result of hydrolysis of an alkyl hydrogen sulphate. The diamylenes did not condense with primary or secondary alkyl halides when heated at 100° with calcium oxide or zinc oxide. β -Methyl- Δ^{β} -butene condensed with tertiary alkyl halides under these conditions, but γ -methyl- Δ^{α} -butene did not; in general, the diamylenes, although olefines, are much less reactive than the amylenes. A study of the decomposition of the ozonide indicates that the diamylene from β -methyl- Δ^{β} -butene is $\text{CMe}_2\text{:CMe}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Me}$.

F. G. WILLSON.

Reaction of magnesium and tribromopropane.

W. KRSTINSKI (J. Russ. Phys. Chem. Soc., 1926, 58, 1078—1080; cf. A., 1913, i, 1145; 1915, i, 365).—The action of metallic magnesium on symmetrical tribromopropane gives, under the conditions of Grignard's synthesis, an 85% yield of diallyl, which crystallises from a mixture of alcohol and ether in two forms, m. p. 53—54° and 64°.

M. ZVEGINTZOV.

Semi-hydrogenation of the acetylenic linking and dependence of the geometrical configuration of the ethylenic compound so formed on the rate of reaction. E. OTT and R. SCHRÖTER (Ber., 1927, 60, [B], 624—642).—During the preparation of ethylenedicarboxylic acids by reduction of acetylenedicarboxylic acid by (accidentally) impure hydrogen in presence of palladised charcoal, it is found that a gradual change in the proportion of maleic to fumaric acid is induced by repeated use of the same catalyst in the sense that the proportion of the latter acid increases as the activity of the catalyst decreases (cf. Zalkind, A., 1923, i, 176). It is shown that alteration in the amount of catalyst and the method of agitation influences the period of reaction within wide limits, but does not affect the relative proportion of the stereoisomeric ethylenic compounds, provided the activity of the catalyst remains unchanged. In the heterogeneous system, therefore, the rate of reaction does not bear the same relationship to the period as in a homogeneous system, and the rate of addition of hydrogen to the multiple linking is influenced definitely only by the activity of the catalyst. In all cases, the product formed when the rate of reaction is greatest is the most labile stereoisomeride with the highest energy content, whether this be the *cis*- or the *trans*-form. Zalkind's observation that *cis*- β -dihydroxy- β -dimethyl- Δ^{γ} -hexene is preferentially produced by rapid reduction of the corresponding hexinene is not connected with the rate of the reaction, but is due to diminution of the period by increase in the amount of catalyst; with the most highly active catalysts, *trans*- β -dihydroxy- β -dimethyl- Δ^{γ} -hexene is produced. Reduction of diphenyldiacetylene with highly active palladised charcoal affords up to 90% of the most labile *cis-trans*-

diphenylbutadiene; increasing diminution of the activity of the catalyst increases the yield of the moderately stable *cis-cis*-form to more than 50%. Controlled and reproducible limitation of the activity of the catalyst has been achieved towards β -dihydroxy- β -dimethyl- Δ^{γ} -hexinene, diphenyldiacetylene, and phenylpropargyldenemalonic acid; simple exposure to air or previous use in the reduction of sparingly soluble acetylenic compounds suffices to reduce the activity of the palladium. Hydrogen sulphide or carbon monoxide does not alter the proportion of maleic to fumaric acid produced from acetylenedicarboxylic acid in presence of palladium, whence it follows that a portion of the metal is completely poisoned, whereas the remainder retains its efficiency, the net result being the reduction of the amount of catalyst.

Reduction of diphenyldiacetylene in presence of colloidal palladium, nickelised charcoal, and highly active palladised charcoal gives 25%, 33%, and 8%, respectively, of the moderately stable *cis-cis*-diphenylbutadiene. Tolane yields exclusively *isostilbene* in presence of colloidal palladium or nickelised charcoal, whereas cobalt affords 8% of *stilbene*. Zalkind's β -dihydroxy- β -dimethyl- Δ^{γ} -hexinene is equally sensitive to change in the catalyst, but irregularities in the action render it unsuitable as a standard for comparison of activities.

Comparison of the effects of highly active palladised charcoal and colloidal palladium shows that the latter never exhibits the maximum activity of the metal, the protective colloid causing delay in the reaction. The period of reaction under equivalent conditions is shorter with the colloidal metal than with the activated charcoal by reason of the greater surface exposed.

The most suitable standard for the comparison of the activities of catalysts is diphenyldiacetylene; methods for the approximate separation of the labile *cis-trans*-, moderately stable *cis-cis*-, and stable *trans-trans*-diphenylbutadienes are given. Tolane is less suitable, whilst acetylenedicarboxylic and phenylpropionic acids cannot be used on account of the readiness with which they lose carbon dioxide.

The laws governing the addition of hydrogen to the acetylenic linking cannot be stereochemical, as universally assumed; the course of the change is a question of energy.

H. WREN.

Thermal investigation of certain olefinic and acetylenic derivatives. W. A. ROTH and F. MÜLLER (Ber., 1927, 60, [B], 643—645).—In connexion with the work of Ott and Schröter (preceding abstract), the heats of combustion of β -dihydroxy- β -dimethyl- Δ^{γ} -hexinene, m. p. 94°, and of the β -dihydroxy- β -dimethyl- Δ^{γ} -hexenes (α -form, m. p. 76—77°, β -form, m. p. 68—69°) have been found to be 8028 ± 4 , 8122 ± 5 , and 8145 ± 2 g.-cal./g., respectively. As expected from other lines of reasoning, the β form of the hexene is found to be richer in energy.

H. WREN.

Propylene-halogen hydride reaction. B. P. SUTHERLAND and O. MAASS (Trans. Roy. Soc. Canada, 1927, [iii], 20, III, 499—505).—In the mixture of products obtained when propylene and hydrogen chloride are allowed to react in the liquid state,

isopropyl chloride was identified by vapour-pressure measurements. A new *hexyl chloride*, $C_6H_{13}Cl$, which from vapour-pressure measurements appeared to have a b. p. of 110.0—110.8°, was also separated, but its structure was not ascertained. A third product was probably a hydrocarbon of mol. wt. about 260, and b. p. about 163°. R. CUTHILL.

Preparation of substituted vinyl bromides. A. KIRRMANN (Bull. Soc. chim., 1927, [iv], 41, 316—323).— α -Bromo- Δ^a -olefines are obtained by the general method of Lespicau (A., 1921, i, 490) and Bourguel (A., 1923, i, 1170). The β -bromo- Δ^a -isomerides are less readily obtained. Kirrmann's method (A., 1926, 934) affords mixtures which in the case of the higher members are incapable of separation. Bruylant's method (Ber., 1875, 8, 406) gives poor yields in consequence of by-reactions affording the α -bromo-substituted aldehyde, and the tribromo-derivative, $R\cdot CHBr\cdot CHBr_2$ or $R\cdot CBr_2\cdot CH_2Br$ through addition at the double linking. By use of the acetals in place of the aldehydes, the β -bromo- Δ^a -olefine is ultimately obtained in at least 25% yield free from its isomeride. The acetals are readily obtained in 90% yield, and with phosphorus trichloro-dibromide afford upwards of 60% of the $\alpha\beta$ -tribromo-derivative, $R\cdot CHBr\cdot CHBr_2$. Excess of the reagent affords a tetrabromo-derivative. The $\alpha\beta$ -tribromo-derivative is then treated with zinc dust, $R\cdot CHBr\cdot CHBr_2 + Zn \rightarrow R\cdot CH\cdot CHBr + ZnBr_2$.

By the above methods, a number of known vinyl bromides have been prepared in a greater state of purity. No attempt was made to separate the *cis*- and *trans*-forms of the α -bromo- Δ^a -olefines. The following compounds are new: $\beta\gamma$ -dibromo- Δ^a -propene, $d^{21(6)}$ 1.9794, n_D^{20} 1.15352; $\alpha\alpha$ -dibromobutane, b. p. 53°/13 mm., 158°/760 mm., d 1.733, n_D^{20} 1.4991; n - $\alpha\alpha$ -dibromoheptane, b. p. 98—99°/11 mm., d 1.500, n_D^{15} 1.4959; $\alpha\alpha\beta$ -tribromo- γ -methylbutane, b. p. 106—108°/16 mm., d 2.032, n_D^{21} 1.5522; $\alpha\alpha\beta$ -tribromoheptane, b. p. 144—145°/19 mm., d 1.792, n_D^{21} 1.5293, n -heptaldehyde-dimethylacetal, b. p. 75°/17 mm., 182°/760 mm., d 0.849, n_D^{20} 1.4130, α -bromo- β -methylbutaldehyde, b. p. 43—44°/16 mm., d 1.353, n_D^{21} 1.4610, α -bromoheptaldehyde, b. p. 80°/11 mm., d 1.256, n_D^{20} 1.4652. The tetrabromo-derivative, $C_5H_8Br_4$, b. p. 150—152°/17 mm., d 2.305, n_D^{17} 1.5940, was isolated from the action of phosphorous trichlorobromide on the acetal of isovaleraldehyde, b. p. 128—129°, d 0.847, n_D^{15} 1.3992 (cf. Alsberg, Jahresber., 1864, 486). Octane and butyl alcohol afford an azeotropic mixture, b. p. 110°, d^{17} 0.778, n_D^{17} 1.4022 (cf. Young, J.C.S., 1902, 81, 760).

R. BRIGHTMAN.

Action of phosphorus pentahalides on derivatives of *as*-methylethylethylene glycol. W. F. SEYER and W. CHALMERS (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 337—341).—By the action of phosphorus pentachloride on the oxide, glycol, and chlorohydrin of *as*-methylethylethylene (β -methyl- Δ^a -butylene), or by the action of thionyl chloride on the oxide, there is produced, not the dichloride, but a *chlorinated amylene*, (?) $CH_2Me\cdot CMe\cdot CHCl$, b. p. 102—104°. Distillation of the chlorohydrin gives the same substance with an *isomeride*, (?) $CHMe\cdot CMe\cdot CH_2Cl$, b. p. 117—120°. Further

action of phosphorus pentachloride on the chloroamylene yields a *trichloride*, $C_5H_9Cl_3$, b. p. 180—184°.

R. CUTHILL.

Action of halogen acids and phosphorus halides on the acetylenic γ -glycols. W. N. KRESTINSKI (J. Russ. Phys. Chem. Soc., 1926, 58, 1067—1077).—The physical properties and reactions of $\beta\epsilon$ -dibromo- $\beta\epsilon$ -dimethyl- Δ^a -hexinene (cf. Dupont, A., 1911, 173) and of the product of the action of phosphorus tribromide on $\beta\epsilon$ -dimethyl- Δ^a -hexinene- $\beta\epsilon$ -diol are studied, to determine the structure of the bromo-compounds. Dupont's dibromide, m. p. 39°, is inert towards bromine and potassium permanganate. The mol. refractivity is 55.7 in alcohol, 54.83 in toluene. It gives a yellow colour with tetranitromethane and is oxidised by potassium permanganate on boiling to acetone and oxalic and α -hydroxy- α -methylpropionic acids. The ethylenic structure, $CMe_2\cdot CBr\cdot CBr\cdot CMe_2$, and not Dupont's acetylenic structure, is therefore probably correct. Reduction with zinc dust in alcohol is rapid, giving a solid hydrocarbon, m. p. 35°, which rapidly passes in air into an amorphous mass, insoluble in organic solvents, which explodes when strongly heated and contains oxygen. Phosphorus tribromide and the glycol give in benzene solution at 0° a mixture of isomeric bromo-compounds, b. p. 100—118°/13 mm. No dibromide, m. p. 39°, is obtained, but the fraction boiling below 104°/13 mm. deposits an *isomeride*, m. p. 46—48°. It is very unstable, and does not give a yellow colour with tetranitromethane. It probably has the acetylenic structure, and readily passes into the ethylenic isomeride. The fractions of b. p. 110—111°/13 mm. and 116—118°/13 mm. seem to contain two dibromides with an ethylenic structure, differing in colour and density. The second fraction on reduction gives a liquid hydrocarbon, C_8H_{12} , b. p. 126—127°, d_4^{20} 0.768, n_D^{20} 1.48143, mol. ref. 40.09, which rapidly resinifies on keeping in air. The original γ -glycol on oxidation gives oxalic and α -hydroxy- α -methylpropionic acids together with traces of acetic and formic acids. The possible structures of the glycol and its bromides, together with the mechanism of the reactions, is discussed. M. ZVEGINZOV.

Trifluoro-alcohols. I. Trifluoro-*tert*-butyl alcohol. F. SWARTS (Bull. Soc. chim. Belg., 1927, 36, 191—205).—*isoAmyl trifluoroacetate*, b. p. 119.3°/757 mm., d_4^0 1.1047, n_D 1.35295, reacts with magnesium methyl iodide to form *trifluoro-*tert*-butyl alcohol*, m. p. 20.75°, b. p. 81.6—81.7°/761 mm., d_4^{20} 1.1903, n_D 1.33241, the fluorine being unattacked. The alcohol is converted by phosphorus pentabromide at 50—60°, but not by concentrated sulphuric acid, into $\gamma\gamma\gamma$ -trifluoroisobutylene, b. p. 6.3—6.4°, d_4^0 1.056; which combines slowly with bromine to give $\gamma\gamma\gamma$ -trifluoro- $\alpha\beta$ -dibromoisobutane, m. p. —53—55°, b. p. 130.8°/754 mm., d_4^{15} 1.9825, n_D 1.44104, and with hydrogen bromide to give a *trifluorobromoisobutane*, b. p. 79—81°, d^{17} 1.550. By the action of phosphorus pentabromide on trichloro-*tert*-butyl alcohol, a small quantity of a *substance*, $C_4H_9Cl_3Br_2$, b. p. 243°, is obtained.

C. HOLLINS.

Action of halogen acids on acetylenic glycols. (I) Hydrobromic and (II) hydriodic acids and

$\beta\epsilon$ -dimethyl- Δ^7 -hexinene- $\beta\epsilon$ -diol. J. S. SALKIND and (I) M. P. SIGOVA and (II) B. RUBIN and A. A. KRUGLOV (J. Russ. Phys. Chem. Soc., 1926, 58, 1039—1043, 1044—1051).—I. The action of hydrobromic acid in water and glacial acetic acid solutions at different temperatures and concentrations on $\beta\epsilon$ -dimethyl- Δ^7 -hexinene- $\beta\epsilon$ -diol gives the same products under all conditions, the best yield being obtained with excess of aqueous hydrobromic acid on keeping for several hrs. at the ordinary temperature. On pouring into cold water, a solid dibromide, m. p. 36—37°, separates (together with some oil). It is very inert, does not react with chlorine or bromine, decolorise cold permanganate, lose bromine on prolonged treatment with potassium hydroxide, or add hydrogen in presence of palladium or platinum-black. Prolonged oxidation with potassium permanganate gives, on warming, formic and acetic acids, together with traces of α -hydroxy- α -methylpropionic acid. Treatment of the glycol with excess of cold phosphorus tribromide yields an isomeric dibromide, m. p. 46°. If the residual oil is purified by steam distillation, a further yield of the crystalline isomeride, m. p. 37°, is obtained. The isomeride of higher m. p. is also very inert, but reacts slowly with potassium hydroxide. It is never obtained by the action of hydrobromic acid. The formulæ $\text{CMe}_2\text{Br}\cdot\text{C}\cdot\text{C}\cdot\text{CMe}_2\text{Br}$ and $\text{CMe}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CMe}_2$, respectively, are suggested for the isomerides of higher and lower m. p. The latter formula accounts for the production of the α -hydroxy- α -methylpropionic acid on oxidation, *vid* the formation of a dibromoglycol by the addition of hydroxyl groups in the $\alpha\delta$ -position.

II. The action of excess of aqueous hydriodic acid in the cold and on warming on $\beta\epsilon$ -dimethyl- Δ^7 -hexinene- $\beta\epsilon$ -diol gives in every case a crystalline product, $\text{C}_8\text{H}_{14}\text{I}_2$, m. p. 75°, inert and analogous in properties to the dibromide, m. p. 37°. On reduction by zinc dust in boiling alcohol, a white solid, decomp. 180—190°, is obtained which contains oxygen, but not halogen. It does not give reactions for either a hydroxyl or a carbonyl group, and is rapidly oxidised by permanganate, giving acetic, traces of formic, and a little α -hydroxy- α -methylpropionic acids. If the di-iodide is reduced in absence of air, an unsaturated hydrocarbon, m. p. 105—106°, is obtained. It is rapidly oxidised in air to the compound containing oxygen.

Cautious oxidation of the hydrocarbon with permanganate in absence of air gives mainly acetone and oxalic acid, with traces of formic and acetic acids.

The formulæ $\text{CMe}_2\cdot\text{C}\cdot\text{C}\cdot\text{CMe}_2$ and $\text{CMe}_2\cdot\text{C}\cdot\text{C}\cdot\text{CMe}_2$ or $\text{CMe}_2\cdot\text{C}\text{---}\text{C}\cdot\text{CMe}_2$ are suggested for the hydrocarbon

and its oxide, although the latter is probably a polymeride. Prolonged oxidation of the di-iodide with potassium permanganate gave a product (b. p. 135—138°), probably α -hydroxy- α -methylpropaldehyde. It gave on keeping a solid, m. p. 59—63°, probably a polymeride, and a semicarbazone, m. p. 156°. Besides the aldehyde, small quantities of formic, acetic, oxalic, and α -hydroxy- α -methylpropionic acids were obtained. The formula suggested for the di-iodide is $\text{CMe}_2\cdot\text{CI}\cdot\text{CI}\cdot\text{CMe}_2$. M. ZVEGINZOV.

Action of halogen acids on acetylenic glycols. III. Hydrobromic acid and $\alpha\delta$ -diphenyl- Δ^8 -butinene- $\alpha\delta$ -diol. J. S. SALKIND and A. A. KRUGLOV (J. Russ. Phys. Chem. Soc., 1926, 58, 1052—1061).—The action of acetic acid solutions of hydrobromic acid at different temperatures and concentrations on one of the stereoisomerides (m. p. 140°) of $\alpha\delta$ -diphenyl- Δ^8 -butinene- $\alpha\delta$ -diol yields five products. Solid dibromide I, m. p. 114—115°, is obtained in 90% yield by treating the glycol for 30 min. at the ordinary temperature with a large excess of hydrobromic acid in 95% acetic acid solution. It slowly decolorises alkaline permanganate, does not react with cold bromine or potassium hydroxide, and is very slowly hydrolysed by moist silver oxide. On oxidation for 4 days at the ordinary temperature with potassium permanganate, only benzoic acid is obtained. Alcoholic potassium hydroxide gives some $\alpha\delta$ -diphenyl- Δ^8 -butinene, m. p. 87°, together with an amorphous polymeride containing bromine. Solid dibromide II, m. p. 92—95°, is obtained if the original reaction mixture is kept at 0° and poured into ice-water. On boiling the solution in most solvents except benzene and cooling, the isomeride of higher m. p. separates.

The action of alcoholic potassium hydroxide is the same as with dibromide I. Liquid dibromide III is obtained by the action of a saturated solution of hydrogen bromide in 95% acetic acid on the solid dibromide I. On pouring into water, the liquid dibromide separates as an oil, together with some solid tribromide. It decomposes on distillation under 50 mm. A liquid monobromide, $\text{C}_{16}\text{H}_{13}\text{OBr}$, is obtained as an oily by-product in the preparation of solid monobromide I. Larger yields result if a saturated solution of hydrogen bromide in glacial acetic acid is used. The liquid decomposes on distillation under 80 mm. It gives no reaction for a hydroxyl group, and is oxidised to the extent of about 50% by potassium permanganate, benzoic acid only resulting. The

formula suggested is $\begin{matrix} \text{CH-CHPh} \\ | \\ \text{CBr-CHPh} \end{matrix} > \text{O}$. A solid tribromide,

m. p. 155°, is obtained by the action for 1—2 days of a saturated solution of hydrogen bromide in glacial acetic acid on the glycol, or by the further action of such a solution on the mono- and di-bromides. It does not decolorise permanganate or react with bromine, and is very slowly hydrolysed by potassium hydroxide and moist silver oxide on heating. Potassium permanganate in acetone solution oxidises it very slowly, giving benzoic acid only. Alcoholic potassium hydroxide gives a product similar to that with the dibromides.

The theoretical significance of these results is discussed. The monobromide gives on further bromination only the tribromide and no dibromides, so that the formation of the latter must be an independent parallel reaction. The tribromide is formed from the monobromide and the dibromide I by the direct addition of hydrogen bromide and consequently must be $\text{CHPhBr}\cdot\text{CH}\cdot\text{CBr}\cdot\text{CHPhBr}$, and dibromide I $\text{CHPh}\cdot\text{CBr}\cdot\text{CH}\cdot\text{CPhBr}$. Dibromide II can either be $\text{CHPhBr}\cdot\text{C}\cdot\text{C}\cdot\text{CHPhBr}$ or $\text{CPhBr}\cdot\text{CH}\cdot\text{CH}\cdot\text{CPhBr}$.

M. ZVEGINZOV.

Syntheses of glycol derivatives of ethers. M. GODCHOT (Compt. rend., 1927, 184, 820—822).—The action of magnesium methyl iodide on ethyl diglycollate affords *di-β-hydroxy-β-methylpropyl ether*, m. p. 65°, b. p. 125—128°/25 mm., 230—235°/760 mm., which is not dehydrated in acetic acid. Similarly, magnesium phenyl bromide affords *di-β-hydroxy-β-β-diphenylethyl ether*, m. p. 126°, converted on warming in acetic acid alone into *αα'α'-tetraphenyldiethylene dioxide*, $O \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CPh}_2 \\ \text{CH}_2 \cdot \text{CPh}_2 \end{array} \right\rangle O$, m. p. 178—179°; in presence of hydrochloric acid also the glycol affords *di-β-β-diphenylvinyl ether*, an oil, oxidised to benzophenone by chromic acid. Ethyl *α-methyl-α'-ethyl diglycollate* (A., 1908, i, 126) and magnesium phenyl bromide afford the *ether*, $\text{OH} \cdot \text{CPh}_2 \cdot \text{CHEt} \cdot \text{O} \cdot \text{CHMe} \cdot \text{CPh}_2 \cdot \text{OH}$, m. p. 142—143°, which loses water on warming in acetic acid and affords *αα'α'-tetraphenyl-β-methyl-β'-ethyldiethylene dioxide*, m. p. 65°. Ethyl methyl diglycollate and ethyl dimethyl diglycollate afforded only viscous products with magnesium phenyl bromide.

R. BRIGHTMAN.

Displacement of alkyl groups from sulphurous esters. E. BOURGEOIS and A. V. CASTELE (Bull. Soc. chim. Belg., 1927, 36, 149—152).—Compounds of the type $\text{Cl} \cdot \text{S}(\text{O}) \cdot \text{OR}$ are obtained in good yield by the action of phosphorus pentachloride on sulphurous esters. The following compounds are described in which R is the alkyl group: ethyl, b. p. 72°/117 mm.; *n-propyl*, b. p. 87·5°/88 mm.; *isobutyl*, b. p. 93°/68 mm.; *isoamyl*, b. p. 87·5°/25 mm. These react in the cold with alcohols, forming normal sulphites, $\text{R} \cdot \text{SO}_2 \cdot \text{R}'$. The mixed sulphites obtained when R and R' are different are converted on keeping into equilibrium (?) mixtures of the two simple normal esters and the mixed ester. *Methyl ethyl sulphite*, b. p. 139—144°, *methyl isoamyl sulphite*, b. p. 121°/76 mm., and *ethyl isoamyl sulphite*, b. p. 120—121°/50 mm., are described.

When ethyl sulphite is heated at 100° with excess of *isoamyl alcohol* for some hrs. it is converted completely into ethyl alcohol, *isoamyl sulphite*, and ethyl *isoamyl sulphite*. Under similar conditions, excess of ethyl alcohol has little action on *isoamyl sulphite*.

C. HOLLINS.

Interaction of sulphur dichloride with substances containing the reactive methylene group or substituted methylene group. K. G. NAIK and G. V. JADHAV (J. Indian Chem. Soc., 1926, 3, 260—272).—The action of sulphur dichloride on substituted malonamides and methylmalonamides in benzene solution has been investigated. With malon-dianilide and *-di-o-tolylamide*, both hydrogen atoms of the methylene group react to yield *compounds* of the type $(\text{CO} \cdot \text{NHR})_2 \text{C}(\text{SCl})_2$, m. p. 164—165° (R=Ph) and 160—161° (R=C₆H₄·Me), respectively, which are less stable than those obtained by the action of sulphur monochloride (Naik, J.C.S., 1921, 119, 379), and on treatment with fuming nitric acid yield, respectively, *malon-dinitroamilide*, m. p. 90° (decomp.), and *-dinitro-o-tolylamide*, m. p. 85° (decomp.). Methylmalon-dianilide and *-di-o-tolylamide* yield the *compounds* $(\text{CO} \cdot \text{NHR})_2 \text{CMe} \cdot \text{SCl}$, m. p. 132° (R=Ph) and 150° (R=C₆H₄·Me). With malon-di-*n-propylamide*,

-di-α-naphthylamide, and *-di-β-naphthylamide*, only one methylene hydrogen atom reacts, yielding *compounds* of the type $(\text{CONHR})_2 \text{CH} \cdot \text{SCl}$, m. p. 141—142° (R=Pr^a), m. p. 145° (decomp.) (R=α-naphthyl), m. p. 230—231° (decomp.) (R=β-naphthyl). The latter on nitration yields *malondinitro-β-naphthylamide*, m. p. 185° (decomp.). Malon-di-*p-tolylamide* and *-dibenzylamide* react to yield chlorinated *compounds* of the type $(\text{CO} \cdot \text{NHR})_2 \text{CCl} \cdot \text{SCl}$, m. p. 158° (R=C₆H₄Me), m. p. 149—150° (R=C₆H₄Ph), which in presence of a trace of moisture are reconverted into the original amides. On nitration, the former *compounds* yield *malondinitro-p-tolylamide*, m. p. 120° (decomp.). In the case of methylmalon-di-*p-tolylamide*, the methyl group is also attacked to yield the *compound* $(\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me})_2 \text{C} \left\langle \begin{array}{c} \text{CH}_2 \\ \text{SCl}_2 \end{array} \right\rangle$, m. p. 157—158°, which is similarly decomposed with traces of moisture. The authors conclude that sulphur dichloride is a definite compound, SCl_2 .

J. W. BAKER.

Varying valency of platinum with respect to mercaptanic radicals. IV. Inadequacy of Werner's theory to explain certain anomalous cases. P. C. RAY, B. C. GUHA, and K. C. BOSE-RAY (J. Indian Chem. Soc., 1926, 3, 358—370).—In continuation of previous work (A., 1926, 1023), the action of primary, secondary, and tertiary bases on the mercaptanic platinum compounds previously described (A., 1925, ii, 1121) has been investigated. The action of ethylamine on the isomerides, m. p. 77° and 104°, of the compound $(\text{Et}_2\text{S})_2\text{PtCl}_2$, and of benzylamine on those of m. p. 77°, 96°, and 100°, yields *compounds* of the type $\text{PtCl}_2 \cdot 4\text{B}$, which have m. p. 142° (B=NH₂Et) and 196° (B=NH₂·CH₂Ph), respectively. Diethylamine on the isomeride, m. p. 108°, yields the *compound* $\text{PtCl}_2 \cdot \text{Et}_2\text{S} \cdot \text{NHEt}_2$, m. p. 176°, quinoline on the form, m. p. 77°, yields the *compound* $\text{PtCl}_2 \cdot 2\text{C}_9\text{H}_7\text{N}$, m. p. 165°. Pyridine acts on the *compound* $(\text{Et}_2\text{S})_2\text{PtCl}_2$ to give the *compounds* $\text{PtCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, $\text{PtCl}_2 \cdot 4\text{C}_5\text{H}_5\text{N}$, and, probably, $\text{PtCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$; benzylamine yields $\text{PtCl}_2 \cdot 4\text{NH}_2 \cdot \text{CH}_2\text{Ph}$ (above), and aniline the *compound* $\text{PtCl}_2 \cdot 2\text{NH}_2\text{Ph}$. The action of benzylamine on the *compound* $\text{PtCl}_4 \cdot 2\text{Et}_2\text{S}$ yields the *compound* $\text{PtCl}_2 \cdot 4\text{NH}_2 \cdot \text{CH}_2\text{Ph}$, whilst aniline yields two isomeric *compounds*, $\text{PtCl}_2 \cdot 2\text{NH}_2\text{Ph}$, m. p. 100° and 190°, respectively. All the above *compounds* can be represented in accordance with Werner's co-ordination theory. The *compound* $\text{Et}_2\text{S} \cdot \text{PtCl}_2$, however, cannot be so represented, and a mol. wt. determination shows that it is bimolecular and most probably has the structure $(\text{SEt}_2 \cdot \text{PtCl}_2)_2$. With benzylamine, it yields the *compound* $\text{Pt}_2\text{Cl}_4 \cdot \text{NH}_2 \cdot \text{CH}_2\text{Ph} \cdot \text{Et}_2\text{S}$, together with $\text{PtCl}_2 \cdot 4\text{NH}_2 \cdot \text{CH}_2\text{Ph}$ and a *substance*, m. p. 110°. Pyridine yields the *compound* $\text{Pt}_2\text{Cl}_4 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{Et}_2\text{S}$ and the *compound* $\text{PtCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ (*loc. cit.*). Piperidine yields the *compound* $\text{Pt}_2\text{Cl}_4 \cdot 2\text{C}_5\text{H}_{11}\text{N} \cdot 0 \cdot 5\text{Et}_2\text{S}$, whilst ethylamine yields the *compound* $\text{Pt}_2\text{Cl}_4 \cdot \text{NH}_2\text{Et} \cdot \text{Et}_2\text{S}$ and the *compound* $\text{PtCl}_2 \cdot 4\text{NH}_2\text{Et}$. In each case, simultaneous oxidation and reduction have occurred. The action of pyridine on the *compound* $\text{Et}_2\text{S} \cdot \text{PtCl}_2 \cdot 2\text{H}_2\text{O}$ yields the *compound* $\text{PtCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$, and ethylamine gives the *compound* $\text{PtCl}_2 \cdot 2\text{NH}_2\text{Et}$.

J. W. BAKER.

Catalytic decomposition of formic acid. J. B. SENDERENS (Compt. rend., 1927, 184, 856—859).—Decomposition of formic acid by sulphuric acid is catalytic, since the latter acid may be used in as small a proportion as 0.05 vol., even when diluted with water. Aluminium sulphate favours the decomposition only when sulphuric acid is present, but potassium hydrogen sulphate and orthophosphoric acid are both catalysts in its absence. The products of decomposition, carbon monoxide and water, are also obtained when alumina is used as catalyst (cf. Wescott and Engelder, A., 1926, 693).

E. W. WIGNALL.

Manufacture of acetic acid. H. DREYFUS.—See B., 1927, 268.

Optical resolution of chloriodoacetic acid. A. M. McMATH and J. READ (J.C.S., 1927, 537—543).—*dl*-Chloriodoacetic acid has been resolved, using *l*-hydroxyhydrindamine and brucine, the less soluble diastereoisomeride in each case being of the form *l*BA. Ammonium *d*- and *l*-chloriodoacetates racemise rather less readily than ammonium *d*- and *l*-chlorosulphoacetates. Slow racemisation occurs in hot aqueous solution, and in presence of an equivalent of sodium hydroxide complete racemisation takes place in a few hrs. at the ordinary temperature. The following are described: *l*-hydroxyhydrindamine *l*-chloriodoacetate, m. p. 149° (decomp.), $[M]_D -126^\circ$ in dilute aqueous solution, $[M]_D$ declining from -135° to -103° in 5 days in methyl alcohol, $[M]_D -118^\circ$ in chloroform containing a little methyl alcohol; *l*-hydroxyhydrindamine *d*-chloriodoacetate, $[M]_D -7^\circ$ in dilute aqueous solution, giving $+53.5^\circ$ for the acid ion; *brucine l*-chloriodoacetate, m. p. 158—160° (decomp.); *brucine d*-chloriodoacetate; *ammonium l*-chloriodoacetate, $[M]_D -60^\circ$, and *ammonium d*-chloriodoacetate, decomp. 149—150°, $[M]_D +56^\circ$ in dilute aqueous solution. M. CLARK.

Determination of mixtures of isomeric unsaturated compounds. I. Bromine additive method. R. P. LINSTAD (J.C.S., 1927, 355—362).—The rate of addition of bromine to four pairs of isomeric unsaturated acids in an inert solvent has been determined. Previous observations that addition takes place more rapidly at the $\beta\gamma$ than at the $\alpha\beta$ double linking are confirmed. Substitution of positive groups for hydrogen increases the velocity of reaction. The statement of Kon and Linstead (A., 1925, i, 633) that β -ethyl- Δ^2 -pentenoic acid (*p*-toluidide, m. p. 94°; *amide*, m. p. 114°) is a $\beta\gamma$ -unsaturated acid is confirmed. Measurements have been made of the amount of bromine adding to known mixtures of the isomerides in a standard time, the results being used to determine the percentage of each isomeride in equilibrium mixtures obtained by boiling the acids in potassium hydroxide solution. M. CLARK.

Undecenoic acid and its homologues. II. P. CHUIT, F. BOELSING, J. HAUSSER, and G. MALET (Helv. Chim. Acta, 1927, 10, 113—131).—Undecenyl bromide (this vol., 40) yields successively *dodecenoitrile*, $\text{CH}_2\text{:CH}\cdot[\text{CH}_2]_9\text{CN}$, b. p. 142—143°/12 mm., $d^{15} 0.844$, and *dodecenoic acid*, m. p. 19°, b. p. 171—172°/13 mm., $d^{20} 0.907$ (*barium* salt; *methyl ester*, b. p. 138—139°/13 mm., $d^{15} 0.885$; *ethyl ester*, b. p.

154.5—155.5°/18 mm., $d^{15} 0.879$), which on ozonisation yields nonane- α -dicarboxylic acid and sebacic acid in yields corresponding with the presence of 10% of *isododecenoic acid*, $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{H}$, b. p. 166—168°/9 mm. (*methyl ester*, b. p. 138—140°/14 mm., $d^{15} 0.888$). The latter is also obtained (1) by the hydrolysis of the nitrile obtained by the action of alcoholic potassium cyanide solution on $\beta\lambda$ -dibromoundecane (together with undecane- $\beta\lambda$ -dinitrile); (2) by hydrolysis of dodecenoitrile (together with the Δ^2 -acid and hydroxydodecenoic acid); and (3) by heating the Δ^2 -acid with potassium hydroxide at 230° for several hrs. At 350—370°, the main product of the fusion is decenoic acid, but fission also occurs at all other points in the chain. By reduction of the corresponding esters with sodium and alcohol are obtained Δ^2 -*dodecenol*, b. p. 138—140°/11 mm., $d^{15} 0.848$ (*phenylurethane*, m. p. 59—60.2°), and Δ^2 -*dodecenol*, b. p. 143—144°/13 mm., $d^{15} 0.850$, respectively. *Dodecalactone*, b. p. 170—171°/11 mm., $d^{15} 0.9382$, is obtained by the action of sulphuric acid at 90° on dodecenoic acid, and on hydrolysis yields γ -*hydroxydodecenoic acid*, m. p. 62.5—63.5°. Heated for 4 hrs. at 150° with ethyl sodiomalonate in alcohol solution, undecenyl bromide yields *ethyl undecenylmalonate*, b. p. 185°/8 mm., which on hydrolysis yields *tridecenoic acid*, m. p. 38—38.2°, b. p. 185°/15 mm. (*methyl ester*, b. p. 143°/8 mm., $d^{15} 0.885$; *ethyl ester*, b. p. 150°/8 mm., $d^{15} 0.880$; *tridecenyl ester*, m. p. 18°; b. p. 230—235°/13 mm.). Reduction of the methyl ester yields Δ^2 -*tridecenol*, m. p. 15°, b. p. 149—150°/9 mm. (*acetate*, b. p. 154—155°/9 mm., $d^{15} 0.8795$; *phenylurethane*, m. p. 58.2—58.6°), which with hydrogen bromide yields *tridecenyl bromide*, b. p. 141—143°/8 mm., $d^{15} 1.037$, and $\beta\gamma$ -*dibromotridecane*, b. p. 185°/8 mm., $d^{15} 1.217$. The latter on acetylation yields the *diacetate*, b. p. 180—190°/8 mm. (together with some *isotrizecenyl acetate*, b. p. 140°/8 mm.), which on hydrolysis yields *tridecane- $\beta\gamma$ -diol*, m. p. 60—61°. This glycol is readily oxidised with chromic and acetic acids to λ -*ketotrizecenoic acid*, m. p. 70—71°, b. p. 185—186°/1 mm. (*methyl ester*, m. p. 30°, b. p. 185—186°/15 mm.). *Tridecalactone*, m. p. 17—18°, b. p. 178—180°/9.5 mm., $d^{15} 0.9327$, obtained by the action of sulphuric acid on tridecenoic acid, on hydrolysis yields γ -*hydroxytridecenoic acid*, m. p. 66—66.5°. *isotrizecenoic acid*, $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2]_9\cdot\text{CO}_2\text{H}$, m. p. 28—29°, b. p. 183—185°/13.5 mm., $d^{15} 1.62^\circ/4$ mm., is obtained as a by-product in the reaction between ethyl sodiomalonate and $\beta\lambda$ -dibromoundecane (cf. following abstract), or by the action of potassium hydroxide at 220° on the Δ^2 -acid. At 300—360°, fission of the chain occurs as in the analogous cases of the lower homologues. Reduction of *methyl isotrizecenoate*, b. p. 147—148°/10 mm., yields Δ^2 -*tridecenol*, m. p. 6°, b. p. 150—152°/11 mm., $d^{15} 0.852$ (*phenylurethane*, m. p. 64—64.5°). Condensation of ethyl methylmalonate with undecenyl bromide in presence of dry sodium ethoxide yields *ethyl methylundecenylmalonate*, b. p. 160°/3 mm., $d^{15} 0.939$, which on hydrolysis yields α -*methyl- Δ^2 -tridecenoic acid*, m. p. 8—9°, b. p. 182—184°/10 mm., $d^{15} 0.893$ (*methyl ester*, b. p. 148—149°/10 mm., $d^{15} 0.879$; *ethyl ester*, b. p. 160.4—161°/10 mm., $d^{15} 0.873$; *amide*, m. p. 86—86.5°), which on oxidation yields

undecane- $\beta\kappa$ -dicarboxylic acid. By analogous methods are obtained: β -methyl- Δ^{Λ} -tridecenol, b. p. 159—160°/12 mm., d^{15} 0.848 (phenylurethane, m. p. 66.5—67.5°); methyltridecenyl bromide, b. p. 140—144°/4 mm., d^{15} 1.014; α -dibromo- β -methyltridecane, b. p. 161—162°/2.5 mm., d^{15} 1.129; β -methyltridecane- α -diol, b. p. 195—196°/12 mm., m. p. -2°, d^{15} 0.911; λ -keto- α -methyltridecanoic acid, m. p. 46.5—47.2°, b. p. 198—199°/3 mm. (methyl ester, b. p. 181—183°/11 mm., d^{15} 0.936); methyltridecen- α -ol, b. p. 159—161°/13 mm., d^{15} 0.852 (phenylurethane, m. p. 69.5—70.5°); methyl tridecenylmalonate, b. p. 178—180°/3 mm., d^{15} 0.947; pentadecenoic acid, m. p. 49.8—50°, b. p. 195°/8 mm. (methyl ester, b. p. 167—168°/8 mm., d^{15} 0.881; ethyl ester, b. p. 174—176°/8 mm., d^{15} 0.875; pentadecenyl ester, m. p. 35—35.5°, b. p. 290—295°/10 mm.); Δ^{ξ} -pentadecen- α -ol, m. p. 32—33°, b. p. 170—172°/10 mm. (phenylurethane, m. p. 60.5—61°); pentadecenyl bromide, b. p. 180—185°/3 mm., d^{15} 1.009; $\alpha\xi$ -dibromopentadecane, b. p. 180—185°/3 mm., d^{15} 1.170; pentadecane- $\alpha\xi$ -diol, m. p. 70.6—71.6°, b. p. 205—207°/10 mm. (diacetate, b. p. 195—200°/8 mm.); ν -ketopentadecanoic acid, m. p. 78.4—79.5° (methyl ester, m. p. 43.2—43.8°, b. p. 205—206°/15 mm.); isopentadecenoic acid, m. p. 42.2—43°, b. p. 174—176°/1.25 mm. (methyl ester, 166—168°/8 mm., d^{15} 0.883; ethyl ester, b. p. 175—177°/8 mm., d^{15} 0.877); Δ^{ν} -pentadecenol, m. p. 40—40.5°, b. p. 170—172°/8 mm. (phenylurethane, m. p. 68—68.4°); methyl γ -methylpentadecanoate, b. p. 167—173°/10 mm.; δ -methyl- Δ^{ξ} -pentadecenol, b. p. 176—182°/12 mm., d^{15} 0.831; α -methylheptadecenoic acid, m. p. 43—43.5°, b. p. 186—187°/3 mm. (methyl ester, b. p. 158—159°/3 mm., d^{15} 0.876).

J. W. BAKER.

Monomethylated polymethylenedicarboxylic acids and their derivatives. P. CHUIT, F. BOEL-SING, and G. MALET (Helv. Chim. Acta, 1927, 10, 167—194; cf. Ruzicka, this vol., 57).—Condensation of ethyl sodiomethylmalonate and methyl θ -bromopelargonate and hydrolysis of the ester, b. p. 200°/2 mm., formed yields decane- β -dicarboxylic acid, m. p. 80—80.5°. Ozonisation of α -methyltridecenoic acid (preceding abstract) yields the aldehydo-acid, b. p. 184—186°/1 mm. (semicarbazone, m. p. 129.5—130.5°), which is readily oxidised to undecane- $\alpha\kappa$ -dicarboxylic acid, m. p. 76—76.5° (dimethyl ester, b. p. 187—188°/13 mm., d^{15} 0.966; diethyl ester, b. p. 197°/12 mm., d^{15} 0.940), which is also obtained by the interaction of ethyl methylmalonate and methyl ι -bromodecoate, and on hydrolysis of the dinitrile obtained by the action of potassium cyanide on $\beta\lambda$ -dibromoundecane (preceding abstract). The action of chloromethyl ether on the magnesium compound of $\beta\lambda$ -dibromoundecane yields α -dimethoxy- β -methylundecane, b. p. 156—168°/12 mm. (together with a little methoxy-dodecenol, b. p. 77—88°/11 mm.), which, treated with hydrogen bromide at 170—180°, yields α -dibromo- β -methylundecane, b. p. 190—200°/8 mm., d^{15} 1.275; this, converted into the diacetate and hydrolysed, yields β -methylundecane- α -diol, b. p. 186—189°/8.5 mm., 169—172°/1 mm., m. p. 18°, d^{15} 0.917, which changes spontaneously to a white, crystalline mass, m. p. 42°. The same glycol is better obtained by the reduction of methyl α -methylundecane- $\alpha\kappa$ -dicarboxylate. Condensation of ethyl malonate with methyl bromoundecate (Walker

and Lumsden, J.C.S., 1901, 79, 1191) and hydrolysis of the product yields β -methylundecane- $\alpha\kappa$ -dicarboxylic acid, m. p. 82°, b. p. 237—238°/7 mm., 210—211°/1 mm. (dimethyl ester, b. p. 175—176°/8 mm., d^{15} 0.975; diethyl ester, b. p. 187—189°/8 mm., d^{15} 0.947; cf. Komppa, A., 1901, i, 365, who described this acid as the normal undecanedicarboxylic acid). Reduction of the methyl ester yields γ -methylundecane- α -diol, b. p. 190—191°/8 mm., d^{15} 0.916 (dibromide, b. p. 187.5—189°/7 mm., d^{15} 1.272). By the continued application of these methods, the following are obtained: dodecane- $\alpha\lambda$ -dicarboxylic acid, m. p. 87.5—88.5° (dimethyl ester, b. p. 185°/9 mm.); β -methyltridecane- α -diol, m. p. 46—47°, b. p. 195°/9 mm. (dibromide, b. p. 198—200°/9 mm., d^{15} 1.229); β -methylundecane- $\alpha\lambda$ -dicarboxylic acid, m. p. 68.5—69.5°, b. p. 182—185°/8 mm., d^{15} 0.958; β -bromo- λ -cyanoundecane, d^{15} 1.100 (decomposes on distillation); γ -methyltridecane- α -diol, b. p. 196—197°/8 mm., d^{15} 0.912, which spontaneously changes into a white, crystalline mass, m. p. 24° (corresponding dibromide, b. p. 196—197°/8 mm., d^{15} 1.241); β -methylundecane- α -dicarboxylic acid, m. p. 75.2°, b. p. 239—241°/4 mm. (dimethyl ester, b. p. 194—196°/9 mm., d^{15} 0.957; diethyl ester, b. p. 205—207°/9 mm., d^{15} 0.938), which was also obtained by hydrolysis of the dinitrile, b. p. 229—232°/16 mm., d^{15} 0.901; γ -methyltetradecane- α -diol, m. p. 17°, b. p. 204—205°/8 mm., d^{20} 0.909; α -dibromo- γ -methyltetradecane, b. p. 207—208°/8 mm., d^{15} 1.218; α -methyltridecane- $\alpha\nu$ -dicarboxylic acid, m. p. 93.5—94.5°, b. p. 228—230°/4 mm. (dimethyl ester, b. p. 193—195°/5 mm., d^{15} 0.941). Dodecane- α -diol yields a monoacetate, b. p. 185°/8 mm., which with hydrogen bromide is converted into a bromoacetate, b. p. 160—161°/3.5 mm., d^{15} 1.083; this on hydrolysis yields the bromohydrin, m. p. 28.6°, b. p. 155—156°/4 mm., which is converted into α -cyanododecan- μ -ol, m. p. 23—24°, b. p. 173—175°/4 mm., which on treatment with hydrogen bromide yields a mixture of the bromonitrile, bromoamide, m. p. 42—43°, and the hydroxyamide, m. p. 82—84°; the first two on hydrolysis with methyl-alcoholic sulphuric acid yield methyl μ -bromotridecoate, b. p. 174—179°/4 mm., d^{15} 1.090; β -methyltridecane- $\alpha\nu$ -dicarboxylic acid, b. p. 215—220°/1 mm. (dimethyl ester, b. p. 203—204°/8 mm., d^{15} 0.950; monoamide, m. p. 110—111°; dinitrile, b. p. 227°/9 mm., d^{15} 0.908); γ -methyltridecane- $\alpha\nu$ -dicarboxylic acid, b. p. 226—227°/3 mm. (dinitrile, b. p. 177—178°/3 mm., d^{15} 0.905). Condensation of ethyl malonate with $\beta\theta$ -dibromo-octane, b. p. 137—138°/15 mm., d^{15} 1.449, yields isodecenoic acid, $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2]_6\cdot\text{CO}_2\text{H}$, b. p. 155—157°/14 mm., d^{15} 0.930 (methyl ester, b. p. 121—123°/20 mm., d^{15} 0.896), and β -methylnonane- α -dicarboxylic acid, b. p. 210—215°/5 mm. (m. p. 40—42°, but sample may not be pure) (dimethyl ester, b. p. 174—178°/15 mm., d^{15} 0.955); γ -methylundecane- $\alpha\lambda$ -diol, b. p. 192—195°/15 mm., d^{15} 0.923 (corresponding dibromide, b. p. 185—188°/15 mm., d^{15} 1.297); δ -methyltridecane- $\alpha\nu$ -dicarboxylic acid, b. p. 229—230°/2.5 mm. (dimethyl ester, b. p. 210—215°/14 mm.). Pentadecane- $\alpha\xi$ -dicarboxylic acid, m. p. 89—90°, b. p. 223—225°/0.2 mm. (dimethyl ester, b. p. 172—180°/1 mm., d^{15} 0.9465, m. p. 3—4°, but changes spontaneously into a white, crystalline mass, m. p. 19—21°), is pre-

pared by the ozonisation or permanganate oxidation of α -methylheptadecenoic acid and by the oxidation of *o*-hydroxy- α -methylpentadecanecarboxylic acid, m. p. 62—63°, obtained by the condensation of α -bromotetradecan-*o*-ol, m. p. 46.4°, b. p. 192—195°/12 mm., d^{25} 1.123, with ethyl sodiomethylmalonate; β -methyltetradecane- α , β -dicarboxylic acid, m. p. 77.2—77.4°, b. p. 250°/3 mm. (dimethyl ester, b. p. 198—200°/3.5 mm., d^{15} 0.946; diethyl ester, b. p. 209—211°/3.5 mm., d^{15} 0.931). γ -Methyltetradecane- α , β -dicarboxylic acid, m. p. 78—78.4° (dimethyl ester, b. p. 203—204°/4 mm., d^{15} 0.948; diethyl ester, b. p. 223—225°/8 mm., d^{15} 0.934; dinitrile, m. p. 36.6—36.8°, b. p. 235—245°/8 mm.); δ -methyltetradecane- α , β -dicarboxylic acid, m. p. 78.8—79°, b. p. 252—253°/3 mm. (dimethyl ester, b. p. 200—202°/3 mm., d^{15} 0.950; diethyl ester, b. p. 234—236°/9 mm., d^{15} 0.931). Methyl κ -bromoundecate, m. p. 15.8°, b. p. 164.5°, and ethyl κ -bromoundecate, m. p. 10°, b. p. 172—174°, d^{15} 1.1295, are described. J. W. BAKER.

Oxidation of oleic acid by perbenzoic acid. G. W. FIGULEVSKI and M. A. PETROVA (J. Russ. Phys. Chem. Soc., 1926, 58, 1062—1066).—Oleic acid was oxidised at 0° in ethereal solution of perbenzoic acid and the benzoic acid removed by gaseous ammonia. The ethereal mother-liquor gave a 78% yield of a solid oxide, m. p. 57.5—58°. On hydrolysis by boiling with dilute acids, or heating in a sealed tube at 150°, this gave a solid dihydroxystearic acid, m. p. 94—94.5°, which corresponds, not with oleic, but with elaidic acid. Hydrolysis of the oxide corresponding with elaidic acid, on the other hand, according to Albitzky (A., 1899, i, 862), gives dihydroxystearic acid, m. p. 137°, corresponding with oleic acid. It is probable that the isomerisation takes place during hydrolysis. M. ZVEGINTZOV.

Oxidation of ricinoleic acid with nitric acid. Conditions underlying the formation of suberic acid. P. E. VERKADE (Rec. trav. chim., 1927, 46, 137—143).—The relative amounts of suberic and azelaic acids produced in this oxidation vary considerably. The following factors influence the reaction. (1) It is immaterial whether the ricinoleic acid is added to the nitric acid, or *vice versa*. (2) A higher temperature lowers the total yield. (3) A higher temperature or less concentrated nitric acid gives a mixture in which suberic acid predominates. (4) Prolonged oxidation reduces the amount of azelaic acid, since it undergoes further oxidation more rapidly than suberic acid. On the basis of these facts, methods of preparing suberic and azelaic acids are described. J. M. GULLAND.

Preparation of α -ketonic acids. BARRÉ (Compt. rend., 1927, 184, 825—826).—Ethyl diethyloxamate, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{NET}_2$, and magnesium ethyl bromide (1.5 mols.) in 1 hr. at -15° afford 75—80% of the theoretical yield of α -hydroxy- α -ethylbutyrdiethylamide, b. p. 120°/11 mm., together with 5—10% of propionylformdiethylamide, b. p. 100°/11 mm. (semicarbazone, m. p. 140°). Excess of Grignard reagent, higher temperatures, and prolonged reaction favour formation of the latter compound. Traces of dipropionyl are formed and about 10% of the ethyl diethyloxamate is unchanged. Rapid hydrolysis of the ketone amide with hydrochloric acid affords the α -ketonic acid in

70% yield. Propionylformic acid has m. p. 31—32°, b. p. 80—82°/16 mm. (phenylhydrazone, m. p. 161°; oxime, m. p. 167°; semicarbazone, m. p. 210°); on slow heating these derivatives give m. p. 152°, 161°, and 190°, respectively). R. BRIGHTMAN.

Electrolysis of aqueous solutions of pure oxalic acid. E. DOUMER.—See this vol., 427.

Preparation of maleic and succinic acids from furfuraldehyde. ZAIDAN HOJIN RIKAGAKU KENKYUJO.—See B., 1927, 268.

Effect of gem-dialkyl groups on the formation and stability of the anhydrides of dicarboxylic acids. E. H. FARMER and J. KRACOVSKI (J.C.S., 1927, 680—685).—Adipic and β -methyladipic acids form unimolecular anhydrides readily hydrolysed by atmospheric moisture when the acids are boiled with acetic anhydride. The stability is progressively increased in the anhydrides of $\beta\beta\beta'\beta'$ - and $\alpha\alpha\alpha'\alpha'$ -tetramethyladipic acids, the former anhydride being unaffected by boiling water or by sodium carbonate solution. Ring closure of ethyl α -bromo- $\beta\beta\beta'\beta'$ -tetramethyladipate could not be effected by treatment with potassium hydroxide in methyl alcohol. The following are described: adipic anhydride, m. p. 97°; β -methyladipic anhydride, b. p. 165°/1 mm.; $\alpha\alpha\alpha'\alpha'$ -tetramethyladipic anhydride, m. p. 166° (anilic acid, m. p. 218°); $\beta\beta\beta'\beta'$ -tetramethyladipic anhydride, m. p. 189° (anilic acid), when heated gives 1 : 1 : 2-tetramethylcyclopentan-4-one, b. p. 186—189°. M. CLARK.

Shellac. Constitution of aleuritic acid. W. NAGEL (Ber., 1927, 60, [B], 605—609; cf. Harries and Nagel, A., 1923, i, 120).—Oxidation of aleuritic acid by 3% potassium permanganate affords azelaic acid and non-crystalline ζ -hydroxyheptoic acid, identified by further oxidation to pimelic acid. With 1% potassium permanganate at the atmospheric temperature, aleuritic acid gives azelaic acid and non-crystalline aldehydic acids, which are oxidised further to pimelic acid. More drastic oxidation with Beckmann's mixture or potassium permanganate yields mainly azelaic and pimelic acids, whereas with hydrogen peroxide and ferrous sulphate, non-crystalline, aldehydic compounds are formed. Aleuritic acid is therefore regarded as ω -trihydroxypalmitic acid. H. WREN.

Ring-chain tautomerism. XV. Hydroxylactone type. E. ROTHSTEIN and C. W. SHOPPEE (J.C.S., 1927, 531—534).—Introduction of a second gem-dimethyl group into Balbiano's acid (cf. *ibid.*, 1922, 121, 654) leads to stabilisation of the hydroxylactone form,

$$\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \quad | \\ \text{CMe}_2 \text{---} \text{CMe}_2 \end{array} > \text{C}(\text{OH})\cdot\text{CO}_2\text{H.} \quad \alpha\text{-Keto-}$$

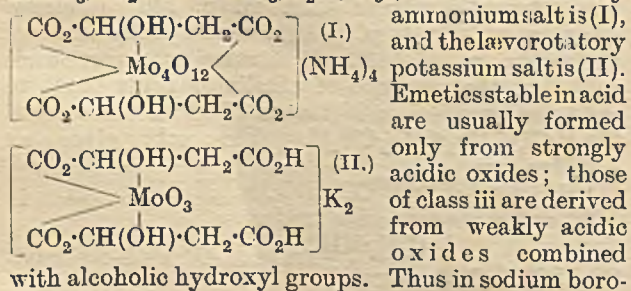
$\beta\beta\gamma\gamma$ -tetramethylglutaric acid, m. p. 140° (dimethyl ester, m. p. 103°, b. p. 170°/15 mm.), yields an acetyl derivative, m. p. 149°. It titrates as a monobasic acid, but the presence of alkalis or acids tends to shift the equilibrium in favour of the ketonic form, $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. The acid gives an additive product, $\text{CO}_2\text{H}\cdot[\text{CMe}_2]_2\cdot\text{C}(\text{OH})(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, m. p. 160°, and a condensation product, $\text{CO}_2\text{H}\cdot[\text{CMe}_2]_2\cdot\text{C} \begin{array}{c} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \\ | \quad \quad | \\ \text{C} \text{---} \text{CO} \end{array}$, m. p. 240°, with *o*-phenylenediamine. M. CLARK.

Oxidation [of organic compounds]. W. H. HATCHER (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 327—335).—The action of alkaline permanganate on tartaric acid yields 2 mols. of oxalic acid, whilst acid permanganate gives carbon dioxide and 2 mols. of formic acid, and sodium hypiodite has no effect. Dihydroxymaleic acid is oxidised by alkaline permanganate to oxalic acid, and by acid permanganate to carbon dioxide, formic acid not being produced in either case, whereas with sodium hypiodite the product is mesoxalic acid. With all three oxidising agents, dihydroxytartaric acid is formed as an intermediate stage. Permanganate oxidises mesoxalic acid to oxalic acid or carbon dioxide, and sodium hypiodite slowly converts it into oxalic acid. Mesoxalic acid does not seem to be formed in the oxidation of dihydroxymaleic acid by permanganate. Formic acid is rapidly and completely oxidised by alkaline permanganate, but with acid permanganate the reaction is not complete. R. CUTHILL.

Compounds of the tartar emetic type. Classification. E. DARMOIS (Bull. Soc. chim. Belg., 1927, 36, 64—75; cf. A., 1923, i, 299, 535, 751; 1924, ii, 618; 1925, ii, 184, 357; 1926, 337, 457, 559, 661, 778, 1201).—Compounds of the tartar emetic type are formed from a variety of oxides of metals or metalloids (beryllium, boron, aluminium, titanium, zirconium, arsenic, antimony, bismuth, copper, molybdenum, tungsten, uranium) and all organic compounds containing two adjacent hydroxyl groups, whether alcoholic, phenolic, or acidic. The constitution, $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OSbO})\cdot\text{CO}_2\text{H}$, suggested by Jungfleisch for tartar emetic does not account for the immediate change in optical rotation on adding alkali to tartar emetic or yellow molybdic acid to malic acid, nor the inability of tartaric esters to form emetics until hydrolysis has occurred. Co-ordination formulæ of a single type are also not satisfactory for all emetics.

Emetics are grouped in three classes: (i) those possessing a p_H of maximum stability; e.g., the compound $[\text{4MoO}_3\cdot\text{2C}_4\text{H}_4\text{O}_5]\text{Na}_4$, formed by gradual addition of alkali to a solution of molybdic and tartaric acids, represents a point of maximum stability at p_H 3.7; (ii) those stable in acid media, and (iii) those stable in basic media; e.g., tartar emetic and mixtures of antimony trioxide or boric acid with mannitol, form stable complexes on addition of excess of concentrated alkali.

The formation of complexes of the emetic type is readily followed by means of polarimetric measurements. The molybdomalates are derivable from acids $\text{4MoO}_3\cdot\text{2H}_2\text{O}$ and $\text{MoO}_3\cdot\text{H}_2\text{O}$; e.g., the dextrorotatory



mannitol, $[\text{C}_6\text{H}_{13}\text{O}_5\cdot\text{B}_2\text{O}_3\cdot\text{C}_6\text{H}_{13}\text{O}_5]\text{Na}_2$, neighbouring pairs of hydroxyl groups are linked to the boric oxide group, and one hydroxyl group of each pair becomes acidic, and the hydrogen atom is replaced by sodium. In the alkali-stable complex from tartar emetic, neutral potassium tartrate takes the place of mannitol.

C. HOLLINS.

Muconic and hydromuconic acids. IV. Geometrical form and reducibility. E. H. FARMER and W. M. DUFFIN (J.C.S., 1927, 402—412).—Addition of bromine to *trans-trans*-methyl muconate gives two isomeric *dibromides*, A, m. p. 104—105°; B, m. p. 50°. When treated with diethylamine in ether, A gives (i) *trans-trans*-methyl α -bromomuconate, m. p. 89° (*amide*, m. p. 235°), whilst B gives (ii) *cis-cis*-methyl α -bromomuconate, m. p. 68° (*amide*, m. p. 197°), and (iii) *cis-trans*-methyl α -bromomuconate, m. p. 55° (*amide*, m. p. 156°). The geometrical configurations of these isomerides are determined by the relative ease of formation of the amides. Reduction with zinc and acetic acid readily gives with (i) and (iii) methyl Δ^β -dihydromuconate, m. p. 16°, whilst with (ii) no reduction occurs. Treatment with zinc dust in alcohol or acetone removes bromine from (i) to give *trans-trans*-methyl muconate, but does not affect (ii) or (iii). Reduction of the three isomeric ethyl $\alpha\alpha'$ -dibromomuconates and of the analogous dichloro-compounds with zinc and acetic acid gives, in each case, ethyl Δ^β -dihydromuconate (*trans*?), m. p. 2°. The two isomeric methyl muconates (J.C.S., 1923, 121, 2531), on reduction with zinc and acetic acid, give methyl Δ^β -dihydromuconate, with sodium amalgam give Δ^β -dihydromuconic acid, and with palladium and hydrogen give methyl adipate. The isomeric methyl $\alpha\alpha'$ -dibromoadipates (*loc. cit.*) treated with zinc and acetone give methyl Δ^β -dihydromuconate, m. p. 16°. *meso*- and *r*-Ethyl $\beta\beta'$ -diphenyl- $\beta\beta'$ -dihydroxyadipates (Beschke, A, 1912, i, 889) react with phosphorus tribromide to give two isomeric ethyl $\beta\beta'$ -diphenylmuconates, (iv), m. p. 136°, and (v), m. p. 174°. These are also produced by the action of zinc dust and acetone or of acetic anhydride on the dihydroxy-compounds; (v) rapidly changes on keeping to a third isomeride (vi), m. p. 72°. Hydrolysis of (iv) yields $\beta\beta'$ -diphenylmuconic acid, m. p. 142°, whilst (vi) gives 2:3-diphenylcrotonolactone-3-acetic acid (?), m. p. 181° (Beschke, *loc. cit.*). Reduction of (iv) with sodium amalgam after hydrolysis gives *cis*- $\beta\beta'$ -diphenyl- Δ^β -dihydromuconic acid, m. p. 195° (ethyl ester, m. p. 56°), whilst (vi) under similar treatment gives a mixture of this acid with *trans*- $\beta\beta'$ -diphenyl- Δ^β -dihydromuconic acid, m. p. 297° (ethyl ester, m. p. 86°). Oxidation of each of these acids with ozone gives the same benzoylacetic acid.

M. CLARK.

Catalytic oxidation by air of alcohols to aldehydes or ketones in presence of zinc oxide. R. OTTENSOOSER (Bull. Soc. chim., 1927, [iv], 41, 324—325).—The following yields of aldehydes or ketones are obtained by oxidation by air of the alcohol named in the presence of zinc oxide catalyst prepared from ammonium zincate (cf. Adkins and Lazier, A., 1925, i, 878). The optimum temperature is indicated: Propyl alcohol, 85.6% (315—325°); isopropyl, 84.5% (315—325°); *sec*-butyl, 93.0% (335—340°); *n*-

butyl, 85.7% (335—340°); *isobutyl*, 74.0% (340—350°), *isoamyl*, 60.5% (345—355°); *sec.-octyl*, 79.1% (330—340°); *n-decyl*, 70% (390—400°), *benzyl*, 67.2% (330°), *phenylethyl alcohol*, 50% (430—440°). In the first three cases, yields are calculated on the air used, less than the theoretical amount being employed. In the last two cases, the reaction was effected under reduced pressure. R. BRIGHTMAN.

Catalytic condensation of acetone at high temperatures and pressures. II. W. N. IPATIEV and A. D. PETROV (Ber., 1927, 60, [B], 753—755; cf. A., 1926, 1130).—Mesitylene is the main product formed when acetone is heated with aluminium oxide at 350° under high pressure; in addition, mesityl oxide, *isophorone*, *xylitone*, and a terpene hydrocarbon are obtained. Hexamethylbenzene is not produced by the condensation of acetone with methyl alcohol in presence of aluminium oxide under pressure. H. WREN.

Catalytic condensation of acetone at high temperatures and pressures. I. W. N. IPATIEV and A. D. PETROV (J. Russ. Phys. Chem. Soc., 1926, 58, 1028—1033)—See. A., 1926, 1130, and preceding abstract.

Condensation of acetaldehyde with methyl *n*-propyl ketone. J. COLONGE (Bull. Soc. chim., 1927, [iv], 41, 325—328).—Methyl propyl ketone and acetaldehyde in presence of methyl-alcoholic potassium hydroxide at 10° afford (yield 50—55%) γ -ethylpentan- δ -ol- β -one, b. p. 80—82°/3 mm., d^{15} 0.977, n_D^{15} 1.4418, which gives iodoform with sodium hypiodite, but does not form a hydrogen sulphite compound. Dehydration in presence of iodine or oxalic acid at 145° affords γ -ethyl- Δ^{γ} -penten- β -one, b. p. 85—86°/80 mm., $d^{17.5}$ 0.865, $n_D^{17.5}$ 1.4479 (*oxime*, b. p. 110—113°/5 mm.; *semicarbazone*, m. p. 200°), which does not give a hydrogen sulphite compound, but on hydrogenation in presence of nickel is converted into γ -ethylpentan- β -one. Reduction with sodium in moist ether affords γ -ethyl pentan- β -ol (yield 30%), and oxidation with sodium hypochlorite, α -ethylcrotonic acid, m. p. 42°.

R. BRIGHTMAN.

Study of the molecular constitution of certain organic compounds by the absorption of light. H. E. ACLY and H. S. FRENCH (J. Amer. Chem. Soc., 1927, 49, 847—856).—The absorption of acetylacetone, acetylacetone dioxime, acetylacetone monoxime anhydride, copper acetylacetone, dimethyl diketone monoxime, dimethylglyoxime anhydride, and copper dimethylglyoxime, dissolved in 95% alcohol, was investigated in the ultra-violet; the visible absorption of the copper compounds was also studied. The conclusion is reached that acetylacetone in 95% alcohol is an equilibrium mixture of keto- and enolic forms, about 55.7% of the latter being present. Dimethyl diketone monoxime also appears to be an equilibrium mixture.

F. G. WILLSON.

Ring-chain tautomerism. XVI. Effect of two adjacent gem-dimethyl groups on the ease of formation of the cyclopentane ring. I. VOGEL (J.C.S., 1927, 594—600).— α -Diacyl- $\beta\beta\gamma\gamma$ -tetramethylbutane, $\begin{matrix} \text{CMe}_2\text{-CH}_2\text{Ac} \\ | \\ \text{CMe}_2\text{-CH}_2\text{Ac} \end{matrix}$ (I), reacts exclusively in

the form of the ring isomeride, $\begin{matrix} \text{CMe}_2\text{-CH}_2 \\ | \\ \text{CMe}_2\text{-CHAc} \end{matrix} > \text{CMe-OH}$

(II), as would be expected from the modified strain theory of Thorpe and Ingold. In addition to purely chemical evidence, confirmation of the structure (II) is obtained from measurements of the parachor. This compound, obtained by reduction of mesityl oxide by moist aluminium amalgam (cf. Law, J.C.S., 1912, 101, 1016), exists in two modifications, a solid (α) and a liquid (β) form, to which *cis* and *trans* configurations, respectively, are ascribed. The α -form, m. p. 45°, gives a monosemicarbazone, m. p. 185°, and a *monobenzoyl* derivative, m. p. 115°. The β -form, b. p. 122—124°/20 mm., gives a *monosemicarbazone*, m. p. 165°, and a *monobenzoyl* derivative, m. p. 42°. Oxidation of either form with chromic acid gives tetramethylsuccinic acid. Sodium hypochlorite and potassium permanganate are almost without effect. Oxidation with sodium hypobromite gives a quantitative yield of bromoform corresponding with one acetyl group and a small quantity of *acid*, m. p. 122—123° (sparingly soluble *silver* and *barium* salts).

M. CLARK.

Selenoketones. R. E. LYONS and W. E. BRADT (Ber., 1927, 60, [B], 824—826).—Selenoketones are obtained as heavy red oils by the action of hydrogen selenide on ketones mixed with concentrated hydrochloric acid. They cannot be distilled without decomposition. Chlorine decomposes them with production of selenium tetrachloride. *Diselenoacetone*, $(\text{CH}_3\text{-CSe-CH}_3)_2$, *di(methyl ethyl selenoketone)* and *diselenoacetophenone* are described. H. WREN.

Constitutional studies in the monocarboxylic acids derived from sugars. IV. Isomeric lactones obtained from arabinose. J. PRYDE and R. W. HUMPHREYS (J.C.S., 1927, 559—565).—Direct chemical proof of the amylenoxide structure of trimethyl- β -methylarabinoside is adduced in that this substance, like the α -stereoisomeride, is converted by simultaneous hydrolysis and oxidation with hydrobromic acid and bromine into *d*-2:3:4-trimethylarabonolactone (cf. A., 1925, i, 366). The isomeric *l*-2:3:5-trimethylarabonolactone is obtained by synthesis of the mixed methyl- γ -arabinosides and subsequent methylation, followed by simultaneous hydrolysis and oxidation. It is obtained alternatively by bromine oxidation of arabinose, followed by methylation. The results of Baker and Haworth (A., 1925, i, 365) and of Haworth and Nicholson (A., 1926, 1025) are confirmed. Simultaneous formation of amylenoxide and butylene oxide derivatives occurs when arabinose is condensed with methyl alcohol in presence of hydrogen chloride at 100°, since both *d*-2:3:4- and *l*-2:3:5-trimethylarabonolactones can be obtained from the initial condensation product. The auto-condensation of γ -arabinose derivatives to form a dipentoside is described. M. CLARK.

Action of sugar in the organism. II. Decomposition of dextrose by very dilute alkali. F. FISCHLER (Z. physiol. Chem., 1927, 165, 53—67).—The previous observation (A., 1926, 1170) that, on distilling a solution of dextrose in dilute sodium carbonate, methylglyoxal appears in the distillate, is confirmed. If the experiment be conducted in the

absence of air and so that the sugar solution is dropped slowly into boiling sodium carbonate, it is further possible to isolate from the residual solution the osazone of glyceraldehyde (or of dihydroxyacetone); the osazone so obtained was always more or less contaminated with a red pigment. Distillation with dilute sulphuric acid, after treatment of the dextrose with carbonate, yields a further amount of methylglyoxal, which must have been derived from the dihydroxyacetone; moreover, dihydroxyacetone, on distillation with sodium carbonate, gives half the amount of methylglyoxal which is yielded by an equimolecular quantity of dextrose under the same conditions. It is therefore thought that the primary degradation of dextrose, under the influence of very dilute alkali, is into two molecules of glyceraldehyde (or dihydroxyacetone), from which the methylglyoxal is formed secondarily.

C. R. HARRINGTON.

Acetone compounds of the sugars and their derivatives. VIII. **Monoacetone-*l*-arabinose [*l*-arabinose isopropylidene ether].** H. OHLE and G. BEREND (Ber., 1927, 60, [B], 810—811).—*l*-Arabinose is converted by acetone in presence of anhydrous copper sulphate into *l*-arabinose isopropylidene ether, m. p. 110° after softening at 103° (also *semihydrate*, m. p. 80°, $[\alpha]_D^{20} +128.8^\circ$ in water). Since it reduces Fehling's solution, it appears to represent a new type of "acetone sugar."

H. WREN.

Detection of sugar in presence of proteins and the supposed condensation of carbohydrates with albumin. C. NEUBERG and E. SIMON (Ber., 1927, 60, [B], 817—824).—The observation of Pringsheim and Winter (A., 1926, 1274) that reducing hexoses combine instantaneously with proteins, albumoses, and peptones is not in harmony with the slight optical effect of proteins on sugars and the ready decomposability of amino-acid-sugar complexes (cf. Neuberger and Kobel, A., 1926, 151). If, however, a mixture of a protein with only half the quantity of sugar with which, according to Pringsheim, it can combine is heated with Fehling's solution, reduction is observed. Pringsheim's observations appear to be vitiated by the retention in colloidal solution of a part of the cuprous oxide by the protective action of the albumin or alkali albuminate. That proteins do not combine with sugars in the proportions indicated by Pringsheim and Winter is established by the observations (1) that sugars can be almost completely removed from such mixtures by dialysis, (2) that the sugar remains in solution when the protein is precipitated from neutral solution by colloidal ferric hydroxide, (3) that proteins can be precipitated by alcohol from the protein-carbohydrate mixtures, and (4) by titrimetric determination of the sugar by a method which does not involve the separation of the cuprous oxide formed.

H. WREN.

Constitution of the disaccharides. XII. **Lactose.** W. N. HAWORTH and C. W. LONG (J.C.S., 1927, 544—548).—Methylation of the barium salt of lactobionic acid, obtained by oxidation of lactose, yields *methyl octamethyl-lactobionate*, b. p. 157—164°/0.05 mm., $[\alpha]_D +34^\circ$, $n_D^{20} 1.4632$. Hydrolytic cleavage of this product gives 2 : 3 : 4 : 6-tetramethylgalactose

and 2 : 3 : 5 : 6-tetramethyl- γ -gluconolactone. The biose linking in lactobionic acid must therefore occupy the 4-position in the hexonic acid chain, and the constitution already ascribed to lactose by Charlton, Haworth, and Peat (A., 1926, 273) is confirmed.

M. CLARK.

Synthetic melibiose. A. PICTET and H. VOGEL (Helv. Chim. Acta, 1927, 10, 280).—The following additional data are given concerning the synthetic melibiose previously obtained (A., 1926, 1229): $[\alpha]_D +127.1^\circ$ in water (after 24 hrs.); *hydrazone*, m. p. 142°; *osazone*, m. p. 177°; *octa-acetate*, m. p. 175°, $[\alpha]_D +97.3^\circ$ in alcohol-chloroform solution.

J. W. BAKER.

Melezitose and turanose. G. C. LEITCH (J.C.S., 1927, 588—594; cf. Zemplén and Braun, A., 1926, 1229).—Treatment of melezitose with methyl sulphate and sodium hydroxide gives hendecamethylmelezitose, b. p. 236°/0.01 mm., $n_D 1.4680$, $[\alpha]_D +114^\circ$ in methyl alcohol, +108.6° in ethyl alcohol. Hydrolysis with hydrochloric acid gives amyleno-oxidic tetramethylglucose and trimethyl- γ -fructose, $n_D 1.4660$, $[\alpha]_D +55.5^\circ$ in alcohol (Zemplén gives +24°) in the proportion 2:1. From the behaviour of the trimethylfructose on distillation, a definite structure, agreeing with that already suggested by Zemplén and Braun, is ascribed to it. An improved method of isolating the hexose derivatives after hydrolysis is given.

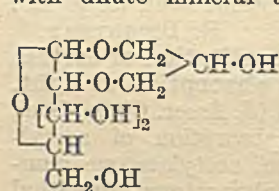
M. CLARK.

Complete depolymerisation of starch. A. PICTET and R. SALZMANN (Helv. Chim. Acta, 1927, 10, 276—279).—Trihexosan, obtained from starch, when heated with twice its weight of glycerol for 15 hrs. at 200—210°, yields an exceedingly hygroscopic compound, m. p. about 40°, $[\alpha]_D +69.21^\circ$, of α -glucosan and glycerol (*tetrazobenzoate*, m. p. 65°; *tetra-acetate*, m. p. 36—37°) which does not reduce Fehling's solution or form an osazone. The same compound is obtained when an equimolecular mixture of glucosan and glycerol is heated at 165° in a vacuum for 10 hrs. It yields dextrose on hydrolysis with dilute mineral acids and acraldehyde when heated with potassium hydrogen sulphate, and, therefore, is probably represented by the annexed formula. Thus α -glucosan is the ultimate depolymerisation product of trihexosan (and therefore of starch),

but careful search failed to detect the presence of any β -glucosan in the product, as would be expected, since trihexosan is probably β -glucosylmaltosan (Pictet and Salzmänn, A., 1926, 52). The formation of the glucosan is, however, in good agreement with the author's relation between the rotatory power and mol. wt. of starch depolymerides (Pictet, A., 1926, 387).

J. W. BAKER.

Catalytic and specific dynamic actions of certain amino-acids. J. M. ORT and J. L. BOLLMAN (J. Amer. Chem. Soc., 1927, 49, 805—810).—The action of 0.03% hydrogen peroxide on dextrose in presence and absence of certain amino-acids was studied by the method of oxidation potentials. Cystine, glycine, alanine, phenylalanine,



leucine, histidine, and valine were found to catalyse this action; glutamic acid, aspartic acid, and tyrosine were without effect. This division of amino-acids closely parallels their division *in vivo* according to their specific dynamic actions. F. G. WILLSON.

Structure of amino-acids, polypeptides, and related compounds. E. ABDERHALDEN and R. HAAS (Z. physiol. Chem., 1927, 164, 1—9; cf. A., 1926, 959).—A significant rise in the absorption of ultra-violet light by amino-acids takes place on formation of salts, but no appreciable increase occurs on salt formation by polypeptides. In polypeptides, therefore, the amino-carboxyl form is the principal type, and this would account for the greater ease of chlorination of these compounds compared with amino-acids. Great differences are exhibited in the absorption curves of creatine and creatinine, and this is attributed to the closure of the ring and the consequent loss of its "Zwitterion" properties. From absorption curves, it is shown that solutions of amino-acids react with freshly-precipitated ferric hydroxide, since there is a distinct increase in the absorption. Large quantities of ferric hydroxide, however, cause a decrease, due to the adsorption of glycine, and possibly the iron compound also, by the ferric hydroxide. A. WORMALL.

Copper salts of optically active amino-acids and similar polypeptides in polarised light. E. ABDERHALDEN and E. SCHNITZLER (Z. physiol. Chem., 1927, 164, 37—49).—The specific rotatory powers of the copper salts of amino-acids, and those of polypeptides, increase with decreasing concentration. The significance, with regard to the structure of these substances in solution, is briefly discussed. A. WORMALL.

Copper salts of amino-acids and polypeptides. E. ABDERHALDEN and E. SCHNITZLER (Z. physiol. Chem., 1926, 163, 94—119).—Copper salts of glycine, sarcosine, *d*-alanine, *dl*-serine, α - and β -aminobutyric acids, α -aminoisobutyric acid, *dl*-valine, *l*-leucine, *d*-, *l*-, and *dl*-tyrosines, aspartic acid, asparagine, *d*-glutamic acid, glycyglycine, leucylglycine, and leucyl-leucine are prepared by boiling a concentrated aqueous solution of the amino-acid with a neutral aqueous suspension of freshly-precipitated copper oxide for some time and crystallising from the dark blue filtrate or precipitating with alcohol. For the cystine salt, the components are shaken together in the cold and excess of copper oxide is removed from the sparingly soluble copper salt by means of hydrochloric acid. The copper salt of histidine cannot be dried without decomposition. The electrical conductivities of the copper salts of the monobasic acids at varying concentrations are of the order of 10^{-5} , and differ little for different acids, that of copper leucine being the smallest for simple amino-acids, and that of copper leucyl-leucine one tenth as great. The copper salts of dibasic amino-acids show special behaviour. The conductivity of monocopper glutamate, $(C_5H_8O_4N)_2Cu$, is ten times that of the other amino-acid copper salts examined. The normal copper salts of aspartic and glutamic acids have about the same conductivity as salts of monobasic acids. Copper *l*-tyrosine shows a higher conductivity than the *d*-salt. C. HOLLINS.

β -Amino- β -aryl-aliphatic acids. II. β -Amino- β -arylisosuccinic ester. W. M. RODIONOV and A. M. FEDOROVA (Ber., 1927, 60, [B], 804—807; cf. this vol., 137).—Ethyl malonate is converted by benzaldehyde and boiling alcoholic ammonia into a mixture of benzylidenemalondiamide, m. p. 190°, ethyl benzylidenemalonate, and ethyl α -aminobenzylmalonate isolated as the *hydrochloride*, m. p. 158—160°, which is converted by boiling hydrochloric acid into β -amino- β -phenylpropionic acid hydrochloride, m. p. 223°. Ethyl piperonylidemalonate and *ethyl α -aminomethylenedioxybenzylmalonate hydrochloride*, m. p. 155°, converted by hydrochloric acid into β -amino- β -piperonylpropionic acid hydrochloride, m. p. 233°, are derived similarly from piperonal. *Ethyl α -methylaminomethylenedioxybenzylmalonate hydrochloride*, m. p. 130°, is described. *Ethyl α -amino-m-nitrobenzylmalonate hydrochloride* has m. p. 150°. H. WREN.

Influence of groups and associated rings on the stability of certain heterocyclic ring systems. I. Substituted glutarimides. S. S. G. SIRCAR (J.C.S., 1927, 600—605).—The rate of hydrolysis of various $\beta\beta$ -disubstituted glutarimides shows that, in accordance with Thorpe and Ingold's modified strain theory, there is an increase in stability in the ascending series, H, H; Me, H; Et, H; Me, Me; Me, Et; Et, Et; cyclopentane; cyclohexane.

The following compounds are new: $\beta\beta$ -*Dimethyl-, β -methyl- β -ethyl-, and $\beta\beta$ -diethyl-glutarimide; cyclopentanediacetimide [$\beta\beta$ -(α' δ' -tetramethylene)glutarimide] and cyclohexanediacetimide [$\beta\beta$ -(α' ϵ' -pentamethylene)glutarimide]. They melt, respectively, at 147°, 127°, 146—147°, 153—154°, and 169°.*

B. W. ANDERSON.

Mustard oils. II. [Reactions with semicarbazide and piperazine.] L. ROSENTHALER (Arch. Pharm., 1927, 265, 111—114; cf. A., 1924, i, 949).—The mustard oils react with semicarbazide and piperazine, giving stable compounds of the types $NHR \cdot CS \cdot N(NH_2) \cdot CO \cdot NH_2$ (I), and (II),

$NHR \cdot (S)CN < \begin{matrix} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \end{matrix} > NC(S) \cdot NHR$. The compounds, m. p. 195—196° and 203—204°, were obtained from semicarbazide and allyl- or phenylthiocarbimides in aqueous alcoholic solution. The sparingly soluble piperazine derivatives, m. p. 219°, 156°, and 255—260° (decomp.), were prepared from ethyl-, allyl-, and phenylthiocarbimides, respectively. S. COFFEY.

Reactions of magnesium alkyl halides. E. SPÄTH (Ber., 1927, 60, [B], 702—704).—The fission of the methylenedioxy-group into hydroxyl and methoxyl under the action of magnesium methyl iodide (Kafuku, A., 1925, i, 1413) has been observed previously by the author (A., 1914, i, 506, 650). The assumption that the product of high b. p. obtained by the action of magnesium methyl iodide on benzyl chloride is α -phenyl- β -*p*-benzylphenylethane, and not $\alpha\beta\gamma$ -triphenylpropane, appears arbitrary (cf. Späth, A., 1914, i, 1; Fuson, A., 1926, 1237; this vol., 46).

H. WREN.

Formation of peroxides in the oxidation of organo-magnesium compounds. H. WUYTS (Bull. Soc. chim. Belg., 1927, 36, 222—238; cf. A.,

1909, i, 448).—Peroxides can be detected in the products of the action of pure, dry oxygen on Grignard reagents in dry ether, especially if the ether solution is diluted with dry toluene. The peroxide is less persistent in the case of magnesium phenyl bromide than in that of the corresponding ethyl and cyclohexyl compounds, and numerous by-products of oxidation are formed, including diphenyl, *p*-diphenylbenzene, ethyl alcohol, and α -phenylethyl alcohol, the last two involving reaction of the ether present.

C. HOLLINS.

Reactions of lead tetraethyl. O. H. BROWNE and E. E. REID (J. Amer. Chem. Soc., 1927, 49, 830—838).—Lead triethyl chloride can be obtained in 86% yield by the gradual addition of lead tetraethyl to concentrated hydrochloric acid below 34°. Lead triethyl hydroxide is obtained in 74% yield by treatment of the chloride, in benzene solution, with aqueous sodium hydroxide (cf. Buckton, Annalen, 1859, 112, 226), but the product is not free from chlorine. The hydroxide absorbs atmospheric carbon dioxide. The decomposition of lead tetraethyl by acids is catalysed by silica gel, and the following lead triethyl salts were obtained by boiling lead tetraethyl with the appropriate acid in presence of silica gel, the fourth ethyl group being always eliminated as ethane: acetate, m. p. 160.4° (decomp.) (cf. Klippel, J. pr. Chem., 1881, [i], 81, 287); propionate, m. p. 141—142°; isobutyrate, m. p. 119.4—121.8°; isovalerate, m. p. 119.4—119.8°; hexoate, m. p. 94.7—95.8°; heptoate, m. p. 90.0—90.8°; octoate, m. p. 85.0—87.5°; and nonoate, m. p. 88.0—90.0°; chloroacetate, m. p. 146—146.5°; dichloroacetate, m. p. 113.5—114.5°; trichloroacetate, m. p. 135.5—138.6°; bromoacetate, m. p. 121°, and dibromoacetate, m. p. 98.6—101.8°. The following salts were prepared by double decomposition from lead triethyl acetate and the appropriate sodium or potassium salt in aqueous solution: cyanide, m. p. 194°; benzoate, m. p. 127°; ferrocyanide, buff-coloured, decomp. above 200°; ferricyanide, brick-red, similar, and valerate, m. p. 115.6—117.0°. All the above m. p. are dependent on the rate of heating. Attempts to prepare the chromate or dichromate always yielded products which appeared to be mixtures of these two salts. A solution of lead tetraethyl in carbon disulphide deposits a black, flocculent precipitate, m. p. not below 300°. Acetyl chloride, phosphorus pentachloride, aluminium chloride, and silicon tetrachloride react with lead tetraethyl, with formation of lead triethyl chloride. Treatment of the latter with sodium phenoxide, *p*-nitrophenoxide, β -naphthoxide, and ethoxide, in absolute alcohol, gave oils. The above lead triethyl salts of the halogenated acetic acids, the reaction of which with lead tetraethyl is vigorous, are strongly sternutatory.

F. G. WILLSON.

Spontaneous oxidation of a saturated cyclic hydrocarbon. G. CHAVANNE (Bull. Soc. chim. Belg., 1907, 36, 206—221; cf. A., 1926, 1130).—Dry 1:3-dimethylcyclopentane absorbs oxygen at the ordinary temperature in diffused light even under reduced pressure, giving a compound of the peroxide type, which on decomposition with potassium iodide yields a mixture of methyl isoamyl ketone, b. p. 143—145° (semicarbazone, m. p. 145°), and δ -methylhexan-

β -one, b. p. 146—147° (semicarbazone, m. p. 129°). The mixture is not separated, but its components are synthesised, the first by catalytic reduction of isobutyrideneacetone, the second by the action of magnesium ethyl bromide on ethylideneacetone.

C. HOLLINS.

Transformation of phenols into hydrocarbons by hydrogen under pressure in presence of catalysts. A. KLING and D. FLORENTIN (Compt. rend., 1927, 184, 885—887; cf. A., 1926, 381).—When heated at 480° with alumina and hydrogen under a pressure of 70—80 kg./cm.², phenol gives mainly benzene; a mixture of the cresols, mainly toluene; cyclohexanol, a mixture of hydrocarbons, only slightly unsaturated, and containing aliphatic hydrocarbons of low b. p. (cf. Ipatiev, A., 1911, i, 25).

E. W. WIGNALL.

Halogenation. I. Iodination. P. S. VARMA and D. A. KULKARNI. **II. Direct iodination in the presence of sodium nitrite and fuming sulphuric acid.** P. S. VARMA and K. G. R. PANICKAR (J. Indian Chem. Soc., 1926, 3, 291—296, 342—344).—I. The yields of aromatic iodo-compounds obtained by the method of Datta and Chatterjee (A., 1917, i, 327) are considerably increased by the addition of glacial acetic acid and 50% nitrosulphonic acid (obtained by passing sulphur dioxide into nitric acid, *d* 1.5). The authors believe that the iodine reacts with nascent nitrobenzene.

II. A 70% yield of iodobenzene may be obtained by the gradual addition of fuming sulphuric acid (10% SO₃) to a mixture of sodium nitrite, iodine, and benzene, and a little glacial acetic acid. Iodination of toluene and xylene may be similarly effected.

J. W. BAKER.

Preparation of *p*-bromobenzyl chloride. R. QUELET (Bull. Soc. chim., 1927, [iv], 41, 329—331).—*p*-Bromobenzyl chloride is obtained in 50% yield by the action of hydrogen chloride on a mixture of trioxymethylene and bromobenzene in presence of stannic chloride. In presence of zinc chloride (cf. Blanc, A., 1923, i, 549), only traces of *p*-bromobenzyl chloride are formed. The crude product (yield 80%) contains about 30% of the *ortho*-isomeride. Böeseken's method (A., 1904, i, 384) affords only 35% of *p*-bromobenzyl chloride, higher chlorinated compounds forming the bulk of the reaction product. The method of Stephen, Short, and Gladding (J.C.S., 1920, 117, 510) also failed to give the yield claimed.

R. BRIGHTMAN.

***p*-Bromobenzyl chloride and the Grignard reaction.** R. QUELET (Compt. rend., 1927, 184, 888—890).—*p*-Bromobenzyl chloride reacts with magnesium and ether in the side-chain only, to give a monomagnesium derivative, decomposed by sulphuric acid to *p*-bromotoluene, together with *pp'*-dibromo- $\alpha\beta$ -diphenylethane in increasing amounts if the vigorous reaction is not controlled by cooling. The Grignard derivative reacts with allyl bromide to give *p*-bromo- Δ^2 -butenylbenzene, b. p. 106°/12 mm., *d*₄¹⁵ 1.259, *n*_D¹⁵ 1.554, which combines with bromine to give $\alpha\beta$ -dibromo- δ -*p*-bromophenylbutane, b. p. 190—191°/12 mm., *d*₄¹⁵ 1.859, *n*_D¹⁵ 1.610, and reacts with perbenzoic acid to form δ -*p*-bromophenylbutylene oxide, b. p. 142°/10 mm.

E. W. WIGNALL.

Walden inversion. XI. Evidence for the bivalency of carbon from some reactions of α -chloroethylbenzene. $\alpha\alpha'$ -Diphenyldiethyl ether. A. M. WARD (J.C.S., 1927, 445—458).—The displacement of the halogen in r - α -chloroethylbenzene in aqueous-alcoholic solution at 28·7° and at 50°, alone and in presence of sodium hydroxide, yields a mixture of phenylethylcarbinol (identified as the *p*-nitrobenzoate, m. p. 47—48°) and ethyl α -phenylethyl ether. The velocity coefficients are identical in each case, and agree with a unimolecular reaction, the sodium hydroxide playing no part in the halogen replacement. Velocity coefficients obtained from the change in rotation of *d*- α -chloroethylbenzene under comparable conditions confirm this conclusion. r - α -Chloroethylbenzene on boiling with water yields mainly $\alpha\alpha'$ -diphenyldiethyl ether, together with styrene and phenylmethylcarbinol. The same products are obtained by boiling $\alpha\alpha'$ -diphenyldiethyl ether or phenylmethylcarbinol with 0·5*N*-hydrochloric acid. It is concluded that these reactions proceed through a phase, CPhMe<, in which only two groups are momentarily attached to carbon. The mechanism of the Walden inversion is discussed from this point of view. Displacement of halogen from β -chloroethylbenzene is negligibly slow in aqueous-alcoholic solution, but proceeds according to the bimolecular law in presence of sodium hydroxide.

M. CLARK.

Thermal decomposition of sulphonic esters. Z. FÖLDI (Ber., 1927, 60, [B], 656—664; cf. A., 1920, i, 828).—Allyl benzenesulphonate, b. p. 120—122°/1 mm., decomposes somewhat violently at 180°, slowly at the atmospheric temperature, yielding benzenesulphonic acid and an amorphous, saturated hydrocarbon of high mol. wt. which could not be identified and is probably formed by polymerisation of vinylmethylene under the action of benzenesulphonic acid. Attempts to counteract the effect of the latter by addition of magnesium or zinc oxides were unsuccessful. In boiling xylene, the radical enters the benzenoid nucleus, yielding unsaturated hydrocarbons of high b. p. Methyl benzenesulphonate and *p*-toluenesulphonate are thermostable. From ethyl benzenesulphonate, the hydrogen atom required for the production of benzenesulphonic acid is withdrawn from the β -position of the ethyl group, since ethylene is almost quantitatively produced. This is also the case with the β -chloroethyl and $\beta\beta'$ -dichloroisopropyl esters, which yield, respectively, vinyl chloride and γ -chloroallyl chloride. Fission of the halogenated esters is more complex than that of the ethyl ester. *Ethylene dibenzenesulphonate*, m. p. 49—50°, b. p. 190°/1 mm., prepared from ethylene glycol and benzenesulphonyl chloride in presence of aqueous sodium hydroxide (20%), gives benzenesulphonic acid, acetylene, and paracetalddehyde. Benzyl benzenesulphonate, m. p. 59—60°, decomposes at a relatively very low temperature into benzenesulphonic acid and an amorphous, polymeric hydrocarbon; if decomposition takes place at the ordinary temperature, the intermediate phenylated cycloparaffins can be isolated as liquids which are immediately polymerised by concentrated sulphuric acid. *Benzenesulphonylbenzoin*, m. p. 99—100°, decomposes at 160°

without production of recognisable material other than benzenesulphonic acid. H. WREN.

Action of ethyl nitrate on diphenyl and its derivatives. H. RAUDNITZ [with H. BÖHM] (Ber., 1927, 60, [B], 738—743).—Ethyl nitrate acts as a vigorous nitrating agent towards aromatic compounds suspended or dissolved in concentrated sulphuric acid at -5°. Anthraquinone is transformed into dinitroanthraquinone. Diphenyl affords *trinitrodiphenyl*, m. p. 175·5°. Carbazole is converted into 1:3:6:8-tetranitrocarbazole, m. p. 289° after darkening at 200° (cf. Borsche and Scholten, A., 1917, i, 390), and an isomeric *tetranitrocarbazole*, decomp. above 200°. *oo'*-Dimethoxydiphenyl gives 3:3':5':5'-tetranitro-2:2'-dimethoxydiphenyl, m. p. 187° (Borsche and Scholten, *loc. cit.*, record m. p. 177—178°), dealkylated to 3:3':5:5'-tetranitro-2:2'-dihydroxydiphenyl, m. p. 248—249°, which is also obtained by direct nitration of *oo'*-dihydroxydiphenyl. Diphenylene oxide and ethyl nitrate yield *trinitrodiphenylene oxide*, m. p. 228°.

Trinitrodiphenyl is converted by thionyl chloride at 180° into *trichlorodiphenyl*, m. p. 55°; similarly, tetranitrocarbazole yields 1:3:6:8-tetrachlorocarbazole, m. p. 180° after softening at 168°.

H. WREN.

Addition of hydrogen to acetylene derivatives. XVII. **Hydrogenation of tolane.** J. S. SALKIND and N. W. LYN (J. Russ. Phys. Chem. Soc., 1926, 58, 994—997; cf. A., 1922, 1134; ii, 835).—Tolane, m. p. 62—63·5°, was hydrogenated in alcohol solution by Paal's method, the unimolecular constant of the reaction being determined. This remains steady until 80% conversion is reached, and then falls gradually. There is no increase of velocity, as in the case of phenylacetylene (*loc. cit.*), when the triple linking is reduced to a double linking, the presence of a second phenyl group apparently slowing down the reduction of the latter. This is proved by the fact that stilbene is reduced more slowly than either tolane or styrene.

M. ZVEGINZOV.

Hydrogenation of naphthalene and anthracene at high temperatures and under high pressures in presence of non-hydrogenating catalysts. A. KLING and D. FLORENTIN (Compt. rend., 1927, 184, 822—824; cf. A., 1926, 381).—The threshold temperatures for hydrogenation both in presence and absence of a non-hydrogenating catalyst are dependent to some extent on the pressure. Thus at an initial hydrogen pressure of 90—100 kg./cm.², hydrogenation of naphthalene is appreciable at 475—480°, or at 450° in presence of aluminium chloride; the corresponding temperatures for anthracene are 440° and 425—430° (with ferric chloride). The presence of the catalyst increases the proportion of liquid products, and particularly the proportion of benzene hydrocarbons. Thus naphthalene under the conditions cited affords 17·6% of liquid products, 36% of which distil below 160°, whilst in presence of a catalyst 64% of liquid products is obtained, 54% of which distils below 160°. Similarly, anthracene affords 67% of liquid products in presence of a catalyst 19% of which distils below 180°, the corresponding figures in absence of the catalyst being 60% and

3.75%. The fractions of high b. p. consist of hydro-naphthalenes and hydroanthracenes. In the case of anthracene, a crystalline product, m. p. 68—69°, distilling at 200—250°, was isolated.

R. BRIGHTMAN.

Nitration. III. Nitration of naphthalene. P. S. VARMA and C. K. MENON (J. Indian Chem. Soc.; 1926, 3, 328—334).—The maximum yield (86%) of α -nitronaphthalene obtained by using a mixture of nitric and sulphuric acids is also produced when plaster of Paris, quicklime, or phosphoric oxide is used as a dehydrating agent in place of sulphuric acid, although they are not effective in the nitration of benzene. The b.-p. curve for mixtures of naphthalene and α -nitronaphthalene has been plotted, and the percentage of the nitronaphthalene in the product was determined by this means. J. W. BAKER.

Rate of conversion of naphthalene-2:7-disulphonic acid into the isomeric 2:6-acid at 160° in presence of sulphuric acid. J. L. HEID (J. Amer. Chem. Soc., 1927, 49, 844—846).—When heated with 1 mol. of sulphuric acid (95%) at 160° in a glass vessel, naphthalene-2:7-disulphonic acid is converted, to the extent of 42%, into the 2:6-disulphonic acid, in 19 hrs. Further heating results in a diminution of the proportion of the 2:6-isomeride present, due apparently to the formation of sulphonated tars (cf. Ebert and Merz, A., 1876, ii, 408; Fierz-David and Hasler, A., 1923, i, 1190).

F. G. WILLSON.

Constitution of thiocyananiline and some derivatives. J. W. DIENSKE (Rec. trav. chim., 1927, 46, 154—157; cf. Söderbäck, A., 1920, i, 219; Kaufmann and Oehring, A., 1926, 392).—Confirmation is obtained of Söderbäck's conclusion that the thiocyanato-group in thiocyananiline is in the *p*-position. The calculated quantity of bromine in acetic acid converts *p*-thiocyananiline (*acetyl* derivative, m. p. 189°) into 2:6-dibromo-4-thiocyananiline, m. p. 118° (*acetyl* derivative, m. p. 174°; *diacetyl* derivative, m. p. 102°), whilst further bromination yields 2:4:6-tribromoaniline. The thiocyanato-group is not removed by superheated steam in 70% sulphuric acid, but it is oxidised to the sulpho-group by permanganate, and the resulting sulphonic acid yields 2:6-dibromoaniline when distilled in steam. Chlorine water in acetic acid converts 2:6-dibromothiocyananiline into a mixture which probably contains 4-chloro-2:6-dibromoaniline. J. M. GULLAND.

Action of phosphorus, arsenic, and antimony trichlorides on dimethylaniline. H. RAUDNITZ [with H. HELLER] (Ber., 1927, 60, [B], 743—748).—Phosphorus trichloride is converted by the successive action of dimethylaniline and aqueous sodium hydroxide into a mixture of the compound, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{P}\cdot\text{O}$, m. p. 162°, the *substance*, $(\text{NMe}_2\cdot\text{C}_6\text{H}_4)_2\text{P}\cdot\text{OH}\cdot 2\text{H}_2\text{O}$, m. p. 165°, and tridimethylaminophenylphosphine, m. p. about 275°. Similar products are derived from arsenic trichloride. Dimethylaminophenylarsenious oxide, m. p. 95° (Michaelis records m. p. 75°), is identified by reduction with sodium hyposulphite to bisdimethylaminoarsenobenzene, m. p. 202°. Tridimethylaminophenylarsine, m. p. 240°, and *bisdimethylaminophenyl-*

arsenious acid, m. p. 169°, are described. The action of the chlorides of phosphorus, arsenic, and antimony on dimethylaniline is accompanied by the production of crystal-violet, the formation of which is most pronounced in the case of the antimony chloride; in addition, hexamethyltriaminotriphenylmethane and tetramethyldiaminodiphenylmethane (obtained from the former by the action of antimony trioxide formed by hydrolysis) are isolated. H. WREN.

Alternating effect in carbon chains. XII. Nitration of some derivatives of methyl benzylaminoformate. J. W. BAKER (J.C.S., 1927, 565—571).—Nitration of (a) methyl benzylaminoformate, (b) *methyl benzylmethylaminoformate*, b. p. 118°/5 mm., prepared from benzylmethylamine and methyl chloroformate, (c) *methyl dibenzylaminoformate*, b. p. 199°/13 mm., gave the following amounts of *m*-nitro-derivative, calculated by oxidation to the corresponding benzoic acid with subsequent analysis: (a) 11%, (b) 12%, (c) 14%. These values are of the same order as those obtained for the nitration of the acyl substituted benzylamines (Goss, Ingold, and Wilson, A., 1926, 1133). *Methyl p-nitrobenzylaminoformate* and *methyl pp'-dinitrodibenzylaminoformate* have m. p. 109.5° and 140°, respectively. H. BURTON.

Azo dyes [from new derivatives of aminodiphenyl]. I. G. FARBENIND. A.-G.—See B., 1927, 213.

Condensations with alkylene bromides. H. F. LEWIS and C. FORDYCE (Proc. Iowa Acad. Sci., 1925, 32, 323).—The corresponding butylenes and substituted diphenylethylenediamines are among the products of condensation of various butylene bromides with aniline. CHEMICAL ABSTRACTS.

Reducing action of sodium methoxide. H. S. FRY and J. L. CAMERON (J. Amer. Chem. Soc., 1927, 49, 864—873).—Klinger's equation (cf. A., 1882, 1061) for the reduction of nitrobenzene to azoxybenzene by sodium methoxide has been verified by comparison of the relative amounts of azoxybenzene and sodium formate produced. In absence of water, the yield of azoxybenzene is 86—87%. Addition of water progressively reduces this, and in presence of 1 mol. of water the yield is 55%. In presence of pyridine, the yield of azoxybenzene may be increased to 90%, but azobenzene is formed simultaneously, the production of sodium formate then being equivalent to that of the azoxy- and azo-benzene combined. The reducing action of sodium methoxide is ascribed to its acidic dissociation, $\text{MeOH} + \text{NaOH} \rightleftharpoons \text{H}\cdot\text{CO}_2\text{Na} + 2\text{H}_2$, the effects of water and pyridine on the reduction being due to their respective inhibition and promotion of this dissociation (cf. Fry and Schulze, A., 1926, 710). F. G. WILLSON.

Derivatives of 4:4'- and 2:2'-dihydroxyazobenzene. D. BIGIAMI and P. GUARDUCCI (Gazzetta, 1927, 57, 145—159).—4:4'-Dihydroxyazobenzene is benzoylated in presence of sodium carbonate to 4-hydroxy-4'-benzoyloxyazobenzene, m. p. 234—235°, which is acetylated to the 4-acetoxy-derivative, m. p. 130—134°, and on bromination gives 3:5-dibromo-4-hydroxy-4'-benzoyloxyazobenzene, m. p. 168—169°, hydrolysed to 3:5-dibromo-4:4'-dihydroxyazobenzene, m. p. 192°. During bromination, some diazo-scission

occurs: with β -naphthol, the solution gives *p*-benzoyloxyazo- β -naphthol, m. p. 164°. By the action of nitrous acid, the benzoyl derivative gives 3-nitro-4-hydroxy-4'-benzoyloxyazobenzene, m. p. 175—176°, hydrolysed to the 3-nitro-4:4'-dihydroxy-compound, m. p. 170—172°.

4:4'-Dihydroxyazoxybenzene is benzoylated to a mixture, m. p. 180°, of the two benzoyl derivatives, $\text{BzO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m. p. 200—201°, and $\text{BzO}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m. p. 212°. The latter forms an acetyl derivative, m. p. 129—132° to a cloudy liquid, clearing at 220°; it is unaffected by nitrous acid. The former gives an acetyl derivative, m. p. 108—111°, liquid clearing at 210°; with nitrous acid it gives a nitro-derivative, hydrolysed to nitroazoxyphenol (Bigiavi and Carrara, A., 1923, i, 715), which forms a dibenzoyl derivative, m. p. 164°, liquid clearing at 240°, and a monobenzoyl derivative, m. p. 178—179°; the benzoyl-acetyl derivative has m. p. 154—157°, clearing at 164°.

2:2'-Dihydroxyazobenzene gives a 2:2'-diacetoxy-compound, m. p. 150°, which is not affected by peracetic acid; 2:2'-dibenzoyloxyazobenzene is, however, oxidised to the corresponding azoxybenzene, m. p. 108—109°.

E. W. WIGNALL.

cycloHexylhydrazine. M. BUSCH and K. LINSENBIEIER (J. pr. Chem., 1927, [ii], 115, 216—234).—When an alcoholic solution of cyclohexyl bromide and hydrazine hydrate is heated at 140° in a sealed tube, cyclohexene and 25% of the theoretical yield of cyclohexylhydrazine (cf. Kijner and Beloff, A., 1911, i, 678; Harkins and Lochte, A., 1924, i, 435) are obtained. The latter is now the most readily accessible hydrazine derivative of aliphatic nature. It forms a dihydrate, m. p. 36—38°, which readily absorbs oxygen and carbon dioxide. The carbonate has m. p. 70°; the hydrochloride, m. p. 110—111°, hydrogen sulphate, and hydrobromide, m. p. 120°, are stable. The abnormal benzylidene compound, m. p. 183°, of Harkins and Lochte is actually benzaldehyde-cyclohexylhydrazone hydrochloride; the oily free hydrazone rapidly absorbs oxygen, forming a crystalline dioxide, m. p. 72—73° (decomp.). The cyclohexylhydrazones of *p*-anisaldehyde, m. p. 55—56° (hydrochloride, m. p. 159—160°; dioxide, m. p. 79—80°); salicylaldehyde, m. p. 58—59° (hydrochloride, m. p. 166—167°); *p*-dimethylaminobenzaldehyde, oily (hydrochloride, m. p. 190°; dioxide, m. p. 72—73°); *p*-nitrobenzaldehyde, m. p. 110—111° (hydrochloride, m. p. 130—132°); *m*-nitrobenzaldehyde, m. p. 104—105° (hydrochloride, m. p. 137—138°); cinnamaldehyde (hydrochloride, m. p. 158°), and acetaldehyde, oily (hydrochloride, m. p. 83—86°), and acetonecyclohexylhydrazone dioxide hydrochloride, m. p. 224—226°, are described. cycloHexylhydrazine gives an acetyl derivative, m. p. 148—149°, and a dibenzoyl derivative, m. p. 195—196°; with potassium cyanate solution, it forms cyclohexylhydrazinedicarboxylamide, $\text{NH}_2\cdot\text{CO}\cdot\text{N}(\text{C}_6\text{H}_{11})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 135—136°, which is partly converted by boiling water into cyclohexylsemicarbazide, $\text{C}_6\text{H}_{11}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 175—176° (hydrochloride, m. p. 173—174°, but cf. A., 1924, i, 226); and with phenylcarbimide, 2-cyclohexyl-4-phenylsemicarbazide,

$\text{C}_6\text{H}_{11}\cdot\text{N}(\text{NH}_2)\cdot\text{CO}\cdot\text{NHPh}$, m. p. 165—166° (1-benzylidene derivative, m. p. 135°), together with its 1-phenylurethane, m. p. 202°. The so-called thioureide, m. p. 144°, of Kijner and Beloff must be 2-cyclohexyl-4-phenylthiosemicarbazide, since with benzaldehyde it affords the corresponding semicarbazone, m. p. 222°.

H. E. F. NOTTON.

Dicyclohexyl derivatives. H. HARTMANN (Rec. trav. chim., 1927, 46, 150—153).—The interaction of hydrazine sulphate, potassium cyanide, and cyclohexanone at the ordinary temperature yields 1:1'-dicyanohydrazocyclohexane, m. p. 145°, in quantitative yield. Bromine water converts this into the colourless 1:1'-dicyanoazocyclohexane, m. p. 100°, which loses nitrogen in boiling toluene, passing into 1:1'-dicyanodicyclohexyl, m. p. 220°. The hydrolysis of this nitrile is difficult, and proceeds only as far as the formation of 1-cyanodicyclohexyl-1'-carboxylic acid, m. p. 185°; even fusion with potassium hydroxide failed to produce the dicarboxylic acid, and the cyano-group was not reduced by sodium and alcohol. The hydrolysis of 1:1'-dicyanohydrazocyclohexane by alcoholic potassium hydroxide yields 1-amino-1-cyanocyclohexane.

J. M. GULLAND.

Constitution of normal diazo-hydrates. A. HANTZSCH (Ber., 1927, 60, [B], 667—668).—In reply to Angeli (A., 1926, 947), reasons are advanced for considering the normal and isodiazotates to be stereoisomeric and not structurally isomeric. H. WREN.

cis-trans-Isomerism and steric hindrance. IV. 2-IsoPropylcyclohexanols. G. VAVON and A. CALLIER (Bull. Soc. chim., 1927, [iv], 41, 357—367).—In continuance of earlier work (A., 1926, 837, 1033, 1042), the isopropyl radical is shown to exert a marked steric effect on the reactions of the *cis*- and *trans*-forms of 2-isopropylcyclohexanol, the reactions of the *cis*-form being distinctly slower than those of the *trans*-isomeride. To the same influence is attributed the small proportion (14%) of *ortho*- as compared with *para*-derivative (86%) in the nitration of isopropylbenzene with nitric acid (*d* 1.5), acetic acid, and acetic anhydride; with acetyl nitrate (10% excess), the nitration product (yield 83%) consists of 22% *ortho*- and 78% *para*-derivative, whereas the nitration of toluene by this method affords the *ortho*- and *para*-derivatives in the ratio 10:1. *o*-Nitroisopropylbenzene, b. p. 106—107°/9 mm., n_D^{20} 1.5286, d_4^{20} 1.101, on reduction with hydrogen and platinum-black in acetic acid, gives an 84% yield of the amine, b. p. 220—221°/745 mm., 92—94°/8 mm., from which *o*-isopropylphenol, b. p. 90—91°/8 mm., 212—213°/745 mm., is obtained by the diazo-reaction. Hydrogenation of the phenol in presence of platinum-black affords a mixture in which *cis*-2-isopropylcyclohexanol, m. p. 50—50.5°, preponderates. The *cis*-hydrogen phthalate has m. p. 129—130°, the hydrogen succinate, m. p. 61.5—62°, and the phenylurethane, m. p. 95—95.5°. Oxidation of the hexanol with chromic and sulphuric acids affords 80% of 2-isopropylcyclohexanone, b. p. 72—73°/9 mm., n_D^{20} 1.4585, d_4^{20} 0.923 [oxime, b. p. 118—119°/10 mm., m. p. 37—39°, giving, by hydrogenation, the β -hydroxylamine, m. p. 63—64°, semicarbazone, m. p. 178—179° (cf. Bouveault, A., 1906, i, 513; Kötze and Michels, A., 1907, i, 58)],

reduction of which with sodium and boiling alcohol yields mainly *trans*-2-isopropylcyclohexanol, b. p. 86°/10 mm., m. p. 63.5—64°. The latter is also obtained by heating the *cis*-isomeride at 220° for 6 hrs. The *trans*-hydrogen phthalate exists in two forms, m. p. 99—100° and 114—115°; the former undergoes transformation into the latter above its m. p. (cf. A., 1926, 1033). The *trans*-hydrogen succinate has m. p. 84—84.5°, the *phenylurethane*, m. p. 98—98.5°.

The *trans*-2-isopropylcyclohexanol is esterified much more rapidly than the *cis*-isomeride, especially at a low temperature and in presence of a catalyst. Similarly, the *trans*-hydrogen phthalate is hydrolysed much more rapidly than the *cis*-phthalate, the ratio of the velocity constants in 75% alcohol at 69° being 18:1, and 34:1 in water at 69°. Similarly, with the hydrogen succinates, the ratio of the velocity constants for the *trans*- and *cis*-forms is 28:1 in water at 68°, 40:1 at 39°, and 67:1 at 0°. *p*-Nitro-isopropylbenzene has b. p. 124—125°/11 mm., n_D^{20} 1.5400, d_4^{20} 1.096. R. BRIGHTMAN.

Condensation products of phenols and aldehydes. V. Substance, $C_{14}H_{15}O_2N$, isolated from the condensation products of phenol and formaldehyde, using ammonia as catalyst. VI. Decolorisation of the insoluble and infusible condensation product of phenol and formaldehyde. T. SHONO (J. Soc. Chem. Ind. Japan, 1927, 30, 136—143, 143—145; cf. B., 1926, 595).—V. The principal constituent, $C_{14}H_{15}O_2N$ (A), of the condensation product of phenol and formaldehyde, when heated with nitrous acid, yields a brownish-yellow diazo-compound which at about 100° evolves nitrogen, decomposing to a tar and a brownish-yellow powder suspended in the liquid. The percentage of nitrogen evolved is exactly equal to that in A. A gives colour reactions in a neutral or an alkaline alcoholic solution with many metallic salts, mostly chlorides, but not in an acid solution. It shows, in alcoholic solution, a wide absorption band, centre about 281 μ .

VI. The condensation product of phenol and formaldehyde formed by using ammonia and potassium hydroxide simultaneously as condensing agents under the ordinary pressure (B., 1926, 680) is markedly decolorised in proportion to the amount of ultraviolet light to which it is exposed. K. KASHIMA.

Nitration of *m*-iodophenol. H. H. HODGSON and F. H. MOORE (J.C.S., 1927, 630—635).—*m*-Iodophenol is nitrated by sodium nitrate and concentrated sulphuric acid, giving 3-iodo-6-nitrophenol, m. p. 96° (sodium and silver salts; methyl ether, m. p. 92°; acetate, m. p. 95°; benzoate, m. p. 122°), and 3-iodo-4-nitrophenol (sodium salt; methyl ether, m. p. 69—70°; acetate, m. p. 73.7°; benzoate, m. p. 119°). Nitration of *m*-iodophenol in fuming sulphuric acid solution gives poor yields of 3-iodo-2-nitrophenol, m. p. 73.5° (sodium, ammonium, and silver salts; methyl ether, m. p. 82—83°; acetate, m. p. 102.5°). 3-Iodo-4:6-dinitrophenol, m. p. 98° (silver salt), is obtained from *m*-iodophenol, 3-iodo-4- and -6-nitrophenols by the method previously described (A., 1926, 281), as is 3-iodo-2:6-dinitrophenol, m. p. 151—

152° (silver salt), from 3-iodo-2- and -6-nitrophenols. The 2:6-dinitro-compound is also obtained by nitration of *m*-iodophenol in oleum solution. 3-Iodo-2:4:6-trinitrophenol, m. p. 197° (silver salt), sublimes slowly from boiling concentrated sulphuric acid. 3-Iodobenzoquinone-4-oxime is oxidised by potassium ferrieyanide to 3-iodo-4-nitrophenol, thus proving that nitrosation of *m*-iodophenol takes place in the 4-position (A., 1925, i, 1408). H. BURTON.

Separation of *p*-cresol from its isomerides. H. D. GIBBS (J. Amer. Chem. Soc., 1927, 49, 839—844).—Technical *p*-cresol (1 kg.) is mixed with 2:6-dichlorobenzoquinonechloroimide (100 g.) with cooling, the mixture brought to p_H 10 by addition of aqueous 10% sodium hydroxide at 5—10°, and kept at this temperature for 1 hr. The resulting blue solution, the colour of which is due to the indophenols formed from the *o*- and *m*-cresols, is acidified with sulphuric acid and steam distilled. After four similar treatments, the *p*-cresol still gives a trace of blue colour with the chloroimide, probably owing to slight decomposition of the indophenols during steam distillation. The *p*-cresol thus purified, which is very hygroscopic, has b. p. 202.3°/760 mm.

F. G. WILLSON.

Influence of nitro-groups on the reactivity of substituents in the benzene nucleus. IX. 2:3- and 2:5-Dinitro-4-methoxytoluenes. H. E. DADSWELL and J. KENNER (J.C.S., 1927, 580—588; cf. A., 1926, 58).—Nitration of 2-nitro-4-methoxytoluene in sulphuric-acetic acid solution gives 2:3-dinitro-4-methoxytoluene, m. p. 132—133° (Kaufler and Wenzel, A., 1901, i, 590, give m. p. 126—128°), and 2:5-dinitro-4-methoxytoluene. Reduction of the former dinitro-compound gives the *o*-diamine, m. p. 75—76° (Kaufler and Wenzel, *loc. cit.*, give m. p. 72—73°), which condenses with benzil, yielding 8-methoxy-2:3-diphenyl-5-methylquinoxaline, m. p. 196—197°. Nitration of 2-nitro-*p*-cresol in glacial acetic acid furnishes 2:3-dinitro-*p*-cresol (66%), m. p. 157—158°, and 2:5-dinitro-*p*-cresol (33%), m. p. 112—113°, each of which on methylation gives the corresponding methoxy-compound.

Boiling methyl-alcoholic sodium methoxide solution converts 2:5-dinitromethoxytoluene into 5-nitro-2:4-dimethoxytoluene (72%), m. p. 117—118°, characterised by its preparation from 2:4-dichloro-5-nitrotoluene, m. p. 49—50°, by the action of sodium methoxide, and 6-nitro-3:4-dimethoxytoluene (28%), m. p. 119—120° (de Vries, A., 1910, i, 29, gives m. p. 94°). Sodium methoxide converts 3-chloro-6-nitro-4-methoxytoluene, m. p. 94—95°, 4-chloro-5-nitro-*o*-toluidine, and 4-chloro-3-nitro-*o*-toluidine into 6-nitro-3:4-dimethoxytoluene, 5-nitro-4-methoxy-*o*-toluidine, m. p. 158—159° (acetyl derivative, m. p. 154—155°, also obtained by nitration of 4-methoxyacet-*o*-toluidide), and 3-nitro-4-methoxy-*o*-toluidine, m. p. 61—62° (acetyl derivative, m. p. 176—176.5°), respectively. The last compound is converted by nitrous acid into 7-nitro-6-methoxyindazole, m. p. 173—174°.

Methyl-alcoholic ammonia at 145—150° converts 2:3-dinitro-4-methoxytoluene into 3-nitro-4-methoxy-*o*-toluidine (30% isolated as the above indazole)

and 2-nitro-4-methoxy-m-toluidine, m. p. 49—50° (acetyl derivative, m. p. 170—171°). The 2:5-dinitro-compound is decomposed by similar treatment.

2:3-Dinitro-4-methoxytoluene is oxidised by potassium permanganate to 2:3-dinitro-4-methoxybenzoic acid, m. p. 248—250° (decomp.) (methyl ester, m. p. 156°), which is converted by sodium methoxide into 3-nitro-2:4-dimethoxybenzoic acid, m. p. 210—212° (methyl ester, m. p. 118—119°). Oxidation of the mixture of nitrodimethoxytoluenes obtained from the treatment of 2:3-dinitro-4-methoxytoluene with methyl-alcoholic sodium methoxide at 110—115°, gave a mixture of nitrodimethoxybenzoic acids in which 2-nitroveratric acid predominated, thus showing that the 3- rather than the 2-nitro-group is displaced in the 2:3-dinitro-compound, whereas the 2-position in the 2:5-isomeride is more easily attacked. 4-Methoxy-m-oxalotoluidide has m. p. 218°.

H. BURTON.

Aromatic thionyl and chlorothionyl derivatives. II. 1:2- and 2:3-Thionyl-dihydroxy-anthracenes. A. GREEN (J.C.S., 1927, 554—558).—1:2-Thionyl-dihydroxyanthracene,

$C_6H_4 \begin{matrix} \text{CH} \\ \text{CH} \end{matrix} < C_6H_2 \begin{matrix} \text{O} \\ \text{O} \end{matrix} > SO$, m. p. 138—139° (decomp.), and 2:3-thionyl-dihydroxyanthracene, m. p. 188° (decomp.), are obtained from the corresponding dihydroxyanthracenes and thionyl chloride in carbon disulphide-pyridine solution. These compounds are stable to moisture. Boiling acetic acid containing a trace of pyridine converts the latter into the original dihydroxy-compound, whilst acetic anhydride furnishes 2:3-diacetoxyanthracene, m. p. 175° (Lagodzinski, A., 1906, i, 82, gives m. p. 155—160°). 2:3-Dihydroxyanthracene, m. p. 282° (Lagodzinski, *loc. cit.*, gives m. p. 192°), is best obtained by reducing hystazarin with stannous chloride to 2:3-dihydroxyanthranol, m. p. 288—289° (Schrobsdorff, A., 1903, i, 840, gives m. p. 282°), and subsequent reduction of the anthranol by an aluminium-mercury couple (cf. Perkin, J.C.S., 1923, 123, 2035). H. BURTON.

Tricyclohexylcarbinol. N. D. ZELINSKI and M. W. GAVERDOVSKAJA (Ber., 1927, 60, [B], 713—715).—Dicyclohexyl ketone, b. p. 140—141°/12 mm. (oxime, m. p. 157—160°), and tricyclohexylcarbinol, b. p. 208°/10 mm., m. p. 81·5°, are isolated in small amount from the neutral products of the successive action of magnesium and carbon dioxide on cyclohexyl chloride, the main product being hexahydrobenzoic acid. The carbinol is reduced by hydriodic acid to a hydrocarbon, $C_{19}H_{34}$, b. p. 340—345°, in the production of which a cyclohexyl group may have become isomerised to a methylpentamethylene ring. Tricyclohexylmethyl bromide, m. p. 61°, is obtained from the carbinol and hydrobromic acid or from tricyclohexylmethane and bromine. H. WREN.

Elimination of the amino-group of tertiary amino-alcohols. IV. Displacement of the amino- by the hydroxy-group. A. MCKENZIE and R. ROGER (J.C.S., 1927, 571—576).—Deamination of α -amino- α -phenyl- β -ethylbutan- β -ol with nitrous acid gives α -phenyl- β -ethylbutan- α - β -diol, whilst α -amino- α -diphenyl- β -benzylisopropyl alcohol yields a mixture of α -diphenyl- β -benzylpropane-

α - β -diol and benzyl α - β -diphenylethyl ketone. α -Amino- α - β -diphenylbutan- β -ol (*hydrochloride*, m. p. 224—226°) yields diphenylmethyl ethyl ketone, showing that a phenyl group has migrated.

The results show that the phenyl group migrates more easily than ethyl or benzyl groups, and it is suggested that the low saturation capacity of the ethyl and benzyl groups causes a retardation or prevention of the "semipinacolinic deamination" change (see A., 1926, 610).

H. BURTON.

Reduction products of plant sterols. R. J. ANDERSON and R. L. SHRINER (J. Biol. Chem., 1927, 71, 401—406).—Reduction of α - and β -sitosterol with hydrogen and platinum-black yielded identical sitostanols, m. p. 140°, $[\alpha]_D^{25} +24^\circ$; acetyl derivative, m. p. 137—138°, $[\alpha]_D^{25} +14^\circ$; similar treatment of γ -sitosterol gave a sitostanol having m. p. 144—145°, $[\alpha]_D^{25} +18^\circ$, acetyl derivative, m. p. 143—144°, $[\alpha]_D^{25} +9-10^\circ$.

C. R. HARRINGTON.

Properties of cholesterol from different sources. R. J. ANDERSON (J. Biol. Chem., 1927, 71, 407—418).—Preparations of cholesterol from various sources show small differences in m. p. and specific rotation which cannot be eliminated by the ordinary methods of purification; further, the acetyl derivatives of such preparations can be separated by crystallisation into fractions possessing markedly different physical properties. This indicates that ordinary cholesterol may be a mixture of isomeric substances corresponding with the mixture of phytosterols from which it is presumably synthesised in the animal body.

C. R. HARRINGTON.

Hydrogenation of triphenylcarbinol and phenylfluorenylcarbinol under pressure. V. N. IPATIEV and B. N. DOLGOV (J. Russ. Phys. Chem. Soc., 1926, 58, 1023—1027).—See A., 1926, 949.

Thymolbenzein, 4-hydroxy-3-isopropyl-6-methylbenzophenone, and some of their derivatives. W. R. ORNDORFF and H. T. LACEY (J. Amer. Chem. Soc., 1927, 49, 818—826).—Gradual addition of molten thymol to 0·515 mol. of benzotrichloride in presence of stannic chloride (1 mol.) yields 4-hydroxy-6-methyl-3-isopropylbenzophenone (I), m. p. 150—150·5° (acetate, m. p. 73°), and thymolbenzein (II), bright red, m. p. 184° [*hydrochloride*, decomp. 225—235° (open tube) or 235—250° (sealed tube); *sulphate*, m. p. 242—243°; *perchlorate*, decomp. 265—272°; *sodium salt* (2H₂O), dark blue with bronze reflex, softening at 235—245°, m. p. not below 310°; *methyl ether*, orange, m. p. 132—133°; *methyl ether hydrochloride*, m. p. 85—95° (sealed tube); *monoacetate*, orange, m. p. 143—144°]. The constitution of (I) was established by synthesis from benzoyl chloride, thymol, and aluminium chloride, and by fusion with alkali, which yielded *p*-thymotic acid. Bromination of (II) in glacial acetic and formic acids affords *dibromothymolbenzein*, red, m. p. 89—90°, as the *additive compound* with formic acid (1 mol.), m. p. 96—97°, whilst nitration in acetic acid yields *dinitrothymolbenzein*, yellow, m. p. not below 310° after darkening at 100—110° and carbonisation at 150—160°. Reduction of (II) with zinc dust and glacial acetic acid affords 4:4'-

dihydroxy-6 : 6'-dimethyl-3 : 3'-diisopropyltriphenylmethane, m. p. 158—159° (*dimethyl ether*, m. p. 105°; *diacetate*, m. p. 121°), which is also obtained by boiling (II) with phenylhydrazine. In 50% ethyl-alcoholic solution, thymolbenzenin changes from red to yellow at p_H 1.5—2.5, and from yellow to red at p_H 7.6—9.0, whilst the dibromo-derivative changes from yellow to blue at p_H 5.6—7.2. Carbinol forms of thymolbenzenin and the dibromo-derivative could not be obtained.

F. G. WILLSON.

Thymoltetrachlorophthalein and some of its derivatives. R. T. K. CORNWELL and A. J. ESSELYSTYN (J. Amer. Chem. Soc., 1927, 49, 826—830).—Condensation of thymol with tetrachlorophthalic anhydride in presence of stannic chloride yields *thymoltetrachlorophthalein* (I), colourless, m. p. 266° [*monosodium salt*, dark grey; *disodium salt*, black; *barium salt*, black; *lead salt*, tan coloured; *diacetate*, m. p. 184—185°; *dibenzoate*, m. p. 177—178°; *di-(phenylcarbamate)*, m. p. 234—235°; *dimethyl ether*, yellow, m. p. 208—210°]. Bromination of (I) in glacial acetic acid affords *dibromothymoltetrachlorophthalein*, m. p. 223—225°. At p_H 9.2—10.0, (I) becomes blue, whilst the dibromo-derivative changes similarly at p_H 8.4—8.8. A lactoid structure is ascribed to (I) and to the dibromo-derivative, the above coloured derivatives being derived from the tautomeric quinonoid form.

F. G. WILLSON.

cycloButylacetic acid. N. D. ZELINSKI and B. A. KASANSKI (Ber., 1927, 60, [B], 711—713).—*cycloButylmethyl alcohol* is converted by phosphorus and iodine into *cyclobutylmethyl iodide*, and thence by magnesium and carbon dioxide into *cyclobutylacetic acid*, the properties of which indicate the presence of *cyclopentane-carboxylic acid*. Partial isomerisation occurs during the conversion of the alcohol into the iodide, since the action of magnesium and air on the latter affords a mixture of alcohols giving a phenylurethane, m. p. 129°; the phenylurethanes of *cyclopentanol* and *cyclobutylmethyl alcohol* have m. p. 136.5° and 68.5°, respectively.

H. WREN.

Anilides and toluidides of chaulmoogric acid. P. HERRERA-BATTEKE (Philippine J. Sci., 1927, 32, 35—40).—The following derivatives of chaulmoogric acid were prepared by heating chaulmoogric acid with the theoretical quantity of the requisite amine at the boiling temperature: *anilide*, m. p. 89°; *p-bromo-anilide*, m. p. 100°; *o-toluidide*, m. p. 95°; *m-toluidide*, m. p. 88°, and *p-toluidide*, m. p. 100°. S. I. LEVY.

Action of iodine in alkaline media on phenylisocrotonic acid: some new mixed anhydride derivatives of benzoylacrylic acid. E. CATTELAINE (Bull. Soc. chim., 1927, [iv], 41, 352—356).—The following *mixed anhydride* derivatives of benzoylacrylic acid have been prepared from phenylisocrotonic acid by Bougault's method (A., 1908, i, 791, 983): *hydrocinnamic*, m. p. 103°; *p-methoxybenzoic*, m. p. 132°; *o-toluic*, m. p. 141°; *m-toluic*, m. p. 107°; *p-toluic*, m. p. 127—128°; *piperonylic*, m. p. 135—136°; *hexahydrobenzoic*, m. p. 103—104°; *o-benzoylbenzoic*, m. p. 114—115°; *p-chlorobenzoic*, m. p. 122°, and *m-bromobenzoic*, m. p. 116—117°. On hydrolysis with dilute sodium hydroxide, they

afford acetophenone from the benzoylacrylic acid first liberated.

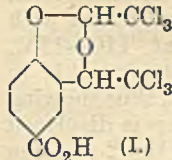
R. BRIGHTMAN.

Condensation of *p*-hydroxybenzoic acid with chloral. F. D. CHATTAWAY and F. C. Y PRATS (J.C.S., 1927, 685—692).—*p*-Hydroxybenzoic acid condenses with chloral (2 mols.) in presence of a large excess of concentrated sulphuric acid, forming *anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene*, (I), m. p. 225.5—226.5° (*acid chloride*, m. p. 98—102°; *amide*, m. p. 195.5—197°; *ethyl ester*, m. p. 100.5—101.5°). *Anhydro-5-cyano-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene*, m. p. 159.5—160.5°, obtained from the 5-amino-derivative (A., 1926, 1242), on hydrolysis with dilute sulphuric acid yields (I). Alcoholic potassium hydroxide converts (I) into a mixture of *5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene*, (II), m. p. 124—126°, *6-hydroxyisophthalic acid* (*ethyl ester*, m. p. 52.5°), and a small amount of *5-carboxy-2-ethoxyphenylglycolic acid*, identified by hydrolysis to *5-carboxy-2-hydroxybenzaldehyde* [*phenylhydrazone*, m. p. 257—258° (decomp.)], and also by oxidation with alkaline potassium permanganate to *6-hydroxyisophthalic acid*. Hot concentrated sulphuric acid converts (II) into *ω-dichloro-5-carboxy-2-hydroxyacetophenone*, m. p. 163—166°. This substance yields a *diacetyl* derivative, m. p. 194—196°; an *osazone*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{CH}\cdot\text{N}_2\text{HPh}$, m. p. 243.5°, and is reduced by hydriodic acid to *5-carboxy-2-hydroxyacetophenone*, m. p. 246—247° (*phenylhydrazone*, m. p. 286°), which is also produced by the action of hydriodic acid on (II).

H. BURTON.

3-Nitro-4-aminobenzoyl-*o*-benzoic acid and derivatives. R. ADAMS, J. M. DAVIDSON, and I. GUBELMANN, Assrs. to NEWPORT Co.—See B., 1927, 212.

Action of magnesium organo-derivatives on *N*-tetraethylphthalamides. N. MAXIM (Compt. rend., 1927, 184, 689—691).—The action of magnesium ethyl bromide on *N-tetraethylisophthalamide*, m. p. 85°, and *N-tetraethylterephthalamide*, m. p. 127°, affords 15—20% of the ketone-amide, $\text{Et}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NEt}_2$, and 25—30% of the diketone, $\text{C}_6\text{H}_4(\text{CO}\cdot\text{Et})_2$. *N-Tetraethyl-*o*-phthalamide*, m. p. 36°, b. p. 204°/10 mm., affords 10% of the ketone-amide and 15% of diethylphthalide. The structure $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NR}_2)_2$ is assigned to these diamides (cf. Piutti, Annalen, 1885, 227, 193), since this structure admits of ready interpretation of the formation of the ketone-amide. The formation of the diethylphthalide is attributed to intermediate formation of the tertiary alcohol, $\text{NEt}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{Et}_2)\cdot\text{OH}$. *m-Propionylbenzdiethylamide*, b. p. 205°/10 mm. (*semicarbazone*, m. p. 145°); *m-dipropionylbenzene*, m. p. 34° (*di-semicarbazone*, m. p. 222°); *p-propionylbenzdiethylamide*, m. p. 82° (*semicarbazone*, m. p. 175°, *oxime*, 105°); *p-dipropionylbenzene*, m. p. 100° (*di-semicarbazone*, m. p. 226°), and *o-propionylbenzdiethylamide*, b. p. 186°/15 mm. (*semicarbazone*, m. p. 195°, *oxime*, m. p. 110°), are described. Magnesium phenyl



bromide does not react with the *N*-tetraethylphthalamides (cf. A., 1926, 837). R. BRIGHTMAN.

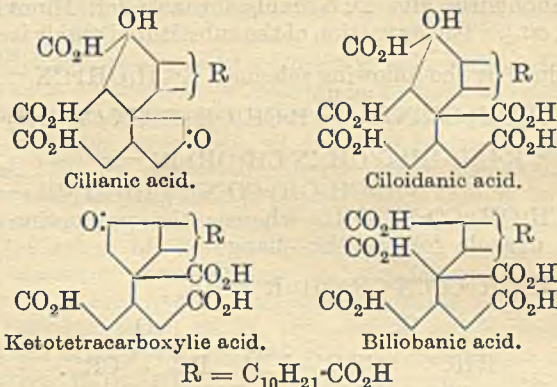
2:5-Diaminobenzene-1:4-dicarboxylic acid. G. SCHROETER.—See B., 1927, 212.

[New diarylamides of 2-naphthol-3:6-dicarboxylic acid] and manufacture of water-insoluble azo-dyes. CHEM. FABR. GRIESHEIM-ELEKTRON.—See B., 1927, 212.

Substitution derivatives of indigotin. II. Ethyl 2-nitro-3:4:5-trimethoxybenzoylacetate and related compounds. C. J. OVERMYER (J. Amer. Chem. Soc., 1927, 49, 499—509; cf. A., 1926, 415).—Modifications are described of Hamburg's method (A., 1899, i, 364) for the preparation of methyl 2-nitro-3:4:5-trimethoxybenzoate, m. p. 67°, and 2-nitro-3:4:5-trimethoxybenzoic acid, m. p. 166°. The acid chloride, m. p. 94°, was used for preparing the corresponding amide, m. p. 186°, and anilide, m. p. 158°, and was converted, by the action of ethyl sodioacetoacetate, into ethyl 2-nitro-3:4:5-trimethoxybenzoylacetate, a reddish-yellow oil (sodium and potassium salts). The sodium salt of the latter, on treatment with aqueous ammoniacal ammonium chloride, yields ethyl 2-nitro-3:4:5-trimethoxybenzoylacetate, m. p. 85° (potassium salt), whilst hydrolysis with dilute sulphuric acid affords 2-nitro-3:4:5-trimethoxyacetophenone, m. p. 118°. Treatment of the potassium salt of ethyl 2-nitro-3:4:5-trimethoxybenzoylacetate with alcoholic methyl iodide yields ethyl α -2-nitro-3:4:5-trimethoxybenzoylpropionate, a red oil, which, on hydrolysis with dilute sulphuric acid, affords 2-nitro-3:4:5-trimethoxypropionophenone, a brown oil. Ethyl 2-nitro-3:4:5-trimethoxybenzoylmalonate, m. p. 96°, and ethyl 2-nitro-3:4:5-trimethoxybenzoylcyanacetate, m. p. 110°, are obtained analogously from the above acid chloride. The cyanoderivative yields, on hydrolysis, 2-nitro-3:4:5-trimethoxybenzoylacetone, m. p. 180°. Reduction of ethyl 2-nitro-3:4:5-trimethoxybenzoylacetate with zinc dust and glacial acetic acid affords 4-hydroxy-6:7:8-trimethoxy-2-ethoxyquinoline oxide, m. p. 61°, whilst ethyl 2-nitro-3:4:5-trimethoxybenzoylacetate yields similarly ethyl 4-hydroxy-6:7:8-trimethoxy-2-methylquinoline-3-carboxylate, m. p. 183°. Hydrolysis of the latter yields the corresponding acid, m. p. 202°, at which temperature it loses carbon dioxide with formation of 4-hydroxy-6:7:8-trimethoxy-2-methylquinoline, m. p. 182°. Reduction of 2-nitro-3:4:5-trimethoxybenzoic acid with ammoniacal ferrous sulphate yields 2-amino-3:4:5-trimethoxybenzoic acid, m. p. 137°. Ethyl 2-nitro-3:4:5-trimethoxybenzoylacetate could not be hydrolysed to the corresponding acid, nor could the latter be obtained from the corresponding malonate. Ethyl 2-nitro-3:4:5-trimethoxybenzoylacetone could not be converted into the corresponding amide or acid. The synthesis of a hexamethoxyindigotin by the method previously described could not therefore be accomplished. F. G. WILLSON.

Constitution of the bile acids. X. Constitution of cilianic acid and certain other polycarboxylic acids of the cholic acid group. W. BORSCHKE and R. FRANK (Ber., 1927, 60, [B], 723—732; cf. A., 1926, 1140).—Contrary to the observ-

ations of Wieland and Schlichting (A., 1922, i, 838), cilioanic acid loses only 1 mol. of carbon monoxide when warmed with concentrated sulphuric acid at 60°. Evolution of carbon dioxide is appreciable only at about 100°, and is accompanied by further loss of 1 mol. of carbon monoxide. These results, considered in conjunction with the author's observation (*loc. cit.*) that cholic acid contains the hydroxyl group attached to the carbon atom 12 instead of 13 in ring III, render the annexed constitutions probable:



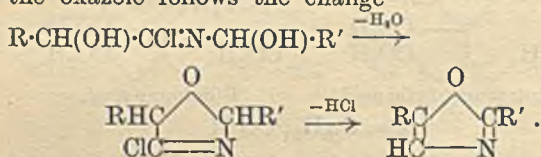
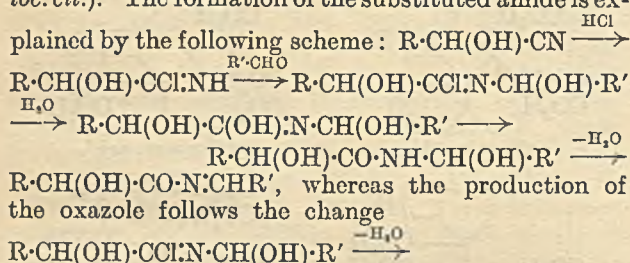
The presence of a hydroxyl group in cilianic acid is established by the evolution of 1 mol. of methane when its tetramethyl ester is treated with magnesium methyl iodide. Bilianic, isobilianic, biloidanic acid, or its hydrate do not evolve carbon monoxide or dioxide to a considerable extent when treated for a protracted period with concentrated sulphuric acid at 100°. Under similar conditions, biliobanic acid slowly gives off oxides of carbon, probably owing to the oxidising action of sulphuric acid. *iso*-Cilianic acid evolves almost 1 mol. of carbon monoxide with varying and not very considerable quantities of carbon dioxide. H. WREN.

Action of aldehydes on azo-compounds. D. BIGLAVI (Gazzetta, 1927, 57, 160—162).—Bamberger's results (Ber., 1924, 57, 2085) are confirmed: the substance, m. p. 161—163°, obtained by the action of benzaldehyde on azobenzene (Barsilowski, A., 1892, 854) is benzanilide. It is suggested that the benzaldehyde condenses with a dissociated radical, PhN₂; intermediate compounds in which oxygen is attached to nitrogen are considered improbable.

E. W. WIGNALL.

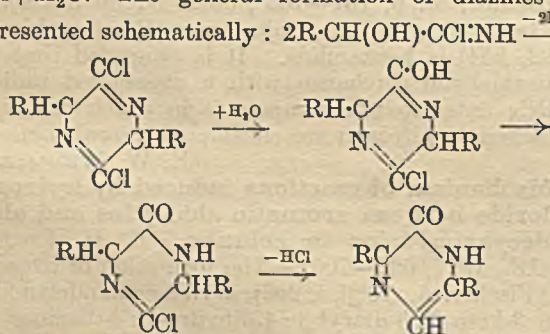
Mechanism of reactions induced by hydrogen chloride between aromatic aldehydes and aldehydecyanohydrins in solution. B. H. INGHAM (J.C.S., 1927, 692—700).—The formation of oxazoles (cf. Fischer, A., 1896, i, 262), arylidenemandelamides, and 3-keto-2:5-diaryl-3:4-dihydro-1:4-diazines (cf. Minovici, A., 1899, i, 890; 1896, i, 703) by the condensation of aromatic aldehydes and aldehydecyanohydrins in presence of moist and dry hydrogen chloride has been studied. It is found that (a) iminochlorides are produced as intermediates, (b) exclusion of moisture favours oxazole formation, whereas presence of moisture favours the production of arylidenemandelamides, (c) no oxazole is formed when the hydroxy-group in the cyanohydrin is benzoylated or replaced by chlorine, (d) diazines are formed

in best yield when there is not a large excess of aldehyde. Thus benzaldehyde and mandelonitrile in ethereal solution, saturated at 0° with hydrogen chloride, condense, giving benzylidenemandelamide, $C_6H_5 \cdot CH(OH) \cdot CO \cdot N \cdot CH \cdot C_6H_5$, unless moisture is rigidly excluded. In a perfectly dry medium, 2 : 5-diphenyloxazole is the predominant product. α -Chlorophenylacetonitrile and benzaldehyde do not react. Benzaldehyde and lactonitrile yield benzylidenelactamide, and anisaldehyde and anisaldehyde-cyanohydrin give 2 : 5-dianisyloxazole (cf. Minovici, *loc. cit.*). The formation of the substituted amide is explained by the following scheme:



Benzoylmandelonitrile and benzaldehyde yield two isomeric benzylidenebisbenzoylmandelamides, $(BzO \cdot CHPh \cdot CO \cdot NH)_2 \cdot CHPh$, having m. p. 250—251° and 223—224°.

m-Nitrobenzaldehydecyanohydrin condenses with *m*-nitrobenzaldehyde, giving two isomeric 2 : 5-*di-m*-nitrophenyloxazoles, m. p. 225—227° and 238°, together with 3-*keto*-2 : 5-*di-m*-nitrophenyl-3 : 4-*dihydro*-1 : 4-*diazine*, m. p. 277—278°; with benzaldehyde yielding 2-*phenyl*-5-*m*-nitrophenyloxazole, m. p. 156—157°, and the above diazine; hydrogen chloride converts the original cyanohydrin into the diazine and the *di-m*-nitrophenyloxazole. This production of the diazine is most probably explained by the change $NO_2 \cdot C_6H_4 \cdot CH(OH) \cdot CCl \cdot NH \cdot HCl \xrightarrow{H_2O} C_{16}H_{10}O_5N_4 + HCl + H_2O$. The general formation of diazines is represented schematically:



3-*Keto*-2 : 5-*di-p*-nitrophenyl-3 : 4-*dihydro*-1 : 4-*diazine*, m. p. 332—334°, and 2 : 5-*di-p*-nitrophenyloxazole, m. p. 228—232°, are obtained from *p*-nitrobenzaldehyde and *p*-nitrobenzaldehydecyanohydrin.

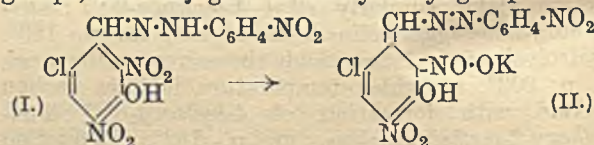
H. BURTON.

Isomerisation of diphenylacetaldehyde into deoxybenzoin. S. DANILOV and E. VENUS-DANILOVA (J. Russ. Phys. Chem. Soc., 1926, 58, 957—965).—See A., 1926, 726.

Alkyl lactolides of salicylaldehyde [α -2-*oxido*-benzyl ethers]. M. BERGMANN and E. VON LIPPMANN (Annalen, 1927, 452, 135—140).—When salicylaldehyde dimethyl acetal (which need not be isolated in the pure condition) is heated at 130° under 0.5—1 mm. for 0.5 hr., methyl alcohol is eliminated with the formation, in small yield, of α -2-*oxido*benzyl methyl ether, $C_6H_4 \begin{array}{l} \diagup O \\ | \\ CH \cdot OMe \end{array}$, m. p. 217—218° (corr.). The

corresponding ethyl ether, m. p. 156° (corr.), is obtained similarly from the diethyl acetal. Both are bimolecular in benzene solution, but unimolecular in phenol solution and in the form of vapour at 234°. Heating with dilute acids or alkali readily splits the oxide ring. J. W. BAKER.

Positional influence of substituents on chemical reactivity and colour. H. H. HODGSON (J. Soc. Dyers and Col., 1927, 43, 72—76).—Mainly a discussion of results already published (A., 1925, i, 674, 1144; 1926, 281, 292, 1039). Chattaway and Clemo's generalisations on the relation between colour and constitution in the hydrazones of nitrobenzaldehydes (J.C.S., 1923, 123, 3043) have been confirmed by the foregoing work (*loc. cit.*) on *p*-nitrophenylhydrazones of chloronitro-substituted *m*-hydroxybenzaldehydes. Chlorine produces a similar effect, which is more pronounced with 6-chloro- than with 2-chloro-substitution. Methylation of the hydroxyl group diminishes the colour except in the case of the 2 : 4 : 6-trichloro-3-methoxybenzaldehyde derivative. A *p*-amino-group has a marked influence, 3-nitro-4-aminobenzaldehyde affording a more intensely coloured *p*-nitrophenylhydrazone than the corresponding 4-halogen-3-nitrobenzaldehydes. The vivid royal-blue colour developed by 6-chloro-2 : 4-dinitro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone in alcoholic solution with alkalis, in contrast with the behaviour of the corresponding hydrazone from 2-chloro-4 : 6-dinitro-3-hydroxybenzaldehyde, which gives no colour in the cold and only a claret colour on warming, is attributed to the position of the chlorine as a terminal member of a chain of five adjacent groups, and conjugate to the hydroxyl group:



The 2-nitro-group therefore exerts its full effect on the methine carbon atom, promoting mobility of the imino-hydrogen atom to give the configuration (II). The intermediate colour of the *p*-nitrophenylhydrazones of 4-chloro-2 : 6-dinitro- and 2 : 4-dichloro-6-nitro-3-hydroxybenzaldehyde is attributed to variations of valency distribution in the conjugate chains. Similarly, the exceptional behaviour of 2 : 5-dichloro-6-nitrobenzaldehydephenylhydrazone (Chattaway and Clemo, *loc. cit.*) is explained by the annexed structure, indicating repression of the effect of the nitro-group on the imino-hydrogen. R. BRIGHTMAN.

Action of trichloroacetic acid on phenols. J. VAN ALPHEN (Rec. trav. chim., 1927, 46, 144—

149).—The replacement by trichloroacetic acid of the chloroform in the Reimer-Tiemann reaction yields the corresponding aldehydes and carbon dioxide in place of the expected α -keto-acids. Phenol yields small quantities of *o*- and *p*-hydroxybenzaldehydes; guaiacol gives a very little vanillin; *p*-cresol yields a small amount of 2-hydroxy-5-methylbenzaldehyde; and *p*-hydroxybenzoic acid gives a rather better yield of 4-hydroxy-3-aldehydobenzoic acid. The following substances yield small quantities of aldehydes (isolated as the *p*-nitrophenylhydrazones only): *p*-chlorophenol, pyrocatechol, resorcinol, quinol, phloroglucinol, thymol, *p*-aminophenol, salicylic acid, phenolphthalein, gallic acid, α - and β -naphthols, and alizarin. The presence of nitro-groups or the replacement of the hydroxyl by an alkyloxy-group inhibits the reaction; picric acid, *p*-nitrophenol, anisole, phenetole, veratrole, anisic acid, and menthol give negative results. The smallness of the yields is due to the production of triphenylmethane dyes, and in the case of guaiacol this reaction takes place almost exclusively. The dyes must be formed from the intermediate substances, $\text{Ar}\cdot\text{CHCl}_2$, not from an aldehyde, because vanillin itself when heated with guaiacol and sodium hydroxide does not yield a dye, whereas a dye is formed when vanillin, guaiacol, and zinc chloride are heated together.

The mechanism of these reactions probably involves the migration of the group $-\text{CCl}_2\cdot\text{CO}_2\text{H}$ from the oxygen atom of the phenol to a nuclear carbon atom. When, however, mono- and di-chloroacetic acids act on phenol or resorcinol, the resulting mono- and di-phenoxyacetic and resorcinol-*OO*-diacetic acids are recovered unchanged after heating with zinc chloride; no migration from oxygen to carbon takes place.

J. M. GULLAND.

Stereoisomerism and isomorphism of the phenyl styryl ketones. C. DUFRAISSE and A. GILLET (Ann. Chim., 1926, [x], 6, 295—312).—A more detailed account of work already published (this vol., 58).

J. W. BAKER.

Hydrogenation of distyryl ketone and di- β -phenylethyl ketone. W. N. IPATIEV and N. A. ORLOV (Compt. rend., 1927, 184, 751—753).—Hydrogenation of distyryl ketone cannot be effected with copper oxide as catalyst or in cyclohexane solution; in the latter case, an unstable amorphous product, C, 84.91%, H, 10.38%, which affords unsaturated products on warming, is formed. In benzene solution and in presence of nickel oxide (cf. Borsche and others, A., 1912, i, 194, 703; 1913, i, 171), the yield of di- β -phenylethyl ketone depends on the concentration, varying from 60% in 15% solution to 10% in 50% solution. In 20% alcoholic solution, the yield is 20%. Hydrogenation of di- β -phenylethyl ketone in cyclohexane at 240° affords α -di-cyclohexylpentane, b. p. 315°.

R. BRIGHTMAN.

Comparative migratory tendencies of phenyl and diphenyl radicals. M. DELAVILLE (Compt. rend., 1927, 184, 462—463).—By the dehydration of the corresponding tertiary alcohol, α -diphenylstyrene, m. p. 93° (dibromide, m. p. 156°; nitrosite, m. p. 136°), was prepared. Silver nitrate acted on the iodohydrin of this compound, forming phenyl diphenylmethyl

ketone, m. p. 140° (oxime, m. p. 151°). The migration of the diphenyl radical was confirmed by the preparation of the isomeric diphenyl benzyl ketone, m. p. 149° (oxime, m. p. 156°), and phenyldiphenylacetaldehyde, m. p. 96° (oxime, m. p. 160°).

B. W. ANDERSON.

Acenaphthene derivatives. P. RUGGLI and A. JENNY (Helv. Chim. Acta, 1927, 10, 228—242).—3-Acenaphthyl benzyl ketone prepared in 65—68% yield by a modification of the method of von Papeke (A., 1888, 701) (oxime, m. p. 138°; phenylhydrazone, m. p. 138—139°; picrate, m. p. 113—116°), treated with phosphorus pentachloride in chloroform solution, yields $\beta\beta$ -dichloro- α -phenyl- β -3-acenaphthylethane, which when heated in methyl-alcoholic solution with potassium hydroxide, or for 0.75 hr. in a vacuum at 140°, is converted into β -chloro- α -phenyl- β -3-acenaphthylethylene, m. p. 77.5°, which cannot be converted into the corresponding acetylene derivative. Oxidation of benzyl 3-acenaphthyl ketone with potassium permanganate in pyridine solution converts it into phenyl-3-acenaphthylglyoxal, m. p. 148.5° (monohydrazone, m. p. 199—200°), which does not yield a dihydrazone, but yields a quinoxaline derivative, m. p. 162°. The monoxime, m. p. 204—205° (decomp.), is obtained by the action of either hydroxylamine on the diketone, or amyl nitrite on the original ketone. The latter, on bromination in chloroform solution, yields 3-acenaphthyl ω -bromobenzyl ketone, m. p. 118°, which on treatment with methyl-alcoholic potassium hydroxide solution yields 3-acenaphthyl ω -hydroxybenzyl ketone, m. p. 138° (benzoyl derivative, m. p. 156°), which on oxidation with potassium permanganate yields phenylacenaphthylglyoxal (above). Nitration of 3-acenaphthyl benzyl ketone in acetic acid and acetic anhydride with nitric acid, *d* 1.4, yields nitroacenaphthyl benzyl ketone, m. p. 189°, which when treated with phosphorus pentachloride yields $\beta\beta$ -dichloro- α -phenyl- β -nitroacenaphthylethane, m. p. 136° (decomp.), which when heated at 140° yields β -chloro- β -nitro- α -phenylacenaphthylethylene, m. p. 160—161°. When treated with hydroxylamine, nitroacenaphthyl benzyl ketone does not yield an oxime, but an isomeric substance, m. p. 136—137°; and on reduction with sodium hydrogen sulphite yields a substance, m. p. 164°. Phenyl- β -naphthylglyoxal (Ruggli and Reinert, A., 1926, 391) yields a monohydrazone, m. p. 136°, and a dihydrazone, m. p. 163°, which when shaken with mercuric oxide in benzene suspension yields phenyl- β -naphthylacetylene (Ruggli and Reinert, loc. cit.). The corresponding phenyl- α -naphthylglyoxal similarly yields a monohydrazone, m. p. 152°, and a dihydrazone, m. p. 217—218° (decomp.), but the latter cannot be converted into the acetylene derivative.

J. W. BAKER.

Nitration of benzil. 3:5:3':5'-Tetranitrobenzil. F. D. CHATAWAY and E. A. COULSON (J.C.S., 1927, 577—579; cf. A., 1926, 728).—3:3'-Dinitrobenzil (monophenylhydrazone, m. p. 171°; osazone, m. p. 269°; quinoxaline derivative, m. p. 213°), on further nitration yields 3:5:3':5'-tetranitrobenzil, m. p. 179° (Christie and Kenner, A., 1926, 408, give m. p. 168°) [monophenylhydrazone, m. p. 236°; quinoxaline derivative, m. p. 285° (Christie

and Kenner, *loc. cit.*, give m. p. 274°), together with 3:5-dinitrobenzoic acid. This acid is produced by oxidation of the tetranitro-compound with chromic acid.

H. BURTON.

Dioximes. XLI. G. PONZIO (*Gazzetta*, 1927, 57, 117—124).—The “ α -form of benzoylformhydroxamic acid oxime,” m. p. 177° or 174° (Gastaldi, A., 1924, i, 733; *Gazzetta*, 1924, 54, 588), is impure phenylhydroxyglyoxime, m. p. 191° [*hydrazine salt*, CPh(N·OH)·C(N·OH)·OH, N₂H₄, m. p. 165°, decomp.], mixed with phenylloximoacetic acid when prepared from ethyl phenylglyoxylate. The “ β -form,” m. p. 183°, of *p*-methylbenzoylformhydroxamic acid oxime (*p*-tolylhydroxyglyoxime) (cf. Gastaldi, A., 1924, i, 1209; Baiardo, A., 1926, 1262) is identical with the α -form, m. p. 186°; the supposed isomerisation of the nickel salt is a gel formation. The single form, m. p. 186°, is also obtained by the hydrolysis of *p*-tolylchloroglyoxime; the single triacetyl derivative has m. p. 122—123°.

3-Hydroxy-5-phenyl-1:2:4-oxadiazole (cf. A., 1926, 1159) is decomposed by nitric acid into benzonitrile, ammonia, and carbon dioxide; heated with aniline in a sealed tube, it gives *s*-diphenylcarbamide; sodium and silver salts, the salt

Ph·C₂N₂O·OAg, Ph·C₂N₂O·OH, m. p. 212° (decomp.), a copper salt, and a basic copper salt, Ph·C₂N₂O·CuOH, are described. The 3-methoxy-derivative, m. p. 26°, is obtained by methylation of the sodium salt, or by the action of sodium methoxide on the 3-chloro- or 3-bromo-compound (see this vol., 470), and, similarly, the 3-ethoxy-derivative, m. p. 64°; these compounds are very stable towards alkali.

E. W. WIGNALL.

New resacetophenone. F. MAUTHNER (*J. pr. Chem.*, 1927, [ii], 115, 274—278).—The third isomeric resacetophenone (cf. Nencki and Sieber, A., 1881, 591; Claus, A., 1896, i, 227), 3:5-dihydroxyacetophenone, m. p. 147—148° (*semicarbazone*, m. p. 205—206°; *p*-nitrophenylhydrazone, m. p. 236—237°; *diacetyl* derivative, m. p. 91—92°), may be obtained by demethylating 3:5-dimethoxyacetophenone (A., 1924, i, 524) with aluminium chloride in chlorobenzene solution.

H. E. F. NOTTON.

Derivatives of methyl α -piperonylidene-ethyl ketone. B. O'DONOGHUE, H. RYAN, and J. KEANE (*Proc. Roy. Irish Acad.*, 1926, 37, [B], 141—148).—Piperonal condenses with methyl ethyl ketone in presence of dry hydrogen chloride at 0° to yield methyl α -piperonylidene-ethyl ketone, MeCO·CMe:CH·C₆H₃:O₂CH₂, m. p. 97—98° (*oxime*, m. p. 130°). In presence of alkali, this condenses with benzaldehyde, anisaldehyde, and piperonal to yield, respectively, 3-phenyl-4-piperonyl-5-methyl-, 3-anisyl-4-piperonyl-5-methyl-, and 3:4-dipiperonyl-5-methyl- Δ^2 -cyclopenten-1-one, m. p. 88.6—89.4°, 112—113°, and 127—128°, respectively [*tetrabromide* of the last-named, m. p. 136° (decomp.)]. In presence of dry hydrogen chloride at 0°, however, the condensation products obtained are, respectively, 3-phenyl-4-piperonyl-2-benzylidene-5-methyl- Δ^3 -cyclopenten-1-one, m. p. 140—141°, 3-anisyl-4-piperonyl-2-anisylidene-5-methyl- Δ^3 -cyclopenten-1-one, m. p. 150—151°, and 3:4-dipiperonyl-2-piperonylidene-5-methyl- Δ^3 -cyclopenten-1-one (I), m. p. 220—222° (cf.

Ryan and Devine, A., 1916, i, 654; Ryan and Lennon, A., 1925, i, 1282), which are also obtained by the action of a further molecule of the aldehyde in presence of dry hydrogen chloride at 0° on the products (above) obtained in presence of alkali. By the action of a concentrated solution of dry hydrogen chloride in alcohol at 40° on 3:4-dipiperonyl-5-methyl- Δ^2 -cyclopenten-1-one, it is converted into the isomeric 3:4-dipiperonyl-5-methyl- Δ^3 -cyclopenten-1-one, m. p. 133.5—134.5°, which condenses with another mol. of piperonal in presence of alkali to yield (I). All these condensation products give colours with concentrated sulphuric acid.

J. W. BAKER.

Derivatives of piperonylidene-methyl ethyl ketone. B. O'DONOGHUE, H. RYAN, and J. KEANE (*Proc. Roy. Irish Acad.*, 1926, 37 [B], 149—153).—Piperonal condenses with methyl ethyl ketone in presence of alkali to yield piperonylidene-methyl ethyl ketone, m. p. 146—147° (*phenylhydrazone*, m. p. 82—83°), which condenses with another molecule of piperonal in presence of alkali to yield the piperonylidene-methyl α -piperonylidene-ethyl ketone, m. p. 186—187° [*tetrabromide*, m. p. 126—128° (decomp.)]. In presence of dry hydrogen chloride, however, the condensation product is 3:4-dipiperonyl-5-methyl- Δ^3 -cyclopenten-1-one (cf. preceding abstract), whilst with anisaldehyde the product is 4-anisyl-3-piperonyl-2-anisylidene-5-methyl- Δ^3 -cyclopenten-1-one, m. p. 220—222°.

J. W. BAKER.

Derivatives of veratrole and of methylvanillin. I. B. L. VANZETTI (*Gazzetta*, 1927, 57, 162—172).—Veratroin is not obtained solid, even when prepared by reduction of veratril (3:4:3':4'-tetramethoxybenzil) (new m. p. 223°). The latter condenses with *o*-phenylenediamine to give a *quinoxaline*, m. p. 198.5—199°; with hydroxylamine to give a *substance*, m. p. 110—113°. Veratrilic acid is not obtained by heating veratroin with potassium hydroxide solution in a current of air, nor by heating veratril with aqueous potassium hydroxide, and only in small quantity, with some veratric acid, when alcohol is present. Fusion of veratril with potassium hydroxide above 234° gives veratrilic acid, which has two forms, m. p., respectively, about 85° and below 68° (decomp.). Veratrilic acid in solution exposed to air resinifies.

Attempts to obtain di-3:4-dimethoxyphenyl ketone by the action of carbonyl chloride, or of veratric acid and zinc chloride, on veratrole, were not very successful. Action of magnesium methyl iodide on the ketone yields α -di-3:4-dimethoxyphenylethyl alcohol, m. p. 95—96°.

Benzilic acid is obtained in 95% yield by the action of sodium hydroxide dissolved in ethyl alcohol on an ethereal solution of benzil. E. W. WIGNALL.

Alkylation of hydroxynaphthaquinone. III. **Synthesis of lapachol.** L. F. FIESER (*J. Amer. Chem. Soc.*, 1927, 49, 857—864; cf. this vol., 155).—Treatment of the silver salt of hydroxynaphthaquinone with α -bromo- γ -methyl- Δ^{β} -butene (isoprene hydrobromide) in cold ethereal suspension yields 2- γ -methyl- Δ^{β} -butenoxy- α -naphthaquinone, pale yellow, m. p. 149—150°, together with 3-hydroxy-2- γ -methyl- Δ^{β} -butenyl- α -naphthaquinone, yellow, m. p. 139—140°, identical with lapachol (cf. Hooker, J.C.S.,

1896, 65, 1355). Crotyl bromide yields similarly 2-crotyl- α -naphthaquinone, (I), yellow, m. p. 137°, 4-crotyl- β -naphthaquinone, (II), orange-yellow, m. p. 120°, and 3-hydroxy-2-crotyl- α -naphthaquinone, yellow, m. p. 132—133°. When treated with cold, concentrated sulphuric acid, the last affords 2-methyl-7:8-benzochroman-5:6-quinone, orange, m. p. 164°, and 2-methyl-6:7-benzochroman-5:8-quinone, yellow, m. p. 122.5°. When heated above the m. p., both (I) and (II) are converted into 3-hydroxy-2- α -methyl- Δ^{β} -propenyl- α -naphthaquinone, m. p. 69°, and this, when treated with cold, concentrated sulphuric acid, yields 1:2-dimethyl-5:6-benzocoumaran-3:4-quinone, m. p. 109—110°.

F. G. WILLSON.

Sulphonation of anthraquinone in presence of mercury. A. MEYER (Compt. rend., 1927, 184, 609—611).—Potassium anthraquinone- α -sulphonate when heated with 80% sulphuric acid at 190° in presence of mercuric sulphate affords about 33% of the theoretical amount of anthraquinone. The liquors obtained on dilution contain the α - and β -anthraquinonesulphonic acids in the ratio 65:35. The theory previously advanced (A., 1926, 1146) regarding the mechanism of the conversion of the α - into the β -sulphonic acid is thus confirmed. Under similar conditions, anthraquinone- β -sulphonic acid is stable. Sulphonation of anthraquinone at 160° in presence of mercuric sulphate (cf. Martinet and Roux, A., 1921, i, 257, 732) affords chiefly anthraquinone- α -sulphonic acid, together with the 1:5- and 1:8-disulphonic acids and a little trisulphonic acid. The presence of the β -monosulphonic acid could not be established.

R. BRIGHTMAN.

Anthraquinonesulphonic acids. H. E. FIERZ-DAVID [with A. KREBSER and W. ANDERAU] (Helv. Chim. Acta, 1927, 10, 197—227).—A summary of an extensive re-examination of the preparation and properties of anthraquinone-mono- and -di-sulphonic acids, their salts and derivatives, in accordance with methods previously described in the literature. A large amount of solubility data for metallic salts in water at 18° and 100° is given, for which the original must be consulted. In presence of mercury salts, monosulphonation of anthraquinone yields 97% of the α -acid (chloride, m. p. 216—218°) and 3% of the β -acid. The sodium (+H₂O), potassium, ammonium, calcium (+3H₂O), strontium (+3H₂O), barium (+H₂O), magnesium (+16H₂O), ferrous (+8H₂O), nickel (+8H₂O), zinc (+8H₂O), cadmium (+16H₂O), copper (+8H₂O), manganous (+16H₂O), and lead (+6H₂O) salts of anthraquinone- α -sulphonic acid are described. Disulphonation in presence of mercury salts yields 40—45% of the 1:5-acid, 23% of the 1:8-acid, the remaining 20—25% consisting of 1:5-, 4:5%; 1:8, trace; 1:6-, about 5%; and 1:7-, 12—15%. The pure 1:5-acid (+4H₂O), m. p. 310—311° (decomp.), yields a disulphonyl chloride, m. p. 265—270° (decomp.); dianilide, m. p. 269—270°; diamide, m. p. above 350°. The pyridine, m. p. 245—246°, aniline, sodium (+4H₂O), potassium, ammonium, calcium (+3H₂O), strontium (+3H₂O), barium (+2H₂O), lead (+4H₂O), magnesium (+8H₂O), zinc (+8H₂O), ferrous (+8H₂O), cobalt (+8H₂O), nickel (+8H₂O), copper (+8H₂O), cadmium (+7H₂O), and

manganese (+7H₂O) salts are described. The 1:8-acid (+5H₂O), m. p. 293—294° (decomp.), yields a disulphonyl chloride, m. p. 222—223°; dianilide, m. p. 237—238° (decomp.); diamide, m. p. above 340°. The aniline, sodium (+4H₂O), potassium (+2H₂O), ammonium (+2H₂O), calcium (+5.5H₂O), strontium (+3.5H₂O), barium (+3.5H₂O), lead (+H₂O), magnesium (+6H₂O), zinc (+6H₂O), ferrous (+6H₂O), cobalt (+6H₂O), nickel (+6H₂O), copper (+7H₂O), cadmium (+5H₂O), and manganese (+4H₂O) salts are described. The 1:6-acid (+5H₂O), m. p. 215—217° (decomp.) (2.5H₂O lost in a vacuum desiccator) yields a disulphonyl chloride, m. p. 197—198° (decomp.); dianilide, m. p. 227—228° (decomp.); additive compound of the dianilide with nitrobenzene, m. p. 142—143°. The sodium (+3H₂O), potassium (+1.5H₂O), ammonium, calcium (+5H₂O), barium (+2H₂O), magnesium (+8H₂O), and nickel (+8H₂O) salts are described. The 1:7-acid (+4H₂O), m. p. 120° (? dissolves in its water of crystallisation), yields a disulphonyl chloride, m. p. 231—232° (decomp.); dianilide, m. p. 237—238° (decomp.); and the sodium (+2H₂O), potassium (+2H₂O), ammonium (+2H₂O), calcium (+6H₂O), barium (+2.5H₂O), magnesium (+10H₂O), and nickel (+10H₂O) salts are described. The chlorination and bromination of the anthraquinonedisulphonic acids were repeated and the following derivatives are described: 1:5-chlorosulphonic acid (+4H₂O), m. p. 236—237° (decomp.) [sodium (+0.5H₂O), potassium (+2H₂O), calcium (+2H₂O), magnesium (+8H₂O), and nickel (+8H₂O) salts]; 1:8-chlorosulphonic acid (+3H₂O), m. p. 183—184° (decomp.) [sodium (+H₂O), potassium (+2H₂O), calcium (+4H₂O), barium (+3H₂O), magnesium (+6H₂O), and nickel (+6H₂O) salts]; 1:6-chlorosulphonic acid (+3H₂O), m. p. 248—249° (decomp.) [potassium and calcium (+2H₂O) salts]; 1:5-bromosulphonic acid (+2.5H₂O), m. p. 265—266° [potassium salt, (+2H₂O)]; 1:6-bromosulphonic acid (+4H₂O), m. p. 268—269°. Attempts to prepare the 6- and 7-chloroanthraquinone-1-sulphonic acids from the corresponding 6-halogen-1-nitro-compounds by means of sodium sulphite were unsuccessful, but the various nitro-, amino-, and acetamido-halogeno- and dihalogeno-anthraquinones were prepared and their properties are summarised. Sulphonation of anthraquinone in absence of mercury salts yields the β -sulphonic acid, of which the sodium (+H₂O), potassium, ammonium, magnesium (+2H₂O), calcium (+2H₂O), strontium (+H₂O), barium (+H₂O), ferrous (+6H₂O), cobalt (+6H₂O), nickel (+6H₂O), manganese (+2H₂O), zinc (+2H₂O), cadmium (+2H₂O), copper (+H₂O), and lead (+3H₂O) salts are described. Disulphonation at 140° yields anthraquinone-2:6- and -2:7-disulphonic acids in the ratio 2:3; at 150° the ratio is 9:11, and with a vanadium catalyst it is 1:1. The 2:6-disulphonic acid yields a disulphonyl chloride, m. p. 186° [sodium (+2H₂O), potassium, ammonium, magnesium (+3H₂O), calcium (+5H₂O), barium (+5H₂O), ferrous (+8H₂O), cobalt (+8H₂O), nickel (+8H₂O), zinc (+6H₂O), copper (+4H₂O), and lead (+5H₂O) salts]. The following salts of the 2:7-disulphonic acid are described: sodium (+4H₂O), potassium (+H₂O), ammonium (+H₂O), magnesium (+5H₂O), calcium (+2H₂O), strontium (+2H₂O), barium (+H₂O),

ferrous (+6H₂O), *cobalt* (+6H₂O), *nickel* (+6H₂O), *zinc* (+4H₂O), *copper* (+6H₂O), and *lead* (+2H₂O). When anthraquinonesulphonic acids are heated with concentrated sulphuric acid in chlorobenzene or nitrobenzene solution for 8 hrs., no elimination of the sulphonic acid groups occurs up to a temperature of 180°, but at 210° in presence of mercury as a catalyst the 1-, 1:5-, and 1:8-acids yield, respectively, 80, 74, and 78% of anthraquinone. At the most, only traces of anthraquinone are produced with the other isomerides or when a vanadium catalyst is used. Sodium anthraquinone-2:6-disulphonate heated with sodium chlorate and hydrochloric acid yields first 2-chloroanthraquinone-6-sulphonic acid [sodium and barium (+H₂O) salts; acid chloride, m. p. 202°] and finally 2:6-dichloroanthraquinone, m. p. 282°. Similarly, 2-chloroanthraquinone-7-sulphonic acid [barium (+H₂O) salt; acid chloride, m. p. 176°] and 2:7-dichloroanthraquinone are obtained.

J. W. BAKER.

Production of anthraquinone derivatives.

H. A. E. DRESCHER, W. SMITH, J. THOMAS, and SCOTTISH DYES, LTD.—See B., 1927, 246.

[Bz-2'-]Hydroxybenzanthrones. K. SCHIRMACHER, K. ZAHN, K. WILKE, and P. OCHWAT, Assrs. to GRASELLI DYESTUFF CORP.—See B., 1927, 275.

Tannins. XXIV. Chebulic acid. III. K. FREUDENBERG and T. FRANK (Annalen, 1927, 452, 303—315; cf. Freudenberg and Fick, A., 1920, i, 849).—Specially purified chebulic acid has the formula C₄₁H₃₄O₂₇ (M 958), [α]_D²⁰ +65.1° in aqueous alcohol. The mol. wt. averages 962 by alkalimetric, 977 by electrometric titration, 875 ebullimetrically in glacial acetic acid or methyl succinate. Fission experiments with 5% sulphuric acid at 100°, with 0.2N-sodium hydroxide at 32°, with boiling water, with tannase, and with boiling water followed by tannase, lead to the equation: C₄₁H₃₄O₂₇+5H₂O=3 mols. of gallic acid + 1 mol. of dextrose + 1 mol. of acid C₁₄H₁₄O₁₁.

C. HOLLINS.

Constitution of α-kirondrin. VOLMAR and SAMDAHL (Compt. rend., 1927, 184, 535—537; cf. this vol., 387).—α-Kirondrin has the formula C₂₄H₃₇O₁₀, and is believed to be a saturated, non-phenolic lactone containing one or more aldehydo-groups. The ready reduction of cold Fehling's solution, Nessler's reagent, and ammoniacal silver nitrate point to the presence of aldehydo-groups, but α-kirondrin gives no osazone either before or after attempted hydrolysis with dilute acid or emulsin, and is therefore not a glucoside. It dissolves in water to a neutral solution which becomes acid on boiling, or in alkali to a yellow solution which becomes colourless on acidification; a lactonic structure is suggested to explain these reactions. It does not decolorise bromine in the cold, or give a colour with ferric chloride. The general properties, and especially the intense greenish-yellow fluorescence in ultra-violet light, are reminiscent of quassine and other substances obtained from the natural order *Simarubaceae*, and therefore an anthracene complex is probably present.

J. M. GULLAND.

Catalytic hydrogenation of carone. S. N. IYER and J. L. SIMONSEN (J. Indian Inst. Sci., 1927, 9A, 169—172).—See A., 1926, 1042.

Enolisation of camphor. II. Camphor-enol ethyl ether (2-ethoxybornylene). M. BREDT-SAVELSBERG and C. RUMSCHEIDT (J. pr. Chem., 1927, [ii], 115, 235—255; cf. A., 1924, i, 530).—Attempts to prepare an ether of enolic camphor by thermal decomposition of 2-methoxycamphane-3-trimethylammonium hydroxide gave only camphor, methyl alcohol, and trimethylamine. Camphoracetal was prepared by Arbusov's method (A., 1908, i, 555); the second compound, b. p. 82—83°/15 mm., obtained by this author was probably a mixture of camphor and ethyl orthoformate. The acetal does not react with sodium or sodium ethoxide; with acetyl chloride and pyridine, camphor is obtained. Treatment with phosphoric oxide and pyridine at 110—130° for 8 hrs. converts it into an unsaturated substance, b. p. 73.9—75.1°/12 mm., *d*₄²⁰ 0.9356, *n*_D²⁰ 1.46795, which must consist mainly of 2-ethoxybornylene, since it is oxidised by potassium permanganate to 3-carbethoxy-2:2:3-trimethylcyclopentane-1-carboxylic acid (*alloethyl* hydrogen camphorate, Brühl, A., 1892, 1100) and camphor. It rapidly absorbs atmospheric oxygen, and is hydrolysed to camphor by water or dilute acids. Catalytic hydrogenation in presence of platinum-black gives camphor and bornyl ethyl ether, b. p. 73—74°/10 mm.

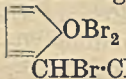
H. E. F. NOTTON.

Essence of camphor. VII. Catalytic action of Japanese acid earth on *l*-linalool. K. ONO and Z. TAKEDA (Bull. Chem. Soc. Japan, 1927, 2, 16—19; cf. this vol., 156).—*l*-Linalool was heated with 10% of Japanese acid earth at 159°. The product volatile in steam contained (?) myrcene, *d*-limonene, *d*-terpineol, and geraniol, whilst the non-volatile residue contained an olefinic sesquiterpene alcohol, C₁₅H₂₆O, b. p. 187—190°/20 mm., *d*₄²⁰ 0.90197, *n*_D²⁰ 1.4942, and a diterpene oxide, C₂₀H₃₄O, b. p. 196—200°/20 mm., *d*₄²⁰ 0.9186, *n*_D²⁰ 1.4946 (cf. Semmler and Jonas, A., 1915, i, 63).

H. E. F. NOTTON.

Hydrogenation of xanthone and xanthen. V. N. IPATIEV and N. A. ORLOV (J. Russ. Phys. Chem. Soc., 1926, 58, 1034—1038).—See this vol., 251.

Action of bromine on furylacrylic acid. C. MOUREU, C. DUFRAISSE, and J. R. JOHNSON (Ann. Chim., 1927, [x], 7, 5—13).—Addition of 4 atoms of bromine to a suspension of furylacrylic acid in chloroform at -15°, in an atmosphere of dry carbon dioxide, yields a crystalline tetrabromide, m. p. 110—111° (decomp.), which decomposes immediately on exposure to air with evolution of hydrogen bromide. It is suggested that two of the bromine atoms enter the side-chain, the other two going to form an

oxonium dibromide, , the

compound being an intermediate product in the formation of the tribromo-acid, C₄H₂OBr·[CHBr]₂·CO₂H, obtained by Gibson and Kahnweiler (A., 1890, 959). On treatment of the chloroform solution with mercury, the original furylacrylic acid is regenerated. Similarly, αβ-dibromo-β-phenylpropionic acid, on treatment with mercury, yields cinnamic acid. Successive treatment of the tetrabromide with sodium sulphate and sodium

carbonate in an attempt to prepare furylbromoethylene (cf. following abstract) probably yielded this substance in solution, but it could not be isolated. Bromofurylbromoethylene prepared by the method of Gibson and Kahnweiler (*loc. cit.*) has the following constants: b. p. 98—99°/10 mm., n_D^{18} 1.6174, d_4^{20} 1.9643, d_4^{18} 1.9373. J. W. BAKER.

Furylacetylene. C. MOUREU, C. DUFRAISSE, and J. R. JOHNSON (*Ann. Chim.*, 1927, 7, 14—42).—Furylethylene, m. p. about —96°, b. p. 99—100°/760 mm., 49—50°/130 mm., 32—33°/57 mm., 25°/27 mm., and 19°/17 mm., d_4^{18} 0.9445, n_D^{18} 1.4992, is obtained as a by-product in the preparation of furylacrylic acid by Gibson and Kahnweiler's method (A., 1890, 959), but is best obtained by heating the latter at 270—280°, rising gradually to 300—320° (yield 40%). It rapidly polymerises in presence of air and light, but is stabilised by the addition of about 0.5% of quinol or pyrocatechol. Under minutely prescribed conditions, which must be closely followed, treatment of furylethylene with bromine in anhydrous ether at —17° yields the *dibromide* (pale green leaflets, m. p. about 20°, which readily decomposes and was not isolated in the pure state); this on treatment with a 50% excess of alcoholic potassium hydroxide solution at 0° (added in one portion because alcohol itself decomposes the dibromide) yields *furylbromoethylene* (probably mainly the α -bromo-compound), b. p. 61—62°/17 mm., 42—43°/3 mm., which in air undergoes spontaneous oxidation to a lachrymatory substance, probably furacyl bromide, $C_4H_3O \cdot CO \cdot CH_2Br$. On treatment with a 10% excess of an 18% alcoholic solution of potassium hydroxide at 100° and subsequent exact neutralisation, furylbromoethylene yields *furylacetylene*, b. p. 105—106°/760 mm., 54—55°/120 mm., d_4^{20} 1.0127, d_4^{20} 0.9919, n_D^{20} 1.5055, which is purified by conversion into its *copper* compound, which gives acetylene when treated with aqueous sodium cyanide. The *mono-* and *di-silver* and *mercury*, m. p. 118—119°, compounds are described. Furylacetylene reacts slowly with sodium but vigorously with potassium to give the *potassium* derivative, which absorbs carbon dioxide to form potassium furylpropiolate(?). Magnesium ethyl bromide converts furylacetylene quantitatively into magnesium furylethynyl bromide (and ethane), which with carbon dioxide yields *furylpropionic acid*, m. p. 113—114° (decomp. on Maquenne block), 108—110° (decomp. in a capillary tube). With alcohol, furylacetylene forms an azeotropic mixture, b. p. 77—78°/760 mm., 37—38°/124 mm., 32—33°/95 mm., d_4^{18} 0.8610, n_D^{18} 1.409, containing 38% of the acetylene. J. W. BAKER.

Preparation and reactions of pyrylium perchlorates. O. DIELS and K. ALDER (*Ber.*, 1927, 60, [B], 716—723).—4 : 6-Di-*p*-tolyl-2-methylpyrylium perchlorate, m. p. 275° (decomp.) after softening, is obtained by warming toluene with a mixture of acetic anhydride and perchloric acid; its constitution is established by its conversion by means of ammonia into 4 : 6-di-*p*-tolyl-2-methylpyridine, m. p. 96° (cf. Thoma, A., 1907, i, 138). It is assumed that the anhydride and perchloric acid yield initially a mixed anhydride, $Ac \cdot O \cdot ClO_3$, which with toluene affords perchloric acid and *p*-tolyl methyl ketone. From the

latter compounds (2 mols.), an unsaturated ketone is derived, converted by the mixed anhydride into a pyrylium perchlorate. In confirmation, 4 : 6-diphenyl- and 4 : 6-di-*p*-tolyl-2-methylpyrylium perchlorates are obtained from acetophenone and *p*-tolyl methyl ketone, respectively. 4 : 6-Di-*p*-tolyl-2-methylpyrylium perchlorate is converted by aniline into 1-phenyl-4 : 6-di-*p*-tolyl-2-methylpyridinium perchlorate, m. p. 217°, and by *as*-phenylmethylhydrazine into 1-methylanilino-4 : 6-di-*p*-tolyl-2-methylpyridinium perchlorate, m. p. 177°; benzylamine behaves similarly. With phenylhydrazine in ethereal solution, it gives primarily the compound

$$CH \left\langle \begin{array}{l} C(C_6H_4Me) - O \\ C(C_6H_4Me) : CH \end{array} \right\rangle CMe \cdot NH \cdot NPh, \text{ m. p. } 129 - 130^\circ,$$

and ultimately a mixture of 2-phenylhydrazino-1-anilino-4 : 6-di-*p*-tolyl-2-methyl-1 : 2-dihydropyridine, m. p. 141°, and the phenylhydrazone of δ -phenylhydrazino- β -*p*-tolyl- $\Delta^{\alpha\gamma}$ -pentadienyl *p*-tolyl ketone, m. p. 241°. Piperidine and dimethylamine transform the perchlorate respectively into 1 : 3' : 5'-di-*p*-tolylphenylpiperidine, m. p. 146°, and 3 : 5-di-*p*-tolyl-dimethyl-aniline, m. p. 106°. Similarly, 2 : 4 : 6-trimethylpyrylium perchlorate, obtained from mesityl oxide or acetone and acetic anhydride and perchloric acid, is converted by dimethylamine into *N*-dimethyl-*as*-methylidene. 4 : 6-Di-*o*-xylyl-2-methylpyrylium perchlorate, m. p. 282° (decomp.), is formed from *o*-xylene and the "mixed anhydride," with which benzene does not appear to react. H. WREN.

β -[4-]Phenylcoumarins. G. BARGELLINI and A. GRIPPA (*Gazzetta*, 1927, 57, 138—145).—2 : 4-Dihydroxy-3' : 4' : 5'-trimethoxybenzophenone, yellow, m. p. 165°, obtained by heating resorcinol with 3 : 4 : 5-trimethoxybenzoic acid and zinc chloride, condenses with sodium acetate and acetic anhydride to give 7-acetoxy-4-(3' : 4' : 5'-trimethoxyphenyl)-coumarin, m. p. 118—120°, which hydrolyses to the corresponding 7-hydroxy-compound [4-(3 : 4' : 5'-trimethoxyphenyl)umbelliferone, cf. Bogert and Isham, A., 1914, i, 532]. This with diazomethane gives the 7-methoxy-compound, m. p. 172—175°, but with methyl sulphate and sodium hydroxide, β -(2' : 4'-dimethoxyphenyl)-3 : 4 : 5-trimethoxycinnamic acid, m. p. 156—158°; by demethylation, 7-hydroxy-4-(3' : 4' : 5'-trihydroxyphenyl)coumarin, m. p. 315—317° (tetra-acetyl derivative, m. p. 146—148°), is obtained.

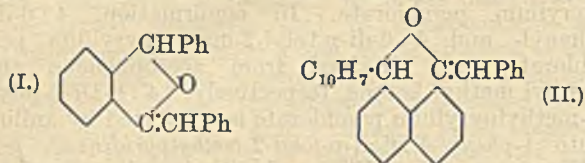
By the method of Bogert and Isham (*loc. cit.*), condensing ethyl 3 : 4 : 5-trimethoxybenzoylacetate with phloroglucinol, 5 : 7-dihydroxy-4-(3' : 4' : 5'-trimethoxyphenyl)coumarin, m. p. 245—247° (diacetyl derivative, m. p. 190—191°), is prepared; this is methylated by diazomethane to the 5 : 7 : 3' : 4' : 5'-pentamethoxy-compound, m. p. 204—206°, and demethylated to impure 5 : 7-dihydroxy-4-(3' : 4' : 5'-trihydroxyphenyl)-coumarin (penta-acetyl derivative, m. p. 170—171°).

Using pyrogallol, 7 : 8-dihydroxy-4-(3' : 4' : 5'-trimethoxyphenyl)coumarin, m. p. 274—276°, is obtained (diacetyl derivative, m. p. 161—162°).

E. W. WIGNALL.

Arylbenzylidenephthalans and naphthalans; disubstituted indones. R. WEISS and P. FASTMANN (*Monatsh.*, 1926, 47, 727—732; cf. A., 1926, 294, 401).—Phenylphthalide is converted by mag-

nesium benzyl chloride in ether-benzene solution into *phenylbenzylidenephthalan* (I), m. p. 128—131°, which



resinifies on keeping. With bromine, this gives 2:3-diphenylindone.

p-Tolylbenzylidenephthalan, m. p. 150—155°, and 2-phenyl-3-*p*-tolylindone, m. p. 136—137°, are obtained in a similar way from *p*-tolylphthalide. Magnesium α -naphthyl bromide and naphthalic anhydride in warm toluene solution form 8- α -naphthoyl-1-naphthoic acid, m. p. 208—212°, which is reduced by hydriodic acid and red phosphorus in boiling glacial acetic acid to α -naphthyl-naphthalide, m. p. 192—194°. The latter is reduced by sodium amalgam and alcohol to 8- α -naphthylmethyl-1-naphthoic acid, m. p. 160—162°, whilst with magnesium benzyl chloride it gives α -naphthylbenzylidenephthalan (II), m. p. 173—177°. 8-*o*-Toluyol-1-naphthoic acid, m. p. 183—184°; *o*-tolyl-naphthalide, m. p. 146—150°, and *o*-tolylbenzylidenephthalan, m. p. 125—127°, are prepared by analogous methods. H. E. F. NOTTON.

Derivatives of 2-phenyl-1:3-benzdithiole. W. R. H. HURTLEY and S. SMILES (J.C.S., 1927, 534—537).—Nitric acid oxidises 2-phenyl-1:3-benzdithiole to the sulphonium nitrate, from which the ψ -base is liberated by alkali (cf. A., 1926, 948). 2-*o*-Nitrophenyl-1:3-benzdithiole does not undergo this oxidation, but 2-*p*-methoxyphenyl-1:3-benzdithiole, m. p. 72°, readily gave the nitrate, which, with sodium hydroxide, yielded 2-*p*-methoxyphenyl-1:3-benzdithiole 2-oxide, m. p. 158° (chloride), and 2-*p*-hydroxy-1:3-benzdithiole, m. p. 118°, is even more easily oxidised to the nitrate. The foregoing nitrate, treated with potassium carbonate, forms 1:3-benzdithiole-2-*p*-benzoquinone, $C_6H_4S_2C:C_6H_4O$, scarlet, m. p. 212—213° (hydrochloride). 1:3-Benzdithiole-2- β -naphthoquinone, is similarly obtained, the normal mercaptol not being formed. 2-Styryl-1:3-benzdithiole, m. p. 80° (nitrate), is also described. B. W. ANDERSON.

Vat dyes [of the thioindigo series]. H. WAGNER and others.—See B., 1927, 212.

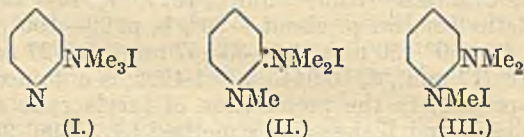
Production of derivatives of oxindole-3-acetic acid and its homologues containing halogens substituted in the aromatic nucleus. CHEM. FABR. VORM. SCHERING.—See B., 1927, 286.

[Compounds of the pyrrole and indole series and isomerisations in these series.] L. ALESSANDRI and M. PASSERINI (Ber., 1927, 60, [B], 807; cf. A., 1926, 1151).—A claim for priority against Putochin (A., 1926, 1151). A plea is entered for the application of the term "formyl" to the aldehydic group when attached to nitrogen. H. WREN.

Oxidation of pyridine and the pyridine nucleus by permanganate. M. DELÉPINE (Bull. Soc. chim., 1927, [iv], 41, 390—393).—See this vol., 254.

Alkyl halides of 2-aminopyridine. A. E. TSCHITSCHIBABIN and R. A. KONOVALOVA (J. Russ. Phys. Chem. Soc., 1926, 58, 1170—1174).—The

possibility of isomerism in the methiodides of dimethylaminopyridine and methylpyridonemethylamine, both of which are mono-acid bases, is discussed. Dimethylaminopyridine and methyl iodide give a *methiodide*, m. p. 183—184°, the solution of which with picric acid gives a *picrate*, m. p. 113°. Moist silver oxide affords a soluble *quaternary base*. On distillation, dimethylaminopyridine was obtained. The methiodide is consequently assigned structure (I). Methyl pyridone-



methylamine and methyl iodide give a *methiodide* decomposing in air. Moist silver oxide gives a silver mirror, together with dimethylamine and methylpyridone. Sodium hydroxide gives dimethylamine. The methiodide is assigned the tautomeric structures (II) and (III). M. ZVEGINTZOV.

Derivatives and oxidation products of 2-aminopyridine. A. KIRPAL and E. REITER (Ber., 1927, 60, [B], 664—666).—2-Aminopyridine is oxidised by sodium hypochlorite in aqueous solution to 2:2'-azopyridine, m. p. 81° [nitrate, m. p. 158° (decomp.); picrate, m. p. 180° (decomp.)], which is reduced by stannous chloride to 2:2'-hydrazopyridine, m. p. 168° (decomp.). Benzaldehyde and 2-aminopyridine afford *benzylidene-2:2'-dipyridylamine*, $(C_5H_4N \cdot NH)_2CHPh$, m. p. 109°, which passes above its m. p. into 2-aminopyridine and *benzylidene-2-aminopyridine*, b. p. 200°/18 mm.; the latter compound is converted by water into benzaldehyde and *benzylidene-2:2'-dipyridylamine*. *Benzylidene-3-aminopyridine* has b. p. 315°/atm. pressure.

H. WREN.

2:5-Diaminopyridine and 2:3-diaminopyridine. A. E. TSCHITSCHIBABIN and A. W. KIRSANOV (Ber., 1927, 60, [B], 766—776).—2:5-Diaminopyridine is conveniently prepared by the action of tin and hydrochloric acid on 5-nitro-2-aminopyridine; when pure, it is reasonably stable towards light and air. The *dihydrochloride*, *chlorostannite*, m. p. 208° after incipient decomposition at 190°, and *diacetyl* derivative, m. p. 289—290°, are described. When suitably treated with nitrous acid, the diamine gives diazonium salts containing an intact amino-group in position 2, from which, by the customary reactions, 5-chloro-2-aminopyridine, m. p. 134—135°, 5-iodo-2-aminopyridine, m. p. 128.5°, and 2-aminopyridyl-5-arsinic acid, m. p. 137—140° when rapidly heated, are obtained; the sodium (+6H₂O), cupric, ferric, and silver salts of the acid are described.

Reduction of 3-nitro-2-aminopyridine with tin and hydrochloric acid affords 2:3-diaminopyridine, m. p. 112—113°, and 4(or 6)-chloro-2:3-diaminopyridine, m. p. 131—132°. 2:3-Diaminopyridine behaves as a typical *o*-diamine, yielding dicyclic derivatives, $C_5H_4N_4$, m. p. 195°, with nitrous acid; $C_7H_7N_3$, m. p. 189.5—190.5° with acetic anhydride; $C_{19}H_{13}N_3$, m. p. 136—138°, with benzil, and $C_{19}H_{11}N_3$, m. p. 217—218° (decomp.), with phenanthraquinone. 4(or 6)-Chloro-2:3-diaminopyridine similarly affords the compounds, $C_5H_3N_4Cl$, m. p. 211—212° after

darkening at 195°, with nitrous acid, $C_7H_6N_3Cl$, m. p. 176—177°, with acetic anhydride, and $C_{19}H_{10}N_3Cl$ with phenanthraquinone.

Reduction of 5-chloro-3-nitro-2-aminopyridine (to be described later) with tin and hydrochloric acid yields 5-chloro-2:3-diaminopyridine, m. p. 164.5—165°, and 5:6(or 4:5)-dichloro-2:3-diaminopyridine, m. p. 165—166° [condensation product with phenanthraquinone, $C_{19}H_9N_3Cl_2$, m. p. 252—254° (decomp.)].

H. WREN.

Indole condensation of phenylhydrazones. A. KORCZYNSKI, W. BRYDOWNA, and L. KIERZEK (Bull. Acad. Polonaise, 1926, A, 149—158).—See this vol., 255.

Synthesis of quinoline and acridine compounds. K. MATSUMURA (J. Amer. Chem. Soc., 1927, 49, 810—818).—Sulphonation of 8-hydroxyquinoline affords the 5-sulphonic acid, which forms a hydrate and has m. p. (anhydrous) 322—323° (cf. Claus and Posselt, A., 1890, 522). An alkaline solution with benzenediazonium chloride gives 8-hydroxyquinoline-7-azobenzene-5-sulphonic acid, dark red, m. p. 310° after darkening at 267° (sodium salt, orange), and this, on reduction with stannous chloride and hydrochloric acid, affords 7-amino-8-hydroxyquinoline-5-sulphonic acid, (+1H₂O), orange, m. p. (anhydrous) not below 310° [N-acetyl derivative, yellow, m. p. 277° (decomp.); N-p-nitrobenzoyl derivative, yellow, m. p. 297° (decomp.)]. Diazotisation of the latter affords the corresponding diazonium derivative, yellow, decomp. above 187°, which, when heated with concentrated sulphuric acid at 120—150°, yields 7:8-dihydroxyquinoline-5-sulphonic acid, yellow, m. p. 302° (decomp.) (cf. Claus and Baumann, A., 1897, i, 580). When heated with hydrochloric acid at 170°, 7-amino-8-hydroxyquinoline-5-sulphonic acid is converted into 7-amino-8-hydroxyquinoline, decomp. above 117°, m. p. 124° [hydrochloride, m. p. 256°; picrate, m. p. 205° (decomp.); N-acetyl derivative, m. p. 177° (methiodide, yellow, m. p. 195°)]. Treatment of an alkaline solution of 8-hydroxyquinoline with iodine in aqueous potassium iodide yields 5-iodo-8-hydroxyquinoline, m. p. 127—128° (methiodide, m. p. 142°), together with 5:7-di-iodo-8-hydroxyquinoline, decomp. above 195°, m. p. 210° (cf. Claus, G.P. 78,880). 5-Nitro-8-hydroxyquinoline yields, similarly, 7-iodo-5-nitro-8-hydroxyquinoline, orange, m. p. 249° (decomp.), which, on reduction with stannous chloride, affords 7-iodo-5-amino-8-hydroxyquinoline, m. p. 157° after softening at 147° [hydrochloride, m. p. 255° (decomp.); picrate, decomp. 159°].

When heated in amyl-alcoholic solution with copper-bronze, o-chlorobenzoic acid and o-phenetidine yield 2-ethoxydiphenylamine-2'-carboxylic acid, yellow, m. p. 160—161°, and this, when treated with concentrated sulphuric acid at 100°, yields 4-hydroxyacridone, yellow, m. p. 300° (cf. Ullmann, A., 1907, i, 842), together with 4-ethoxyacridone, yellow, m. p. 320° (decomp.). Reduction of the latter with sodium and amyl alcohol yields 4-ethoxyacridine, yellow, m. p. 80° [hydrochloride, yellow, m. p. 220° (decomp.); sulphate, yellow, m. p. 250°; picrate, yellow, m. p. 255°; methosulphate, orange-yellow,

m. p. 189°]. 4-Hydroxyacridone yields similarly 4-hydroxyacridine, yellow, m. p. 117° [hydrochloride, orange, m. p. 252° (decomp.); sulphate, orange, m. p. 240°; picrate, orange, m. p. 215°]. Sulphonation of the latter affords 4-hydroxyacridine-1-sulphonic acid, yellow, m. p. 301° (decomp.), and the potassium salt of this, when treated in aqueous solution with potassium iodide and bleaching powder, yields 3-iodo-4-hydroxyacridine-1-sulphonic acid, yellow, decomp. above 240°, m. p. 264°.

F. G. WILLSON.

Quinoline derivatives. III. 2-Phenylquinoline-4-carboxylic acid. H. JOHN [with F. KAHL (J. pr. Chem., 1927, [ii], 115, 279—280)].—Dry distillation of manganese, cobalt, and nickel 2-phenylquinoline-4-carboxylates yields only 2-phenylquinoline, but the beryllium, vanadium, chromium, zirconium, mercury, thorium, and uranium salts give, in addition, the compound of m. p. 303° (cf. this vol., 159).

H. E. F. NOTTON.

Glyoxalone and glyoxalidone as anhydrides of amino-acid derivatives. C. GRÄNACHER and M. MAHLER (Helv. Chim. Acta, 1927, 10, 246—262).—Tripeptide derivatives of the type

$R \cdot CO \cdot NH \cdot C(\cdot CHR') \cdot CO \cdot NH \cdot CH_2 \cdot CO_2 R''$ (I) are smoothly converted into glyoxaline derivatives of the type $CO_2 R'' \cdot CH_2 \cdot N < \begin{matrix} CO \cdot C \cdot CHR' \\ CR : N \end{matrix}$ by simply heat-

ing above their m. p. in a vacuum, providing the asterisked carbon atom is primary. When it is secondary, fission occurs, yielding the lactimide (lactimone, cf. Mohr and Geis, A., 1908, i, 339), $O < \begin{matrix} CO \cdot C \cdot CHR'' \\ CR : N \end{matrix}$, and the amino-ester,

$CHR''' \cdot NH_2 \cdot CO_2 R''$ (R''' =group attached to the secondary carbon). Ethyl α -benzamidocinnamylaminoacetate (I, R and R' =Ph, R'' =Et), m. p. 135—136°, prepared by the condensation of glycine ester with the lactimide of benzylidenehippuric acid in alcoholic solution, on hydrolysis with dilute sodium hydroxide solution, yields the free amino-acid, m. p. 165° (decomp.), and when heated at 170° under 12 mm. for 2 hrs. yields ethyl 2-phenyl-4-benzylideneglyoxal-5-one-1-acetate, m. p. 108—110°. This on hydrolysis with sodium carbonate in aqueous-alcoholic solution yields the free acid, m. p. 200—202° (decomp.) (sodium salt), which on reduction either with sodium amalgam and acetic acid or catalytically yields the fully reduced 2-phenyl-4-benzylglyoxalid-5-one-1-acetic acid, $CO_2 H \cdot CH_2 \cdot NH < \begin{matrix} CO - CH \cdot CH_2 Ph \\ CHPh \cdot NH \end{matrix}$, m. p. 158—

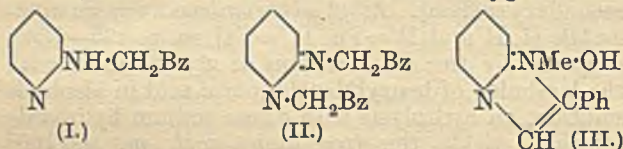
160°, which is stable to hot, dilute alkali, but is readily hydrolysed to benzaldehyde and phenylalanylglycine (or its anhydride) by heating with 0.1N-hydrochloric acid, or with alcohol in a sealed tube for 3 hrs. at 170—180°. Reduction of α -benzamidocinnamylglycine with 2.5% sodium amalgam yields α -benzoyl- β -phenylpropionylglycine (benzoyl-phenylalanylglycine; cf. Mohr and Stroschein, A., 1909, i, 581). By the application of similar methods are obtained α -acetamidocinnamylglycine, m. p. 185—188° (decomp.) (ethyl ester, I, R=Me, R' =Ph, R'' =Et, m. p. 155°); ethyl 2-methyl-4-benzylideneiminazol-5-

one-1-acetate (hydrolysed to the *sodium* salt of the corresponding acid), which on reduction probably yields the iminazolidone derivative, since on preparing the oily *amide* of the product, fission into phenylalanylglycine and acetaldehyde occurs, the same products being obtained by the action of hydrochloric acid. Condensation of leucine ester hydrochloride with the lactimide of hippuric acid in presence of sodium ethoxide yields the *ethyl ester*, m. p. 173°, of the amorphous α -benzamidocinnamyl-leucine, which is obtained on hydrolysis. By a similar method is obtained the amorphous α -benzamidocinnamylalanine (*ethyl ester*, m. p. 116—117°). α -Benzamidoisobutyryl-lactimide condensed with glycine ester hydrochloride yields α -benzamidoisobutyrylglycine ester, m. p. 123—124°, and with alcoholic methylamine yields α -benzamidoisobutyrylmethylamide, m. p. 140—142°.

J. W. BAKER.

Manufacture of barbituric acid derivatives. J. D. RIEDEL.—See B., 1927, 237.

Tautomerism of 2-aminopyridine. V. 2-Phenylpyriminazole and the preparation of the homologues of pyriminazole. A. E. TSCHITSCHIBABIN (J. Russ. Phys. Chem. Soc., 1926, 58, 1159—1169; cf. A., 1921, i, 450; 1924, i, 987; 1925, i, 158, 1328).—The preparation and properties of the products of interaction of phenacyl bromide and 2-aminopyridine are described and discussed from the point of view of ring-chain tautomerism in heterocyclic compounds. This interaction readily yields a bromide, m. p. 129°, which, on treatment with alkali, gives a base, m. p. 140°, which contains no oxygen, so cannot have the structure (I) suggested by Palazzo and Marogna. Both the bromide and the free base give chloroplatinates, which lose water when heated, but otherwise contain no oxygen. The



bromide cannot be benzoylated, so that the interaction of phenacyl bromide and α -aminopyridine must result in ring closure with the formation of 2-phenylpyriminazole. Further action of alkali on the mother-liquor after the separation of the bromide gives a second base, m. p. 120° (*chloroplatinate*, m. p. 242°). The corresponding bromide is obtained by the action of phenacyl bromide on 2-phenylpyriminazole. The insolubility, stability, and precipitation with alkalis of the free base suggest the open-chain structure (II) which gives the pyriminazole ring on treatment with acids. 2-Phenylpyriminazole methiodide, m. p. 220—221°, does not give a base on treatment with alkali, but gives with moist silver oxide a strongly alkaline, very soluble *quaternary ammonium base*, which must therefore have the ring structure (III).

M. ZVEGINTZOV.

Reaction of nicotinic acid with picric and picrolonic (?) acids. Y. SENDJU (J. Biochem. [Japan], 1926, 6, 161—162).—Nicotinic acid (obtained by condensation of glycine with nicotinic acid) with picric acid yields the yellow compound,

$C_8H_8O_3N_2, C_5H_3O_7N_3$, m. p. 167°; with picrolonic (?) acid, the compound $C_8H_8O_3N_2, C_{10}H_8O_5N_4$, m. p. 196°, is obtained.

CHEMICAL ABSTRACTS.

Constitution of thiasine. E. B. NEWTON, S. R. BENEDICT, and H. D. DAKIN (Science, 1926, 64, 602).—Thiasine (Benedict, Newton, and Behre, A., 1926, 421) is identical with ergothioneine (Tanret, A., 1909, i, 671), the betaine of thiolhistidine (Barger and Ewins, J.C.S., 1911, 99, 2336).

A. A. ELDRIDGE.

Triazoles. IV. Mechanism of Brunner's triazole synthesis. K. BRUNNER and J. MEDWETH (Monatsh., 1926, 47, 741—746).—Evidence in favour of the mechanism suggested (A., 1915, i, 1007) for the synthesis of dimethyltriazole from diacetamide and semicarbazide has now been obtained by the synthesis of the hypothetical intermediate product. Cyanic acid does not react with dimethyltriazole in cold ethereal solution, but when potassium cyanate is added to an acetic acid solution of this substance at -5° , 84% of 3:5-dimethyl-1:2:4-triazole-1-carboxylamide, m. p., when freshly prepared, 130° (decomp.), is precipitated. The latter does not show the reactions of the cyanate ion; it is quantitatively decomposed by (a) warm water, (b) alcohol, and (c) aniline, forming in each case 3:5-dimethyl-1:2:4-triazole, with (a) carbon dioxide and ammonia, (b) ethyl allophanate, and (c) *s*-diphenylcarbamide. The corresponding thiocarbamide was not formed from thiocyanic acid and dimethyltriazole. As was expected, a carboxylamide could not be obtained thus from 1-phenyl-3:5-dimethyl-1:2:4-triazole and cyanic acid, and thiocyanic acid gave only a *thiocyanate*, m. p. 116—117°.

H. E. F. NOTTON.

Triazoles. V. Phenyl dimethyltriazole derivatives. W. GABEL and O. SCHMIDEGG (Monatsh., 1926, 47, 747—753).—1-Phenyl-3:5-dimethyl-1:2:4-triazole, prepared by an improved method, gives a *methiodide*, m. p. 158—159°; *methochloride* (*chloroplatinate*; *mercurichloride*, $C_{11}H_{14}N_3Cl_3HgCl_2$); *methohydroxide*; *ethiodide*, m. p. 194°, decomposed into free base and ethyl iodide at 300°; *ethochloride*, m. p. 54° (*chloroplatinate*), and *ethohydroxide*. When heated at 100° with fuming sulphuric acid containing 31% of sulphur trioxide, phenyl dimethyltriazole gives a *monosulphonic acid* ($+H_2O$); the *barium*, *copper*, *potassium*, and *sodium* salts are described.

H. E. F. NOTTON.

Triazoles. VI. Nitration of phenyl- and naphthyl-1:2:4-triazoles. F. HERNLER and F. MATTHES (Monatsh., 1926, 47, 791—802).—1-Nitrophenyl-3:5-dimethyl-1:2:4-triazole (75%), m. p. 149° (*picrate*, m. p. 141—142°, *chloroplatinate*, decomp. 270°), is obtained from phenyl dimethyltriazole and nitric-sulphuric acids at 65°. It is reduced by alkaline stannous chloride to an *azo-derivative*, m. p. 158°, and by tin and hydrochloric acid to *aminophenyl dimethyltriazole*, m. p. 183° [*picrate*, m. p. 177°; *chloroplatinate*, decomp. 250°; impure *acetyl derivatives*, m. p. 91—93°, and 109—116° (mixtures (?) of mono- and diacetyl derivatives), from which pure *acetamidophenyl dimethyltriazole picrate*, m. p. 196°, was isolated; *benzoyl derivative*, m. p. 88—90°]. The amino-group in this substance could be diazotised

and coupled with β -naphthol-3:6-disulphonic acid (red dye), but attempts to replace it by bromine in order to compare the product with 1-*p*-bromophenyl-3:5-dimethyl-1:2:4-triazole, m. p. 92—93° (picrate, m. p. 163—165°), prepared from *p*-bromophenylhydrazine and diacetamide, were unsuccessful. *o*-, *m*-, and *p*-Nitrophenylhydrazines and diacetamide give principally the corresponding acetylnitrophenylhydrazines; only in the case of the *m*-derivative could a triazole, 1-*m*-nitrophenyl-3:5-dimethyl-1:2:4-triazole, m. p. 128°, be isolated. This is not identical with the product of direct nitration. Attempts to establish the constitution of the latter by synthesis from *p*-acetamidophenylhydrazine or by reductive or oxidative fission were also fruitless. The following were obtained by direct nitration: 1-nitro- α -naphthyl-, m. p. 75—76°; 1-nitro- β -naphthyl-, m. p. 85°, and 1-nitrosulphophenyl-3:5-dimethyl-1:2:4-triazole (cf. preceding abstract); also 1-nitrophenyl-3:5-diethyl-1:2:4-triazole, m. p. 105—106°, which is reduced by tin and hydrochloric acid to 1-aminophenyldiethyltriazole, m. p. 119—120° (hydrochloride, m. p. 66—69°; chloroplatinate; benzoyl derivative, m. p. 161—162°). H. E. F. NOTTON.

7-Amino-derivatives of benztriazole and benziminazole. H. LINDEMANN and H. KRAUSE (J. pr. Chem., 1927, [ii], 115, 256—273).—The 7-amino-benztriazoles and -benziminazoles here described, like the 1-aminocarbazoles (A., 1926, 75), do not undergo ring closure in the 1:7-position when treated with nitrous acid or acetic anhydride. Instead, with the former they give diazonium salts which couple in the normal manner with amines or phenols, forming, for example, 2:5-dimethyl-7-benziminazoleazo- β -naphthylamine, red, m. p. 281°, and 2:5-dimethyl-7-benziminazoleazo- β -naphthol, bluish-red, m. p. 210°. 3-Nitro-4:5-diaminobenzoic acid (monoethylchloride; monoacetyl derivative, m. p. 270°) is conveniently prepared by heating 4-chloro-3:5-dinitrobenzoic acid with excess of aqueous ammonia and reducing directly with hydrogen sulphide. It is converted by acetic anhydride in presence of sulphuric acid into 7-nitro-2-methylbenziminazole-5-carboxylic acid, m. p. 305°, which is reduced by tin and hydrochloric acid to the 7-amino-derivative, m. p. 310° (hydrochloride; acetyl derivative, m. p. above 375°); and by nitrous acid into 7-nitrobenztriazole-5-carboxylic acid, m. p. 300° (decomp.), which is reduced similarly to 7-amino-benztriazole-5-carboxylic acid, m. p. 310° (hydrochloride; acetyl derivative, m. p. 315°). 3:5-Dinitro-*p*-toluidine is reduced by sodium sulphide to 3-nitro-4:5-diaminotoluene (I), m. p. 158° (monoacetyl derivative, m. p. 211°), which gives 7-nitro-2:5-dimethylbenziminazole, m. p. 248°, with acetic anhydride; (I) is further reduced by stannous chloride and hydrochloric acid to 3:4:5-triaminotoluene, m. p. 105°. When the triacetyl derivative, m. p. 249°, of this is boiled with hydrochloric acid, or 3:5-dinitro-4-acetamidotoluene is reduced with stannous chloride and hydrochloric acid, 7-amino-2:5-dimethylbenziminazole (+H₂O), m. p. 100°, is formed. Its diacetyl derivative, m. p. 169°, is easily hydrolysed by acids to a monoacetyl derivative, m. p. 160° (hydrochloride, m. p. 235°; acetate, m. p. 125°). On treatment with

nitrous acid, (I) affords 7-nitro-5-methylbenztriazole, m. p. 277° (decomp.), which is reduced to 7-amino-5-methylbenztriazole, m. p. 155° (diacetyl derivative, m. p. 226°, hydrolysed by ammonia to a monoacetyl derivative, m. p. 230°). H. E. F. NOTTON.

Azo-dyes [naphthatriazoles]. I. G. FARBENIND. etc.—See B., 1927, 275.

Synthesis of 8-methyl-7-ethylxanthine from a glyoxaline derivative. F. M. DIAZ DE PLAZA (Anal. Fis. Quim., 1926, 24, 731—737).—From 5-chloro-4-nitro-2-methyl-1-ethylglyoxaline, prepared by the method of Sarasin and Wegmann (A., 1924, i, 1115), 4-nitro-2-methyl-1-ethylglyoxaline-5-carboxylamide, m. p. 272° (decomp.), was obtained by way of 5-chloro-4-nitro-2-methyl-1-ethylglyoxaline, m. p. 77°. By reduction of the above amide, 4-amino-2-methyl-1-ethylglyoxaline-5-carboxylamide, m. p. 166°, was obtained; the hydrochloride has m. p. 195°. By heating the free base with ethyl carbonate, 8-methyl-7-ethylxanthine, m. p. 340° (decomp.), was obtained. G. W. ROBINSON.

Porphyrin syntheses. IX. New porphyrin synthesis. Oxidation of porphyrins. H. FISCHER, P. HALBIG, and B. WALACH (Annalen, 1927, 452, 268—302; cf. A., 1926, 1261).—Porphins are obtained by condensing a dibromobispyrrylmethene salt with an α -dimethylbispyrrylmethene salt in glacial acetic acid at about 200°. Thus, bis-(2-bromo-3:4-dimethylpyrryl)methene hydrobromide and bis-(3:4:5-trimethylpyrryl)methene hydrochloride yield octamethylporphin, together with 5-acetyl-3:4:5-trimethylpyrrole, whilst a hexamethyldiethylporphin (unmelted at 360°) is obtained from the dibromomethene and biscriptopyrrylmethene [bis-(2:3-dimethyl-4-ethylpyrryl)methene]. These porphins and isoetioporphyrin show no observable spectroscopic difference in nitrobenzene solution. Cautious oxidation of octamethylporphin with hydrogen peroxide in concentrated sulphuric acid solution at 10° gives a red, crystalline substance, C₂₈H₂₈ON₄; at 15—20° the product is dimethylmaleinimide, m. p. 118°.

isoEtioporphyris are obtained (i) by air oxidation of bis-(2-carboxy-3-methyl-4-ethyl-5-pyrryl)methane in formic acid; (ii) by condensing bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)methene with bis-(2:3-dimethyl-4-ethyl-5-pyrryl)methene in glacial acetic acid at 180—190°; (iii) by condensing the dibromomethene with bis-(2:4-dimethyl-3-ethyl-5-pyrryl)methene; (iv) by heating bis-(2-carboxy-3-methyl-4-ethyl-5-pyrryl)methane with 20% sodium hydroxide and silver at 180°. All four products give identical spectra, as do their respective copper and iron salts. Crystallographic measurements by STEINMETZ show that (iii) differs from (i) and (ii), which are identical; (iv) is probably different from the other two. Oxidation with hydrogen peroxide in concentrated sulphuric acid gives a substance, C₃₂H₃₆ or 38ON₄, m. p. 236°. isoEtioporphyrin is oxidised by air in bright sunshine to methylethylmaleinimide.

isoMesoporphyrin (methyl ester, m. p. 275°) is obtained by condensing together (i) bis-(2-carboxy-3-methyl-4-ethyl-5-pyrryl)methane and bis-(2-carboxy-3-methyl-4- β -carboxyethyl-5-pyrryl)methane in

formic acid in a current of air, or (ii) bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)methene and bis-(2:3-dimethyl-4-β-carboxyethyl-5-pyrryl)methene in glacial acetic acid at 190°. Crystallographic data by STEINMETZ confirm the identity.

4-Carbethoxy-3:5-dimethylpyrryl-2:4-dimethylpyrrolenylmethene, m. p. 120°, from ethyl 2-aldehyde-3:5-dimethylpyrrole-4-carboxylate and 2:4-dimethylpyrrole; 3:5-dimethyl-4-ethylpyrryl-(3-carbethoxy-2:4-dimethylpyrrolenyl)methene, m. p. 132°, from cryptopyrrolealdehyde and ethyl 2:4-dimethylpyrrole-3-carboxylate; bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)methene, m. p. 182° (hydrobromide, unmelting at 270°), from the methane by bromination, and bis-(2:3-dimethyl-4-β-carboxyethyl-5-pyrryl)methene hydrochloride, m. p. 212° (decomp.), by condensation of 2:3-dimethyl-4-β-carbomethoxyethylpyrrole with formic-hydrochloric acid, are described.

[With M. SCHUBERT and A. OSSENBRUNNER].—Cryptopyrrole, condensed with hydrogen cyanide in chloroform saturated with hydrogen chloride, gives cryptopyrrolealdehyde (azine, m. p. 172°) in 90% yield without isolation of the aldimine. The "amine," formerly (Fischer and Schubert, A., 1924, i, 544) considered to be bis-(2:4-dimethyl-3-ethylpyrryl)methylamine, formed as a by-product in the aldehyde preparation, melts at 148° (not 142°) and has the composition C₁₈H₂₅N₃.

Ethyl 2:4-dimethyl-3-ethyl-5-pyrrylglyoxylate, m. p. 80°, obtained by way of its imine from cryptopyrrole and ethyl cyanofornate, is hydrolysed to the free acid (darkens at 150° and decomposes). Cryptopyrrolealdehyde condenses with hippuric acid to give the azlactone, m. p. 172°, with ethyl cyanoacetate to form the compound C₁₄H₁₈O₂N₂, m. p. 122°, and with oxindole to give the compound C₁₇H₁₈ON₂, m. p. 227° (darkens at 196°). Cryptopyrrolealdehyde is converted by acetic anhydride into α-cyanocryptopyrrole, m. p. 134°. Dicyrptopyrrylmethene, m. p. 151° [perchlorate; hydrobromide; sulphate; arsenate (decomp. 211°); picrate (decomp. 174°)], is prepared by condensing cryptopyrrole with hydrogen cyanide or with formic acid, and also results from the action of arsenic acid on cryptopyrrole. It forms complex salts with nickel, m. p. 200—203°; cobalt, m. p. 198°; copper, 185—187°; zinc, m. p. 197°; ferrous iron, decomp. 215°, and mercury, m. p. 160° (decomp.). By reduction with zinc dust and acetic acid, it regenerates cryptopyrrole; oxidation with nitric acid or chromic acid gives methylethylmaleinimide, m. p. 69°.

C. HOLLINS.

Disulphoisatide. A. WAHL and FÉRICÉAN (Compt. rend., 1927, 184, 826—828).—By the action of hydrogen sulphide on a cold suspension of isatin in 10 parts of alcohol, 90% of the theoretical yield of disulphoisatide is obtained. The amount of sulphur eliminated is in agreement with Laurent's formula, 2C₈H₅O₂N+3H₂S=C₁₆H₁₂O₂N₂S₂+2H₂O+S (cf. A., 1924, i, 322), and not with that recently proposed by Sander (cf. A., 1925, i, 977). Mol. wt. determinations in phenol give 320—324 for disulphoisatide.

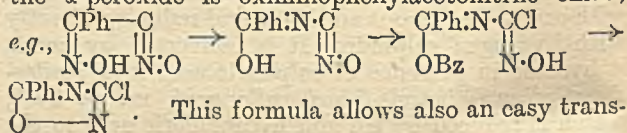
R. BRIGHTMAN.

Dioximes. XLII. G. PONZIO and L. AVOGADRO (Gazzetta, 1927, 57, 124—138).—The arylglyoxime peroxides, regarded by Wieland (A., 1908, i, 108;

1921, i, 605) as 4-aryl-1:2:5-oxadiazole 2- and 4-oxides, or as 2:3-cyclic oxides, have different constitutions. Whilst Wieland's formula is accepted for dibenzoylglyoxime peroxide, α-phenylglyoxime peroxide, m. p. 108—112°, is now regarded as oximino-phenylacetonitrile oxide, and the β-form, m. p. 108°, as a true peroxide, $\begin{array}{c} \text{CPh-CH} \\ \text{N}\cdot\text{O}\cdot\text{O}\cdot\text{N} \end{array}$.

A mixture of the α- and β-forms melts at 65—90°. Whilst the α-peroxide is hydrolysed by sodium hydroxide to phenylmetazonic acid and 3-hydroxy-5-phenyl- and 5-hydroxy-3-phenyl-1:2:4-oxadiazoles, the β-peroxide gives ω-nitrophenylacetonitrile. Whilst benzoyl chloride converts the α-peroxide into 3-chloro-5-phenyl-1:2:4-oxadiazole, m. p. 5.5°, b. p. 171°/134 mm., the β-peroxide does not react. (The diphenyl-, phenylmethyl-, and benzoylmethyl-glyoxime peroxides similarly do not react, in contrast with diacylglyoxime peroxides.) 3-Chloro-5-phenyloxadiazole is also obtained by the action of phosphorus pentachloride, in which process 5-phenyloxadiazole is not formed (cf. Wieland and Semper, A., 1908, i, 108); it is stable to alkali, but reacts with sodium ethoxide or methoxide to give the 3-alkoxy-derivatives (see this vol., 462). Benzoyl bromide does not react with the β-peroxide, but converts the α-peroxide into 3-bromo-5-phenyl-1:2:4-oxadiazole, m. p. 68°, stable to alkali, but reacting with sodium alkoxide to give an alkoxy- and ultimately the hydroxy-derivative, for which this is a convenient method of preparation; the bromo-compound is also obtained by the action of phosphorus pentabromide. By the action of hydriodic acid on either peroxide, but more readily with the α-form, 5-phenyloxadiazole is formed, with ω-aminoacetophenone (phenylhydrazone, new m. p. 163°).

These reactions, with those previously described (A., 1923, i, 472, 855, 1019, 1137; 1926, 1159; this vol., 134, 135), are best explained by assuming that the α-peroxide is oximino-phenylacetonitrile oxide;



This formula allows also an easy transformation into the β, true peroxide form: $\begin{array}{c} \text{CPh-CH} \\ \parallel \\ \text{N}\cdot\text{OH}\text{N}\cdot\text{O} \end{array}$

→ $\begin{array}{c} \text{CPh-CH} \\ \parallel \\ \text{N}\cdot\text{O}\cdot\text{O}\cdot\text{N} \end{array}$. Wieland's formulae involve an

unlikely migration of an oxygen atom: $\begin{array}{c} \text{CPh-CH} \\ \parallel \\ \text{N}\cdot\text{O}\cdot\text{N}\cdot\text{O} \end{array} \rightarrow$

$\begin{array}{c} \text{CPh-CH} \\ \parallel \\ \text{O}\cdot\text{N}\cdot\text{O}\cdot\text{N} \end{array}$. Further, the resulting extranuclear oxygen atom would be expected to be reactive.

β-p-Tolylglyoxime, obtained from p-tolyl oximino-methyl ketone (new m. p. 107—108°; +H₂O, 83—84°), gives in nitric acid the corresponding β-peroxide, m. p. 100—101°. This is reduced by zinc and acetic acid, and is converted by sodium hydroxide into the compound C₆H₄Me·C(CN)·NO₂Na.

E. W. WIGNALL.

Anthraquinone vat dyes [thiazines]. I. G. FARBENIND.—See B., 1927, 211.

Conessine. D. D. KANGA, P. R. AYYAR, and J. L. SIMONSEN (J. Indian Inst. Sci., 1927, **9A**, 173—177).—See A., 1926, 1047.

Yohimba alkaloids. II and III. G. HAHN and W. BRANDENBURG (Ber., 1927, **60**, [B], 669—679, 707—711; cf. A., 1926, 1263).—II. A solution of the residues from the technical isolation of yohimbine is rendered just alkaline with ammonia and the precipitate (*A*) is removed; the filtrate is evaporated to dryness, giving a residue *B*. The solution of the latter substance in the requisite quantity of ammonia is placed under diminished pressure at a temperature not exceeding 30°, whereby yohimbenic and allo-yohimboic acids are successively deposited. Complete separation of the two acids from one another is achieved by taking advantage of (*a*) the sparing solubility of yohimbenic acid hydrochloride in dilute, aqueous hydrochloric acid, (*b*) the behaviour of yohimbenic acid towards methyl or ethyl alcohol (*loc. cit.*), or (*c*) the sparing solubility of alloyohimboic acid hydrochloride in methyl alcohol. Isolation of yohimboic and isoyohimboic acids from the residues is effected by esterification with ethyl alcohol and hydrogen chloride, removal of the sparingly soluble ethyl yohimboate hydrochloride, and separation of ethyl isoyohimboate from the filtrate. The precipitate *A* (see above) is treated with benzene and hydrogen chloride is passed into the solution. The bases are liberated from the precipitated hydrochlorides and hydrolysed with alcoholic potassium hydroxide. Yohimbenic acid and the ethyl esters of yohimboic and isoyohimboic acids are obtained from the solution by the methods just described. The following compounds are described in detail: alloyohimbine, $C_{21}H_{26}O_3N_2$ or $C_{22}H_{28}O_3N_2$, $[\alpha]_D^{20} -72.7^\circ$ in pyridine (also trihydrate, m. p. 98—99°, and monohydrate, m. p. 135—140°), which is considered identical with the dihydroyohimbine of Warnat (A., 1926, 1263) [Warnat's nomenclature is criticised, since the relationship of the substance to yohimbine rests solely on a somewhat indefinite analysis]; alloyohimbine hydrochloride, decomp. 278—279°; alloyohimboic acid, $C_{20}H_{24}O_3N_2 \cdot H_2O$, m. p. 248—250°, $[\alpha]_D^{20} -79.5^\circ$ in pyridine (Warnat's dihydroyohimboic acid), and its hydrochloride, $C_{20}H_{24}O_3N_2 \cdot HCl \cdot H_2O$, m. p. 288—290° (decomp.); ethyl alloyohimboate hydrochloride; isoyohimboic acid, $C_{20}H_{24}O_3N_2 \cdot H_2O$, decomp. 268—269°, $[\alpha]_D^{20} +147^\circ$ in pyridine (also $+1.5H_2O$); isoyohimbine, m. p. 239—240°, $[\alpha]_D^{20} +57.6^\circ$ in pyridine, and its hydrochloride, m. p. 298—299° (decomp.); ethyl isoyohimboate, m. p. 243°.

III. Further analyses of "methyl-yohimbenic acid methylbetaine" (A., 1926, 1263) indicate the formula, $C_{21}H_{26}O_3N_2 \cdot 4H_2O$, whence the substance must be regarded as yohimbenic acid methylbetaine. To yohimbenic acid and yohimbene the formulae $C_{20}H_{24}O_3N_2 \cdot 2H_2O$ and $C_{21}H_{26}O_3N_2$ are assigned. The compounds are thus isomeric with yohimbine, allo- and iso-yohimbine, and yohimboic acid, respectively. The identity of Spiegel's meso-yohimbine (A., 1916, i, 286) with isoyohimbine is confirmed (cf. Warnat, A., 1926, 1263), but the supposed identity of isoyohimbine with corynanthine

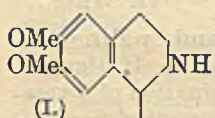
(cf. Fournau and Fiore, A., 1912, i, 49) cannot be maintained.

isoYohimbine hydrochloride has $[\alpha]_D^{20} +103.8^\circ$ in water. Yohimbine and isoyohimbine have $[\alpha]_D^{20} +84.11^\circ$ and $+57.6^\circ$ in pyridine, whereas the corresponding acids have $[\alpha]_D^{20} +79^\circ$ and $+147^\circ$ in the same solvent. Yohimbene has $[\alpha]_D^{18} +43.7^\circ$ in pyridine [a negative value was previously (*loc. cit.*) reported erroneously]. The following compounds are new: silver yohimbenate; yohimbenic acid hydrochloride, m. p. 299—300°; the perchlorate of yohimbenic acid methylbetaine; ethyl yohimbenate, m. p. 250—251°, and its hydrochloride, decomp. 223—225°.

H. WREN.

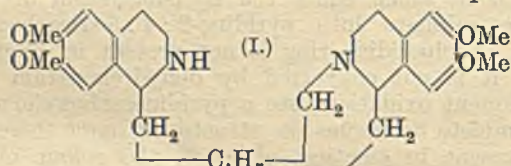
Ipecacuanha alkaloids. I. Constitution of emetine and cephaline. E. SPÄTH and W. LETTHE (Ber., 1927, **60**, [B], 688—702).—The possibility that emetine resembles palmatine in structure is discounted by the observation that it fails to yield hemipinic acid in addition to *m*-hemipinic acid when oxidised. The presence of a berberine-like complex is improbable, since it is oxidised to oxalic acid under conditions which cause the transformation of berberine sulphate into pyridine-2 : 4 : 5-tricarboxylic acid. A piperidine ring is not present in emetine, since it is not converted by dehydrogenation and subsequent oxidation into a pyridinecarboxylic acid. A complete berberine-like structure cannot therefore be present in emetine, although the colour of its dehydro-derivative indicates a close relationship. Since oxidation of emetine in faintly alkaline solution affords 1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline, the complex (I) must be present in the alkaloid. Since *N*-benzoylemetine is oxidised to 3 : 4-dimethoxy-6- β -benzamidoethylbenzoic acid, m. p. 172—173° (decomp.), the imino-group is present as such in the alkaloid. Since Carr and Pyman (J.C.S., 1914, **105**, 1591) obtained 6 : 7-dimethoxyisoquinoline-1-carboxylic acid by the oxidation of emetine, it appears either that an unusual instance of dehydrogenation of a dimethoxytetrahydroisoquinoline has been encountered or that the acid originates from a second nitrogenous complex. Evidence of the presence of a second tetrahydroisoquinoline group is obtained by the production of *m*-hemipinic acid from emetine in 65% of the amount derivable theoretically on the supposition of the presence of only one such nucleus, whereas, under similar conditions, palmatine and papaverine, which actually contain only one dimethoxyisoquinoline nucleus, give 34 and 28% of *m*-hemipinic and hemipinic acids and 25% of *m*-hemipinic acid, respectively. Further confirmation is obtained by treatment with permanganate of the residues left after the conversion of emetine into 1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline (see above); the yield of *m*-hemipinic acid attains 96% (after allowance for the ketonic base). Contrary to the observations of Carr and Pyman (*loc. cit.*) and of Windaus and Herman (A., 1914, i, 721), emetine yields *m*-hemipinic acid in addition to 1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline when oxidised.

Cephaline (of which emetine is the methyl ether)



is converted into cephaline *O*-ethyl ether, which appears to be oxidised by permanganate to a mixture of 1-keto-6 : 7-dimethoxy- and -7-methoxy-6-ethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline; the mixture could not be separated into its components, but its m. p. is raised by the addition of either of them. Further evidence in favour of this view is found in the production of *m*-hemipinic acid and the methyl ethyl ether of nor-*m*-hemipinic acid by more drastic oxidation.

In the second phase of the Emde degradation of emetine, trimethylamine is produced, whereby the presence of a secondary, monocyclic nitrogen atom appears confirmed. In the third stage of the degradation, the second tertiary nitrogen atom is not completely eliminated, hydrocarbons being obtained in poor yield. Since emetine under these conditions is not separated into two approximately similar components, the second tertiary nitrogen atom cannot represent the sole point of union of the two isoquinoline complexes, and the production of 2 mols. of 1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline from emetine indicates that in the second isoquinoline

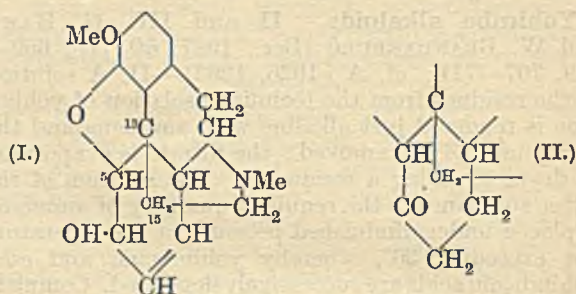


complex also a carbon chain is attached in position 1. The partial formula (I) is therefore suggested. Probably the tertiary nitrogen atom forms a portion of a piperidine ring.
H. WREN.

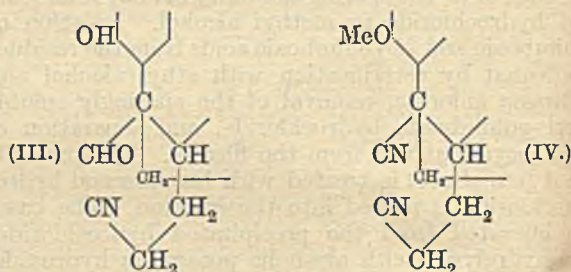
Synthesis of oxyberberine and palmatine. R. D. HAWORTH, J. B. KOEFLI, and W. H. PERKIN, jun. (J.C.S., 1927, 548—554).—Bromination of β -veratrylpropionic acid yielded β -6-bromoveratrylpropionic acid, m. p. 118—119°, which, when treated with sulphuric acid, formed 4-bromo-6 : 7-dimethoxy-1-hydrindone, m. p. 120—121°. From the isonitroso-derivative, m. p. 236° (decomp.), of this hydrindone, 6-bromo-2-carboxy-3 : 4-dimethoxyphenylacetone, m. p. (+H₂O) 98—100°, was obtained, and the anhydride, m. p. 151°, of this hydrolysed to 6-bromo-3 : 4-dimethoxyhomophthalic acid, m. p. 166—167°. This acid, debrominated (sodium amalgam) and treated with acetyl chloride, yielded the required 3 : 4-dimethoxyhomophthalic anhydride (I), m. p. 104—105°. The anhydride was condensed with β -piperonyl-ethylamine, and the methyl ester of the resulting crude amic acid boiled with phosphorus oxychloride, forming oxyberberine. Similarly, palmatine was synthesised by condensing (I) with β -veratrylethylamine, forming *N*- β -veratryl-3 : 4-dimethoxyhomophthalamic acid, the methyl ester of which, when treated with phosphorus oxychloride, yielded oxypalmatine, m. p. 183°. Oxypalmatine was reduced electrolytically to tetrahydropalmatine, and this was oxidised by iodine to palmatine iodide.
B. W. ANDERSON.

Morphine alkaloids. C. SCHÖPF (Annalen, 1927, 452, 211—267). I. **Constitution of morphine and codeine.**—For the linking of the C¹⁵ atom, Gulland and Robinson's suggestion (J.C.S., 1923, 123, 980,

989; A., 1926, 83) is confirmed as against the Knorr-Wieland formula (A., 1925, i, 1090, 1448), and the formula (I) for codeine is considered to be definitely proved. The oxime of dihydrocodeinone



(II) undergoes a Beckmann change when treated with cold thionyl chloride, giving an isooxime (III), m. p. 196—198° [*picrate*, m. p. 207—208°; *acetyl* derivative, m. p. 225° (decomp.); *oxime*, m. p. 218—219°]. This is shown to be a cyano-aldehyde

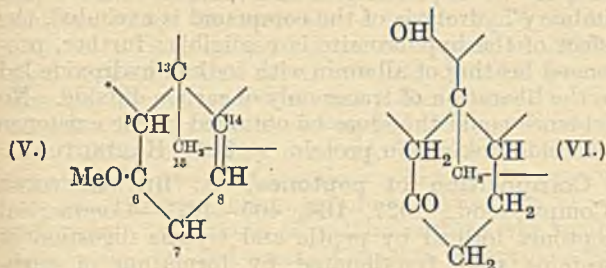


(Robinson structure), and not a cyano-ketone (Knorr-Wieland structure); the oxime of the methyl ether undergoes dehydration to a dinitrile which still contains intact the nitrogen ring, since by Hofmann degradation no loss of carbon atoms occurs. Any dehydration of the cyano-ketone (*cf.* dehydration of camphoroxime) would lead to fission of the nitrogen ring.

The isooxime (III) is methylated by Rodionov's method with phenyltrimethylammonium hydroxide (A., 1926, 532) to form the *methyl ether*, C₁₉H₂₄O₃N₂ [base, amorphous; *hydriodide*, m. p. 249—250°; *picrate*, m. p. 221° (decomp.); *oxime*, amorphous]. The oxime of the methyl ether is converted by cold thionyl chloride or hot acetic anhydride into a *dinitrile* (IV) (*methiodide* sinters at 200°, melts partly at 203—204°, decomposes at 207°). By heating the *methiodide* with sodium hydroxide, there is obtained an oily base, C₂₀H₂₅O₂N₃ (*perchlorate*, m. p. 203—204°; *methiodide* non-crystalline), which is reduced by hydrogen and palladium to a *dihydro-derivative* (*perchlorate*, m. p. 197—198°; *methiodide*, m. p. 190°).

II. **Constitution of thebaine** [with L. WINTERHALDER].—Thebaine, the methyl ether of an enolic codeinone, gives on reduction a mixture of products from which for the first time a pure crystalline tetrahydrothebaine is now isolated. This is found to be identical with Mannich's dihydromorphine dimethyl ether (A., 1917, i, 473). The presence of two double linkings in thebaine is thus demonstrated, since a cyclic bridge linking (*cf.* Wieland and Kotake, A., 1925, i, 1090, 1448) would not be reduced under the mild conditions employed, and the Knorr-Robinson

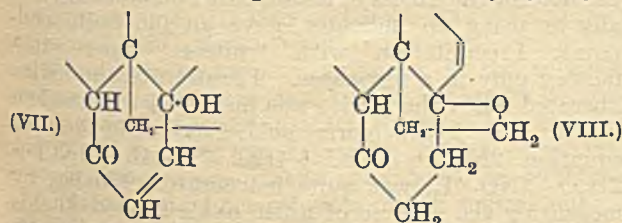
formula for thebaine (V) is established. The mechanism of the reduction is discussed. Dihydrothebaine,



first formed by reduction of $\Delta^{8(14)}$, is further reduced only under energetic conditions, giving dihydrothebaine (VI), the chain $-O\cdot CH\cdot CH\cdot CH-$ being analogous with a system of conjugated double linkings. Dihydrothebainone also results directly from thebaine, 1:6-reduction in the conjugated system $C^{14}-C^6-O$ being followed by 1:4-hydrogenation in the system C^5-C^8 and hydrolysis of the methoxyl. Tetrahydrothebaine is formed by 1:4-reduction in the system $C^{14}-C^6$, followed by reduction of the resulting $\Delta^{7(8)}$. In every case hydrogenation of C^{14} occurs, and indications of the production of stereoisomeric ketones are obtained when palladium-calcium carbonate is the catalyst.

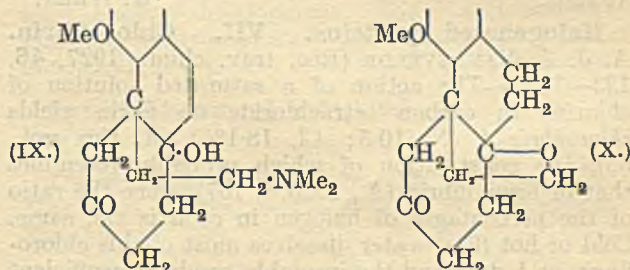
For the isolation of the reduction products, the ethereal solution of the mixed bases is shaken with alkali to remove some dihydrothebainone, m. p. 130—140°, and then deposits dihydrothebaine, m. p. 160—162° (picrate, m. p. 238°). The ether residue with hydroxylamine yields dihydrothebainoneoxime are treated with hydrochloric acid to convert dihydrothebaine into dihydrocodeinone, removed as oxime, m. p. 259°. The ether-soluble residues contain in 20% yield tetrahydrothebaine, m. p. 83°, after purification as picrate, m. p. 222°, or as hydrochloride, m. p. 115—116° (+H₂O). Tetrahydrothebaine methiodide melts at 135—140° (+H₂O) or 212° (anhyd.), and is probably a stereoisomeride of Freund and Speyer's product, m. p. 244—246° (A., 1921, i, 125).

III. Constitution and configuration of hydroxycodeinone [with F. BORKOWSKY].—The structure (VII) assigned by Gulland and Robinson (*loc. cit.*) to hydroxycodeinone is supported by known data and by further experimental evidence. Hydroxydihydrocodeone (VIII) (Freund and Speyer, A., 1917, i, 217), obtained in 33% yield by Hofmann degradation of hydroxydihydrocodeinone, gives a *phenylhydrazone*, m. p. 228°. The intermediate hydroxyde-*N*-methyl-dihydrocodeinone, m. p. 115°, is reduced by hydrogen



and palladium to the corresponding *dihydro*-compound, m. p. 136—137° (*methiodide*, m. p. 280°), which by

Hofmann degradation yields *hydroxytetrahydrocodeone* (as VIII, without double linking), m. p. 150—153°, obtained also by palladium-hydrogen reduction of hydroxydihydrocodeone. Reduction of hydroxydihydrocodeinone with aluminium amalgam, followed by methylation with diazomethane, methyl sulphate, or phenyltrimethylammonium hydroxide, gives hydroxydihydrothebainone methyl ether (Freund and Speyer, *loc. cit.*), m. p. 151—153° (*methiodide*, m. p. 206—208°), which by successive Hofmann degradations yields first a *base*, C₂₀H₂₇O₄N (IX), m. p. 133—135° (*methiodide*, m. p. 209°; *dihydro*-compound, m. p. 83—85°), and then *hydroxydihydrothebaine methyl ether*, m. p. 87—89° (obtainable also by methylation of hydroxydihydrothebaine with methyl sulphate), converted by means of hydrogen and palladium into the *tetrahydromethyl ether* (X), m. p. 74—76°. The latter is also obtained by reduction of the *base* (IX) to its *dihydro*-compound, m. p. 83—85° (*methiodide*, amorphous, m. p. 95—100°), followed by Hofmann degradation.



Hydroxyde-*N*-methyldihydrothebainone (Freund and Speyer, *loc. cit.*), m. p. 239—240°, is converted by dehydration with cold hydrobromic acid into the *hydrobromide*, m. p. 230—231°, of a *base*, C₁₉H₂₃O₃N, which is reduced by hydrogen and palladium to a *tetrahydro*-derivative, m. p. 135—137° (as *base*). The results of the determination of reactive (hydroxylic) hydrogen in a number of ketones and "des-bases" of the hydroxycodeinone series by Zerewitinov's method with magnesium methyl iodide are in accord with the formulæ assigned. C. HOLLINS.

Colour reactions of *apomorphine* and its detection in presence of *morphine*. J. VON MIKO (Pharm. Zentr., 1927, 68, 193—195).—One drop of aqueous ammonia added to 5 c.c. of aqueous *apomorphine* produces a green colour; subsequent shaking with chloroform gives a violet lower layer. A distinct pink tinge in the chloroform is given by 0.0002 g. of *apomorphine* in 1 c.c. of 1% aqueous *morphine*. *apomorphine* is said to be formed during the sterilisation of *morphine* on the water-bath; this is not the case. B. W. ANDERSON.

Opium alkaloids. VII. Synthesis of *laudanine* and *laudanidine*. E. SPÄTH and A. BURGER (Monatsh., 1926, 47, 733—740).—A second synthesis of *laudanine* (cf. A., 1922, i, 568) has now been based on Pictet's synthesis of *laudanidine* (A., 1900, i, 685; 1909, i, 323). The latter is prepared in 70% yield by electrolytic reduction of a solution of crude *papaverine* methosulphate in dilute sulphuric acid, using a lead cathode. The racemic *laudanidine* is partly hydrolysed by heating in a sealed tube with

10 times its weight of hydrochloric acid (d 1.19) for exactly 20 min. at 100°. The product is extracted with sodium hydroxide, when laudanone (50%) remains undissolved, whilst the solution contains a mixture of phenolic bases from which laudanone (12%) may be isolated. *d*- and *l*-Laudanone are converted in the same way into *d*-laudanone, $[\alpha]_D^{25} +93.5^\circ$, and *l*-laudanone, $[\alpha]_D^{25} -94.8^\circ$, the latter being identical with laudanidine. Attempts to resolve laudanone directly were unsuccessful.

H. E. F. NOTTON.

Opium alkaloids. VIII. Synthesis of papaverine. E. SPATH and A. BURGER (Ber., 1927, 60, [B], 704—706).—The final step in Pictet and Gams' synthesis of papaverine (cf. A., 1909, i, 671) is accomplished by the conversion of dihydropapaverine into papaverine by the action of palladised asbestos (40%) at 200° in presence of air. Under similar conditions, tetrahydropapaverine also yields papaverine which is only slightly affected by the reagent at 225°.

H. WREN.

Halogenated proteins. VII. Chlorofibrin. A. J. J. VANDEVELDE (Rec. trav. chim., 1927, 46, 133—136).—The action of a saturated solution of chlorine in carbon tetrachloride on fibrin yields *chlorofibrin-A* (N, 10.5; Cl, 18.1%) (cf. this vol., 65), the constitution of which probably resembles that of bromofibrin (A., 1925, i, 707), since the ratio of the percentages of halogen in each is the same. Cold or hot (61°) water dissolves most of this chlorofibrin in 1 day, and the insoluble residue (insufficient amount obtained for analysis) is scarcely acted on in 15 days. This hydrolysis is due to the conversion of about 90% of the chlorine into an ionised condition, the strong acid converting the fibrin into soluble products. *Chlorofibrin-A* is not decomposed by ether, but when left in contact for 1 day with 0.5*N*-potassium hydroxide it dissolves, and acetic acid precipitates *chlorofibrin-Ac* in small quantity (N, 12.2; Cl, 10.5%). The filtrate contains ionised chlorine to the extent of 83.2% of the total original chlorine, together with a little un-ionised chlorine. Alcohol converts *chlorofibrin-A* into *chlorofibrin-Ad* (N, 11.4; Cl, 16.6%), and the filtrate contains ionised chlorine to the extent of 60.4% of the total original chlorine, but no un-ionised chlorine.

J. M. GULLAND.

Unsaturated dipeptide-anhydrides, and dehydration of amino-acid derivatives. M. BERGMANN (Z. physiol. Chem., 1927, 165, 167—169).—A question of priority.

C. R. HARRINGTON.

Tetrapeptide from gliadin. R. NAKASHIMA (J. Biochem. [Japan], 1926, 6, 55—60).—A substance, m. p. 283—285°, obtained as colourless needles (1 g.) in a peptic digestion of gliadin (16 g.) contains 4.3 mols. of water to 1 mol. of a tetrapeptide apparently consisting of 1 mol. of tyrosine, 2 mols. of glutamine, and 1 mol. of glutamic acid. Of the total nitrogen content of 14.58%, 4.93% is ammonia-nitrogen, and 9.94% is amino-nitrogen. CHEMICAL ABSTRACTS.

Constitution of the proteins. III. S. GOLDSCHMIDT (Z. physiol. Chem., 1927, 165, 149—154).—Under no conditions could the results of Brigl and Held (A., 1926, 630) regarding the oxidation of

carbonyldiglycylglycine by hypobromite be confirmed, and, if the experiment be so conducted that preliminary hydrolysis of the compound is excluded, the effect of the hypobromite is negligible; further, prolonged heating of albumin with sodium hydroxide led to the liberation of traces only of carbon dioxide. No evidence could therefore be obtained of the existence of ureide linkings in protein. C. R. HARRINGTON.

Composition of peptones. A. BLANCHETTERE (Compt. rend., 1927, 184, 405—407).—Commercial peptones formed by peptic and tryptic digestion of proteins were fractionated by formation of carbamates, and 14—33% of the total nitrogen content of the peptones is considered to be present as diketopiperazines.

L. F. HEWITT.

Decomposition of soya-bean protein. III. Decomposition with sodium hydroxide. IV. M. MASHINO (J. Soc. Chem. Ind. Japan, 1926, 29, 248—251, 252—254).—III. Soya-bean protein obtained from four different sources was decomposed by treating with 19.65% sodium hydroxide at 100° for 0.5—12 hrs. and the amounts of ammoniacal and amino-nitrogen liberated were determined. The amount of ammonia liberated increases during the first 4 hrs., but then remains almost constant. Ammoniacal nitrogen (4—12 hrs.) is 16.5, 18.6, 19.5, and 17% in the four cases, respectively, of the total nitrogen. The rate of decomposition of the protein is nearly the same for the four samples. Amino-nitrogen (12 hrs.) is 65.6, 68, 68.6, and 67.6% in the four cases, respectively, of the total nitrogen.

IV. A discussion of the above and previous work (A., 1926, 1048). The violet colour of the biuret reaction for soya-bean protein is apparently related to ammonia in protein. When all the ammonia is evolved, no violet colour is observed. The free carboxyl group in the protein molecule may be present in combination with an amino-group. The rate of decomposition of soya-bean protein is little affected by pre-treatment with superheated steam. Oil-extracted soya-bean cake is therefore used for producing amino-acids.

K. KASHIMA.

Determination of nitrite formed by replacement of nitro-groups in presence of highly-coloured reaction products. R. H. CLARK and N. M. CARTER (Trans. Roy. Soc. Canada, 1926, [iii], 20, III, 429—438).—An attempt has been made to find a method of determining the amount of nitrite formed when nitro-groups in organic compounds are replaced by hydroxyl or ethoxyl groups. Reduction to nitric oxide with mercury and sulphuric acid or to ammonia always gave very low results. Direct titration of the excess of alkali, either conductometrically or using an indicator, gave an indefinite endpoint. Precipitation with "nitron" was satisfactory only in a few cases. Titration of the iodine liberated when the nitrite was mixed with potassium iodide and hydrochloric acid, according to the equation $2\text{NaNO}_2 + 2\text{KI} + 4\text{HCl} = 2\text{NaCl} + 2\text{KCl} + 2\text{H}_2\text{O} + 2\text{NO} + \text{I}_2$, was quite inaccurate. Finally, by measuring the volume of nitric oxide formed in this reaction, fairly satisfactory results (94% and upwards of the theoretical values) were obtained.

R. CUTHILL.

Determination of formic acid. F. OBERHAUSER and W. HENSINGER (Z. anorg. Chem., 1927, 160, 366—372).—Formic acid may be determined bromometrically by treating the solution with sodium acetate or sodium hydrogen carbonate in excess, then with a standard solution of bromine in *N*-potassium bromide until a permanent yellow colour remains, adding a known excess of arsenious acid to discharge this colour, acidifying with hydrochloric acid, and titrating the excess of arsenious acid with the bromine solution, using indigo-carmin-styphnic acid as indicator. In absence of sodium acetate, the hydrobromic acid formed exerts a marked retarding effect on the reaction between bromine and formic acid, even in direct sunlight. Mineral acids also have a retarding influence on the reduction of mercuric chloride to mercurous chloride by formic acid, but this may be overcome as follows: The formic acid solution is treated with at least a 50% excess of mercuric chloride and sufficient to give a 0.5% solution of the mercury salt, followed by sodium hydroxide solution drop by drop until a faint opalescence persists; 10 c.c. of saturated sodium acetate solution are added and the mixture is boiled for 2 hrs. in a water-bath. The precipitated mercurous chloride is collected, washed, and dissolved in an excess of standard bromine solution, the excess being determined as described above.

A. R. POWELL.

Micro-determination of methoxyl. A. FRIEDRICH (Z. physiol. Chem., 1927, 163, 141—148).—A 3% thiosulphate solution is found preferable to the

red phosphorus suspension, and may contain cadmium sulphate for the simultaneous absorption of hydrogen sulphide. The low results are due to incomplete reaction between alkyl iodide and silver nitrate, and it is recommended that for micro-determinations a constant volume (2 c.c.) of alcoholic silver nitrate be used and 0.12 mg. be added to the weight of silver iodide. Results within 0.1% of the theoretical are then obtained. Complete dissolution of the substance is advisable.

C. HOLLINS.

Phenol tests. II. Nitrous acid tests. H. D. GIBBS (J. Biol. Chem., 1927, 71, 445—459).—The colour produced by the action of nitrous acid on phenol is due to the secondary condensation of the *p*-nitrosophenol, which is the primary product of the reaction; the colour development is greatly accelerated by the presence of mercury salts (*e.g.*, with Millon's reagent). The optimum reaction for the colour development is p_H 4—5. Whilst *para*-substituted phenols give similar colour reactions, a somewhat longer time and higher temperature are required for the colour development. The dissociation value, pK_a , for *p*-nitrosophenol, determined spectrophotometrically, is 6.4.

C. R. HARRINGTON.

Determination of uric acid. A. BOIVIN.—See this vol., 488.

Determination of sulphur in proteins. L. C. MAXWELL, F. BISCHOFF, and N. R. BLATHERWICK.—See this vol., 486.

Biochemistry.

Gasometric determination of small amounts of carbon monoxide in blood and determination of blood volume. D. D. VAN SLYKE and F. S. ROBSCHT-ROBBINS (J. Biol. Chem., 1927, 72, 39—50).—The method of Harrington and Van Slyke (A., 1924, ii, 872) has been adapted to the determination of small amounts of carbon monoxide in blood; by the use of this technique, the determination of blood volume by the carbon monoxide method may be carried out after saturation of only 5—10% of the total hæmoglobin with carbon monoxide. Experiments on dogs, in which the carbon monoxide was introduced by intravenous injection of a small amount of blood saturated with the gas, indicate that the blood volume may be determined by this method with an error of 5%. C. R. HARRINGTON.

Physical chemistry of proteins. VI. Activity coefficients of the ions in certain oxyhæmoglobin solutions. E. J. COHN and A. M. PRENTISS (J. Gen. Physiol., 1927, 8, 619—639).—The effect of a neutral salt such as magnesium sulphate on the solubility of oxyhæmoglobin is shown to be similar to its effect on a sparingly soluble salt (*cf.* Brønsted and Petersen, A., 1922, ii, 199), and hence the effect is presumably due to the change in the activity of the oxyhæmoglobin caused by the presence of the neutral salt. It is shown that the solubility of oxyhæmoglobin in phosphate solutions is given by $\log S/S_0 = 2\sqrt{\mu}/(1 +$

$1.5\sqrt{\mu})$, where S is the solubility when the ionic strength is μ and S_0 is the solubility in absence of salt (calculated to be 12.2, 11.2, and 13.1 g. per litre at p_H 6.4, 6.6, and 6.8, respectively).

W. O. KERMACK.

Blood bilirubin. G. FÖRSTER and B. FÖRSTNER (Magyar Orvosi Arch., 1926, 27, 455—465).—There is an individual, physiological variation in the bilirubin content of human blood of 0.2—1.0%. Bilirubin in the serum is oxidised in diffused light, hence the determination should be made soon after withdrawing the sample.

CHEMICAL ABSTRACTS.

Relationship between chemical composition of blood and lymph in the dog. R. M. ARNOLD and L. B. MENDEL (J. Biol. Chem., 1927, 72, 189—211).—In the normal dog, the protein content of the lymph is considerably lower than that of the blood-serum, but the diffusible constituents of the two fluids are closely similar in amount; changes induced in the composition of the blood-serum, by abnormal physiological conditions, are immediately reflected by parallel changes in the lymph; there must therefore exist free interchange of diffusible constituents between the two fluids.

C. R. HARRINGTON.

Characterisation and determination of oxalate in the blood and in the cerebrospinal fluid. C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1927, 9, 247—262).—Methods previously described for the

determination of oxalate in the blood and in the cerebrospinal fluid are shown to contain sources of error, and a modified method is described. The concentration of oxalate in the serum and cerebrospinal fluid of normal individuals is less than 2 mg. per litre, whilst in pathological cases the blood oxalate never exceeds 40 mg. per litre. It is doubtful whether the crystals described by Rodillon (Bull. Sci. Pharmacol., 1920, 249) in the cerebrospinal fluid really consist of calcium oxalate.

W. O. KERMACK.

Action of blood on sulphides. W. DENIS and L. REED (J. Biol. Chem., 1927, 72, 385—394).—Intravenous or parenteral injection of sodium sulphide is followed, in dogs, by a rise in the inorganic sulphate content of the blood, which is particularly marked in absence of renal function, but by no change in the neutral sulphur. Hydrogen sulphide is therefore presumably detoxicated in the animal organism by oxidation to sulphuric acid.

C. R. HARRINGTON.

Determination of carbamide in blood. H. CHABANIER, M. LEBERT, and R. WAHL (Bull. Soc. Chim. biol., 1927, 9, 277—279).—The authors have been unable to confirm the findings of Pagel (A., 1924, ii, 575) and Péchon (A., 1926, 763) to the effect that the concentrations of carbamide may be markedly different in consecutive samples of blood drawn from the same individual.

W. O. KERMACK.

Adrenaline content of blood. H. SCHLOSSMANN (Arch. exp. Path. Pharm., 1927, 121, 160—203).—The hydrodynamic resistance of the vessels of the isolated dog's ear, perfused at a constant pressure of 20—30 cm. of water, is used as a very sensitive measure of the adrenaline content of the perfusing liquid. Results are given for the adrenaline content of arterial blood in the normal state and after excitation of the suprarenal in various ways. Asphyxia and injection of nicotine produce an adrenaline concentration as high as 1 part in 50×10^6 parts.

E. A. LUNT.

Effect of neutral salts on the acid charge of certain substances. L. AMBARD, F. SCHMID, and M. ARNOVLYEVITCH (Bull. Soc. Chim. biol., 1927, 9, 236—246).—A theoretical discussion of the effects of neutral salts on the alkaline reserve in the blood, the rate of hydrolysis of sucrose by acid, the precipitation of protein, the colour assumed by an indicator in solution, the activity of enzymes, and on the rate of lung-ventilation leads to the conclusion that all these effects can be traced to the same cause, viz., an increased appropriation of acid by substances in solution after the addition of neutral salts.

W. O. KERMACK.

Gas and electrolyte equilibria in the blood. IX. **Distribution of electrolytes between transudates and serum.** A. B. HASTINGS, H. A. SALVESEN, J. SENDROY, and D. D. VAN SLYKE (J. Gen. Physiol., 1927, 8, 701—711).—The electrolyte content of serum transudates differs from that of the serum itself in a manner explicable on the assumption of the existence of the Donnan membrane equilibrium between the two fluids. When serum and salt solutions approximating to oedema fluid in composition are equilibrated across a collodion membrane, the

distribution of electrolytes becomes similar to that between serum and oedema fluid *in vivo*.

W. O. KERMACK.

Blood-sugar of cod, sculpin, and pollock during asphyxia. M. L. MENTEN (J. Biol. Chem., 1927, 72, 249—253).—The normal fasting blood-sugar concentration of the above fish was from 0.014 to 0.04%; both under normal and asphyxial conditions, however, this value was greatly influenced by the previous feeding.

C. R. HARRINGTON.

Micro-determination of sugar and reducing substances in blood. V. LAPA (Bull. Soc. Chim. biol., 1927, 9, 310—323).—Treatment of blood or plasma with mercuric acetate in presence of sodium hydrogen carbonate precipitates, not only proteins, but also all nitrogenous components. The reducing power may then be determined by any of the ordinary micro-methods. The reducing power after fermentation is independent of the method used and varies from 3 to 6 mg. (as dextrose) per litre.

W. O. KERMACK.

Determination of small quantities of sugar. Application to blood and to other body-fluids. A. BAUDOIN and J. LEWIN (Bull. Soc. Chim. biol., 1927, 9, 280—309).—To 15 c.c. of the neutral solution to be examined 1 c.c. of a solution containing 3.60 g. of mercuric iodide and 12 g. of sodium iodide per 100 c.c. and 1 c.c. of *N*-sodium hydroxide solution are added. The mixture is heated for 3 min. on the boiling water-bath and then cooled, and there is then added 1 c.c. of a solution containing 1.783 g. of potassium iodate dissolved in sufficient 5% sulphuric acid to make the volume to 1 litre. The iodine liberated converts the mercury formed during the heating into mercuric iodide, and the excess of iodine is then titrated with sodium thiosulphate.

W. O. KERMACK.

Blood-sugar. Fractionation of the reducing substances in blood-filtrates. B. SJOLLEMA (Biochem. Z., 1927, 182, 453—459).—Blood-filtrates obtained by the method of Folin and Wu contain, besides dextrose, an amount of reducing substance much greater than the content of reducing non-sugar substances such as uric acid. A method is described for the determination of dextrose in presence of very small amounts of disaccharides (lactose, maltose). When such sugar solutions are shaken with animal charcoal and a little acetic acid is added, dextrose remains in solution, whereas the disaccharide is almost completely adsorbed. If, in place of acetic acid, the solution is shaken with ether, the disaccharide remains in solution.

P. W. CLUTTERBUCK.

Analytical method of establishing the "nitrogen formula" for blood-serum. M. LAUDAT (Bull. Soc. Chim. biol., 1927, 9, 137—148).—Detailed methods are described for establishing the "nitrogen formula" (cf. Widal and Laudat, Compt. rend. Soc. Biol., 1926, 95, 1233), the determinations including those for total non-protein nitrogen, carbamide, uric acid, creatine, creatinine, ammonia, and amino-acids, and the undetermined nitrogen. Well-known methods, with certain modifications, are recommended, and this method of analysis has proved useful in studying the retention of nitrogenous sub-

stances in renal impermeability. The amount of serum required for the complete analysis is not greater than 15 c.c.

A. WORMALL.

Thiasine ; its structure and identification with ergothioneine. E. B. NEWTON, S. R. BENEDICT, and H. D. DAKIN (J. Biol. Chem., 1927, 72, 367—373).—Thiasine (A., 1926, 421) gives the Pauly reaction, yields trimethylamine on warming with potassium hydroxide, and reduces permanganate in the cold; the sulphur is readily removed by oxidation with ferric chloride, although it is stable towards alkali. Re-determination of the sulphur content indicated 13.4%; the substance was therefore suspected to be identical with ergothioneine (cf. Tanret, A., 1909, i, 671), and the identity was confirmed by direct comparison, and by the identity of the behaviour of the substance with that described by Barger and Ewins (J.C.S., 1911, 99, 2336) for ergothioneine. The compound (which it is proposed to name thioneine) has been isolated also from human blood (cf. Eagles and Johnson, this vol., 369).

C. R. HARRINGTON.

Non-protein sulphur compounds of blood. I. Sympectothion. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1927, 72, 123—132).—Modifications are described in the method of isolation of the compound previously obtained by the authors (A., 1926, 85) from blood; this compound is now shown to contain sulphur, and is named sympectothion, the formula suggested being $C_{18}H_{32}O_5N_5S_2$; it has $[\alpha]_D^{25} +115^\circ$, the previously recorded value being in error. The possible relationship of the compound to the thiasine of Benedict and others (A., 1926, 421) is discussed (cf. preceding abstract).

C. R. HARRINGTON.

Non-protein sulphur compounds of blood. II. Glutathione. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1927, 72, 133—146).—A substance apparently identical with glutathione has been isolated from blood-corpuses by a modification of the original method of Hopkins (A., 1921, i, 635); colorimetric determinations indicate the presence of about 100 mg. of this substance per 100 c.c. of red corpuses.

C. R. HARRINGTON.

Measurement of hæmolysin. C. B. COULTER (J. Gen. Physiol., 1927, 10, 541—544).—A method is described for the measurement of hæmolysin concentration, the principle of which is to compare under standard conditions the percentage of hæmolysis produced by a given amount of the unknown with that produced by varying amounts of a standard hæmolysin solution.

W. O. KERMAK.

Protein associated with hæmolysin in rabbit-serum and -plasma. C. B. COULTER (J. Gen. Physiol., 1927, 10, 545—550).—The hæmolysin of immune serum is associated with the water-insoluble euglobulin. Its activity is retarded by the presence in the solution of fibrinogen. Hæmolysis and hæmagglutinin appear to be distinct entities, since the activity of the former is destroyed, and that of the latter apparently increased by extraction with alcohol.

W. O. KERMAK.

Hæmolysis by the photo-sensitising action of hæmatoporphyrin. R. FABRE and H. SIMONNET (Compt. rend., 1927, 184, 707—709).—Lecithin freed

from cholesterol by the method previously described (A., 1926, 1283), when irradiated in presence of hæmatoporphyrin by means of a mercury-vapour lamp for 60 min., acquires hæmolytic powers towards the red cells of the dog. Partial separation of the hæmolyzing product has been effected by alcohol-ether fractionation.

R. BRIGHTMAN.

Unscaled fibres. A. T. KING (Biochem. J., 1927, 21, 434—436).—A method has been devised for the mechanical removal of the scales or outer layer of wool fibres in such a way as to leave the cortex intact. It consists essentially in drawing the fibre across the edge of a suitable glass plate, or over a series of such plates. The effectiveness of the method is illustrated by photomicrographs of wool fibres in various stages of scale removal.

S. S. ZILVA.

Distribution of unsaturated fatty acids in tissues. II. Voluntary muscle of the ox. W. R. BLOOR (J. Biol. Chem., 1927, 72, 327—343).—Figures are given for the distribution of lipins in various voluntary muscles and in the heart-muscle of the ox. The content of phospholipins, unsaponifiable matter, and cholesterol was highest in the most active muscles; a similar relationship was not observed with respect to the glycerides. Cholesterol esters are often absent from muscle, and, when present, are found in small amounts only. Emphasis is laid on the relationship of the phospholipin content to the mitochondria of muscle-cells, and the probable rôle of the phospholipins as constant constituents of protoplasm is discussed.

C. R. HARRINGTON.

Ovary. XII. Fatty acids of lecithin from corpus luteum. M. C. HART and F. W. HEYL (J. Biol. Chem., 1927, 72, 395—402; cf. this vol., 69, 168).—The lecithin-cadmium chloride compound obtained from the acetone extract of corpus luteum yielded, on hydrolysis, 49.4% of fatty acids, of which 17% was palmitic, 26% stearic, 22% oleic, 26% linoleic, and 7% arachidonic acid; there was also obtained 2% of an acid, $C_{20}H_{34}O_2$, the presence of which had been previously observed in the neutral fat fraction, and for which the name *ovarenic acid* is now proposed. The above figures are similar to those previously obtained for the neutral fat, which supports the hypothesis that a function of the corpus luteum is to maintain a supply of the labile phospholipins which are required during pregnancy.

C. R. HARRINGTON.

Structure of the histone of the thymus. III. Acid- and base-binding power after peptic digestion. K. FELIX and A. HARTENECK (Z. physiol. Chem., 1927, 165, 103—120).—Peptic digestion of the histone of the thymus causes an equal increase in acidic and basic groups and an equal increase in free amino-nitrogen and in formaldehyde-titratable carboxyl groups. The acidic groups liberated appear to be entirely carboxyl groups; the basic non-amino groups set free probably belong to the guanidine group of arginine; this hypothesis is supported by the low figure for the increase in the carboxyl groups titratable in alcohol compared with the increase in base-binding capacity. No ammonia could be detected. Pepsin, therefore, apparently splits acid-basic linkings. After preliminary digestion of the

histone with trypsin, pepsin caused no further increase in acid- or base-binding power, but the nitrogen which could be methylated increased in amount.

C. R. HARRINGTON.

Crystals of Charcot, Leyden, Böttcher, and Neumann. F. WREDE, F. BOLT, and E. BUCH (Z. physiol. Chem., 1927, 165, 155—166).—The crystals described by the above workers (Compt. rend., 1853, 3; Arch. Anat. und Physiol., 1872, 54, 324; *ibid.*, 1865, 32, 525; Arch. mikr. Anat., 1866, 2, 508) were almost certainly those of spermine phosphate.

C. R. HARRINGTON.

Glutathione. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1927, 72, 147—166).—By a method similar in principle to that of Hopkins (A., 1921, i, 635), there was isolated from yeast and from liver a sulphur-containing peptide which is regarded as glutathione; the product from liver was contaminated with cystine, but was otherwise similar to that from yeast and from blood (cf. this vol., 477). The material agreed with that of Hopkins (*loc. cit.*) and with the compound synthesised by Stewart and Tunnicliffe (A., 1925, i, 795) in its optical rotation, but differed from it in possessing a higher content of nitrogen and a lower content of sulphur. The preparations contained total N 11.5—12.0, amino-N 7.8—7.9, S 8.85—10.27%. On hydrolysis, the amino-nitrogen was increased by one half. The optical rotation after reduction was $[\alpha]_D -4.74^\circ$; it is thought that the completely reduced substance may be dextro-rotatory. On the basis of the above results, the authors deduce the presence of a third amino-acid (? serine) in ester combination in the glutathione molecule; the direct evidence adduced by Hopkins (*loc. cit.*) for the constitution of glutathione is questioned on the ground of the present authors' inability to effect a sharp separation of glutamic acid hydrochloride from cystine dihydrochloride after hydrolysis of their products.

C. R. HARRINGTON.

Isolation of glutathione. F. G. HOPKINS (J. Biol. Chem., 1927, 72, 185—187).—Hunter and Eagles (cf. preceding abstract) have omitted to discuss the evidence in favour of the accepted constitution of glutathione which is afforded by the synthesis of the compound by Stewart and Tunnicliffe (A., 1925, i, 795); the sulphur in glutathione is very much more labile than that in cystine; loss of sulphur at some stage in the isolation may therefore explain the results of Hunter and Eagles.

C. R. HARRINGTON.

Colorimetric determination of cystine and glutathione. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1927, 72, 177—183).—The method of Folin and Looney (A., 1922, ii, 539) for the colorimetric determination of cystine has been modified by the substitution of sodium hydroxide for sodium carbonate as the necessary alkali; the modified method is applicable also to the determination of glutathione, which yields 0.464 times the depth of colour given by the same weight of cystine.

C. R. HARRINGTON.

Cystine in liver. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1927, 72, 167—175).—Preparations of glutathione obtained from liver showed a high content of sulphur and a high specific rotation; this was found to be due to contamination with free

cystine, which must therefore occur as such in the liver. The possible relationship of this observation to the physiological synthesis of taurocholic acid, and to the occurrence of cystinuria, is discussed.

C. R. HARRINGTON.

Micro-volumetric determination of sulphur in biological fluids. B. POHORECKA-LELESZ (Bull. Soc. Chim. biol., 1927, 9, 263—276).—Sulphate is precipitated as benzidine sulphate which is titrated in boiling distilled water, in presence of phenol-red, with 0.02*N*-sodium hydroxide solution. The method may be applied for the determination of sulphate in body-fluids, only 0.5 c.c. of urine or 5 c.c. of serum being required, and also for the determination of total sulphur in such fluids if the sulphur is first oxidised to sulphate.

W. O. KERMAK.

Normal excretion of zinc in urine and faeces of man. K. R. DRINKER, J. W. FEHNEL, and M. MARSH (J. Biol. Chem., 1927, 72, 375—383).—The average daily excretion of zinc by the adult human is 0.89 mg. in the urine and 9.8 mg. in the faeces. Ingestion of a single meal rich in zinc causes an immediate and great increase in the faecal excretion of zinc, which may persist for 2—3 days; the urinary excretion of zinc is not perceptibly affected.

C. R. HARRINGTON.

Micro-determination of ammonia in urine. J. WEBER and W. KRANE (Z. physiol. Chem., 1927, 165, 45—52).—The ammonia is precipitated with Nessler's reagent or with sodium cobaltinitrite and alcohol; the ammonia is liberated from the precipitate, in the first case with sodium hydroxide and potassium sulphide, and in the second case with sodium hydroxide alone, steam-distilled into excess of standard acid, and determined by titration. The method is applicable to quantities of ammonia of 0.5 mg. and upwards.

C. R. HARRINGTON.

Determination of oxalic acid in urine by means of the rocking-extraction method of Widmark. C. G. HOLMBERG (Biochem. Z., 1927, 182, 463—469).—Widmark's method (Skand. Arch. Physiol., 1926, 84, 61) for the determination of urinary benzoic acid is adapted to the determination of oxalic acid in urine.

P. W. CLUTTERBUCK.

Effect of light on uroporphyrin. B. T. SQUIRES (Biochem. J., 1927, 21, 437—440).—Over the p_H range 6.2—8.2, there is a differential fading which reaches a maximum at about p_H 7.3. The rate of the general fading of uroporphyrin solutions is greater in the case of those containing crude uroporphyrin than in those containing the purified compound. The fading of crude uroporphyrin is in part associated with the presence of oxygen; this is not the case with pure uroporphyrin. As uroporphyrin solutions fade, there is no change in the positions of the absorption bands, which simply fade away. Within the above range of p_H , the appearance of "Kalilichtreaktion" band described by Schumm at 461 $\mu\mu$ could not be detected. On exposure of crude or purified uroporphyrin solutions in quartz tubes to ultra-violet light, a general fading irrespective of p_H is obtained.

S. S. ZILVA.

Iron in nutrition. IV. Correction of nutritional anaemia with ash of plants and animal

tissues and with soluble iron salts. E. B. HART, C. A. ELVEJHEM, J. WADDELL, and R. C. HERRIN (J. Biol. Chem., 1927, 72, 299—320; cf. A., 1925, i, 1354).—The nutritional anæmia which occurs in young rats on a diet of whole milk and ferric oxide can be cured by the addition of the ash, or an alcoholic extract, of lettuce or cabbage; spleen marrow and an alcoholic extract of maize were efficient supplements, but the ash of these substances was not so. Pure ferrous sulphate had no effect, although a commercial sample of the salt cured the anæmia. The supplementing factor is thus apparently of an inorganic character, but is not connected with the solubility of the iron compounds administered (cf. Mitchell and Schmidt, A., 1926, 1269). C. R. HARRINGTON.

Action of mineral waters on carbohydrate metabolism. Experiments [on diabetics]. O. KAUFFMANN-COSLA, R. ZÖRKENDÖRFER, and W. ZÖRKENDÖRFER (Bull. Soc. Chim. biol., 1927, 9, 174—202).—1000—1500 G. *per diem* of the natural mineral waters of Carlsbad and Marienbad, of which the principal constituent is sodium sulphate, bring about the recovery of mild and moderately severe diabetics. A. WORMALL.

Oxidative processes in the living cell. A. OPARIN (Biochem. Z., 1927, 182, 155—179).—An investigation of the aerobic oxidation of glycine under the influence of the plant respiratory chromogen chlorogenic acid, a dipeptide of caffeic and quinic acids (A., 1922, i, 309). It is concluded that in the living cell the chromogen is oxidised by molecular oxygen and phenoloxylase to a pigment, and that the pigment is then reduced by oxido-reductase to the original chromogen, the necessary hydrogen being derived from water, whilst the hydroxyl remains for the actual oxidation. The oxidation and reduction of the chromogen are normally in equilibrium. A high oxygen uptake by the living cell, following chemical or mechanical injury, leads to deep-seated oxidation of the respiratory chromogen, with the formation of an inactive pigment, and oxidation within the cell ceases. J. PRYDE.

Metabolism of tissues growing *in vitro*. I. Ammonia and urea production by kidney. B. E. HOLMES and E. WATCHORN (Biochem. J., 1927, 21, 325—334).—Growing embryonic rat kidney-tissue produces considerable amounts of ammonia and urea in contrast to "resting" embryonic kidney-tissue, *i.e.*, living but non-proliferating tissue, which produces neither ammonia nor urea. Preliminary experiments with brain-tissue indicate the probable existence of urease in the rat brain. S. S. ZILVA.

Brain metabolism. IV. Carbohydrate metabolism of brain-tissue of depancreatized cats. B. E. HOLMES and E. G. HOLMES (Biochem. J., 1927, 21, 412—418).—The lactic acid values of the brain fall and rise with the blood-sugar. Hyperglycæmia brought about by the administration of anæsthetics is also accompanied by an increased brain lactic acid content. Similarly, the hyperglycæmia of depancreatized cats is responsible for a correspondingly higher value of resting lactic acid in the brain of the cat. The brain-tissue of diabetics, like that of normal

animals, is capable of converting dextrose into lactic acid and of removing lactic acid under aerobic conditions. The lactic acid of the brain is therefore formed from the dextrose supplied by the blood. S. S. ZILVA.

p_H of muscles of marine animals. K. FURUSAWA and P. M. T. KERRIDGE (J. Marine Biol. Assoc., 1927, 14, 657—659).—The average p_H of the muscles of various marine animals was 7.06 in the resting condition and 6.33 in rigor; these figures are in close agreement with those obtained for the muscles of the frog and the cat. C. R. HARRINGTON.

Post-mortem changes in the free sugar, glycogen, phosphates, and lactic acid in mammalian muscle. W. W. SIMPSON and J. J. R. MACLEOD (Trans. Roy. Soc. Canada, 1926, [iii], 20, V, 371—375).—Experiments have been carried out to determine the total reducing substances, the free sugar, and the glycogen content of extracts of the liver and muscle of standard white rats, previously starved for 24 hrs. The free sugar, which accounts for a small percentage only of the total reducing value, is much lower in the liver extracts of insulin-treated rats than with the normals. Insulin treatment causes little, if any, change in the glycogen content or total reducing value. With muscle-extract, on the contrary, there is no reduction in free sugar following insulin. Changes taking place in the glycogen, free sugar, lactic acid, and soluble phosphorus of frozen rabbit muscle, after various short periods of thawing, indicate that some polymerised carbohydrate (perhaps a lower dextrin) must be formed from the disappearing glycogen. A. WORMALL.

Acid formation in thiocyanate rigor in frog's muscle. G. E. SELTER (Z. physiol. Chem., 1927, 165, 18—27).—In thiocyanate rigor in frog's muscle there is a marked increase in lactic acid and no constant change in the phosphoric acid. The phenomenon is therefore probably due to increased acidity. C. R. HARRINGTON.

Significance of ions in muscular function. IX. Influence of different anions on lactic acid formation and phosphoric acid exchange in minced muscle. G. E. SELTER (Z. physiol. Chem., 1927, 165, 1—17).—The effects of additions of various sodium salts to minced muscle on the formation of lactic acid and the amount of free phosphoric acid vary greatly (they may, indeed, be in the reverse direction) according to the concentration of salt employed. A salt which increases the rate of disappearance of phosphoric acid does not necessarily diminish the formation of lactic acid. Complete inhibition of lactic acid formation is obtained only in presence of those anions (fluoride and oxalate) which entirely suppress the degradation of lactacidogen. In view of these results, it is unsafe to deduce the behaviour of the lactic acid, under any given conditions, from the observed behaviour of the phosphoric acid. C. R. HARRINGTON.

Degradation of glycogen in muscle. H. VON EULER, R. NILSSON, and B. JANSSON (Z. physiol. Chem., 1927, 165, 121—129).—The decolorisation of methylene-blue by muscle is influenced to an equal extent by sodium and potassium phosphates. The

rate of decolorisation was not definitely affected by the state of nutrition of the animal; the process of reduction is accelerated to a slight extent by addition of small concentrations of glycogen; it is inhibited by high concentrations of glycogen and by all concentrations of dextrose; in the case of yeast, the reduction is not accelerated by glycogen.

C. R. HARINGTON.

Carbohydrate utilisation. II. Rate of disappearance of carbohydrates from the blood. J. G. REINHOLD and W. G. KARR (J. Biol. Chem., 1927, 72, 345—365).—Oral administration to rabbits of galactose, maltose, sucrose, starch, lactose, and levulose produced hyperglycæmia of descending orders of magnitude; in general, therefore, the magnitude of the effect varies directly with the rate of absorption of the carbohydrate and inversely with its capacity to form glycogen. The hyperglycæmia was increased by preliminary starvation, except in the case of starch, and was diminished by preliminary feeding with gelatin, except in that of maltose. Simultaneous administration of maltose, galactose, or levulose together with dextrose produced less hyperglycæmia than dextrose alone; this effect was not observed with starch or lactose. The typical hyperglycæmia produced by lactose or sucrose could not be reproduced by administration of mixtures of dextrose and galactose or of dextrose and levulose.

C. R. HARINGTON.

Action of glucosone on normal animals (mice) and its possible significance in metabolism. A. HYNÉ (Proc. Roy. Soc., 1927, B, 101, 244—261).—Glucosone produces similar symptoms in mice to those of insulin when injected subcutaneously. The effect is slightly modified by administration of dextrose, and appreciably by adrenaline, pituitrin, and acetoacetic acid injections. Glucosone does not produce hypoglycæmia. The possibility of the significance of glucosone in carbohydrate metabolism is thus confirmed (cf. Thannhauser and Jenke, A., 1926, 317).

L. F. HEWITT.

Effect of glycine on the metabolism of isolated perfused muscle. D. RAPPORT and L. N. KATZ (Amer. J. Physiol., 1927, 80, 185—199).—A preparation is described for the study of the metabolism of the isolated hind limb of the dog perfused with blood. The oxygen consumption of the resting muscles was found to be 0.0024—0.0093 c.c. per g. per min. Addition of 5 g. of glycine to the perfusing blood caused a notable increase in the oxygen consumption which might be sustained for several hours. It is concluded that the specific dynamic action of glycine is a direct effect on the cells of the tissues stimulated. It is argued that the respiratory quotient in this type of experiment is totally untrustworthy as an index of the metabolism of different foodstuffs.

R. K. CANNAN.

Metabolism of women. III. Lipin content of blood in relation to menstrual cycle. R. OKEY and R. E. BOYDEN (J. Biol. Chem., 1927, 72, 261—281).—During, and immediately after menstruation, there was observed a fall in the cholesterol content of the blood; the other lipins remained relatively unchanged in amount.

C. R. HARINGTON.

Influence of nutrition on synthesis and oxidation. A. PALLADIN and D. FERDMANN (Biochem. Z., 1927, 182, 193—203).—Rabbits receiving phenol *per os* excrete more in a combined form when they are fed on an "acid" diet than when fed on a "basic" diet. Intravenously-injected phenol is recovered in greater amount in "basic" than in "acid"-fed rabbits, whilst the relative amount of combined phenol is higher in the latter animals. It is concluded that an acid diet favours the oxidation and conjugation of phenol.

J. PRYDE.

Effect of heat and oxidation on nutritive value of protein. H. GOLDBLATT and A. R. MORITZ (J. Biol. Chem., 1927, 72, 321—326).—The nutritive value of caseinogen was not impaired by heating for 36 hrs. in a current of air at 110—130°.

C. R. HARINGTON.

Dietary value of potato protein. G. A. HARTWELL (Biochem. J., 1927, 21, 282—288).—Potato protein given in a diet consisting mainly of mashed cooked potatoes was found insufficient to promote growth. Reproduction took place, but many of the young were born dead and few could be reared. If this diet was given during lactation only, the young rats were undersized and the mothers lost weight during lactation. The addition of bread to the potato diet during lactation improved the condition of the young, but not of the mother. The dietetic deficiency of the potato diet is due to the insufficient consumption of potato protein and not to its quality.

S. S. ZILVA.

Growth on diets rich in fat. H. LEVINE and A. H. SMITH (J. Biol. Chem., 1927, 72, 223—238).—Normal growth in young rats was obtained on diets in which 86% of the caloric requirements were supplied in the form of fat and the remainder as protein, provided that adequate supplies of salt were maintained; on such diets, the fat was almost quantitatively absorbed, and the caloric intake per 100 g. body-weight was the same as that on an ordinary mixed diet. No abnormalities were observed in the liver after maintenance of the diet rich in fats for 83 days.

C. R. HARINGTON.

Effect of carbon monoxide inhalation on metabolism. F. M. WALTERS (Amer. J. Physiol., 1927, 80, 140—149).—The body temperature and the metabolic rate of the rat were depressed by breathing carbon monoxide to a degree varying with the carbon monoxide saturation of the blood. There is a relation between the fall in metabolic rate and the symptoms of poisoning.

R. K. CANNAN.

Effect of the administration of excessive amounts of water. I. C. H. GREENE and L. G. ROWNTREE (Amer. J. Physiol., 1927, 80, 209—229).—There are reported the effects on the volume and on the concentrations of proteins, electrolytes, and non-electrolytes of the blood of the forced administration of large amounts of water to the dog.

R. K. CANNAN.

Excitability of nervous centres in terms of their hydrochloric acid content. L. AMBARD and F. SCHMID (Compt. rend., 1927, 184, 769—771).—Excess of hydrochloric acid above the normal gives rise to hyper-excitement symptoms, from vasomotor

reactions and high blood pressure to convulsions; deficiency of hydrochloric acid produces the converse symptoms. The concentration relation $\text{Protein HCl} \rightleftharpoons [\text{NaCl} \times \text{H}_2\text{CO}_3] / [\text{HCl} \times \text{NaHCO}_3] = K$ is proposed and its biological applications are discussed.

R. BRIGHTMAN.

Synthetic production of different flavours. E. BARYSCHEVA (Pflüger's Arch., 1926, 215, 103—105).—By means of mixtures of four solutions of saline (sodium chloride), sweet (sucrose), acid (oxalic acid), and bitter (quinine hydrochloride) substances, it is claimed that the taste of any substance may be simulated by varying the proportions of each. The odour of many substances interferes with the experiments.

L. F. HEWITT.

Action of choline and histamine on the excretion of dyes from the blood. G. FARKAS and H. TANGL (Biochem. Z., 1927, 182, 406—410).—Vasodilator substances (choline) increase, and vasoconstrictor substances (histamine) retard the excretion of dyes from the blood. P. W. CLUTTERBUCK.

Potassium, sodium, and calcium content of blood after ingestion of calcium chloride. J. WEBER and W. KRANE (Z. physiol. Chem., 1927, 163, 134—140).—Sub-normal calcium content of human blood is very rapidly restored to normal by food rich in calcium, and is further increased by doses of calcium chloride. Increase in calcium content is not accompanied by increased potassium content.

C. HOLLINS.

Effect of iodine on protein and sodium chloride equilibria in man. A. SLAUCK (Arch. exp. Path. Pharm., 1927, 121, 250—258).—Subjects fed for 8 days on a daily diet of 2.5 litres of milk were treated with doses of sodium and potassium iodides varying from 10 to 18 g. Determinations were made of the nitrogen content of the blood during a period of 3—48 hrs. It was found that the nitrogen content rose to a maximum in 3 hrs. and became normal 24—48 hrs. afterwards; slightly higher maxima were observed for potassium iodide. Corresponding maxima were observed for the iodine and sodium chloride content of the blood 3 hrs. after the administration of sodium or potassium iodide and for the total chlorine and iodine content in the urine excreted during the 24 hrs. following the iodide treatment.

E. A. LUNT.

Iodine as a biological element. IX. Acceleration of the growth of young rats by administration of a diet rich in iodine to the lactating mother. E. MAURER and S. DIEZ (Biochem. Z., 1927, 182, 291—300).—Administration of a diet of maize and milk which had been enriched in iodine to rats did not affect the body-weight of the mother, but the weight of the young was 20% greater than normal by the end of the lactating period. In both mother and young, the dry substance content was increased to a greater extent than the body-weight, but whereas in the mother loss of salts had taken place, the ash content of the young had increased with the body-weight. The changes of calcium, iodine, and phosphorus content of mother and young during the period of iodine-rich feeding are tabulated (cf. A., 1926, 1167).

P. W. CLUTTERBUCK.

Elimination of iodine after oral or intravenous administration of various iodine compounds. F. R. GREENBAUM and G. W. RAIZISS (J. Pharm. Exp. Ther., 1927, 30, 407—427).—After administration of sodium iodide or potassium iodide, 90% of the iodine is excreted by the kidneys within 24 hrs. and the rest within the next few days. After administration of calcium iodide, most of the iodine is similarly eliminated during the first 24 hrs., but in this case a considerable proportion is in the faeces. After ingestion of "pepto-iodine," the iodine is rapidly eliminated by the kidneys in an ionised form, but damage of the kidneys by mercuric chloride does not lessen the elimination, as it does in cases of sodium and potassium iodides. The iodine of organic compounds such as tetraiodophenolphthalein or 4-iodoguaiacol is eliminated by the kidneys and by the faeces, but not in an ionised form. Elimination of iodine after administration of the additive compound of calcium iodide and thiocarbamide is very similar to that observed following administration of calcium iodide alone.

W. O. KERMAK.

Effect of Witte's peptone on blood-sugar. M. L. MENTEN and H. M. MANNING (J. Biol. Chem., 1927, 72, 255—260).—No constant effect on the blood-sugar concentration of the rabbit was observed as the result of intravenous injection of Witte's peptone.

C. R. HARRINGTON.

Proteinogenous toxicosis. L. A. TSCHERKEZ (Biochem. Z., 1927, 182, 35—49).—White mice fed exclusively on a protein diet develop toxic symptoms which are fatal and to which the name proteinogenous toxicosis is given. The addition of fat or carbohydrate to the diet lessens the severity of the toxic effects in a measure more or less proportional to the amount of fat or carbohydrate fed. The toxic effects are not ascribed to the lack of vitamins or to starvation. In the case of white rats and pigeons, an exclusive diet of caseinogen is not followed by the toxic symptoms, but, on the other hand, a diet of egg-albumin does produce the effect in rats.

J. PRYDE.

Influence of urethane narcosis on specific dynamic action of glycine and dextrose in rabbits. M. S. GUTTMACHER and R. WEISS (J. Biol. Chem., 1927, 72, 283—297).—The normal specific dynamic action of glycine and dextrose (caloric equivalents of which produce effects of equal magnitude) is observed in rabbits under urethane anaesthesia, provided that the anaesthesia be not so deep as to abolish nervous reflexes; this indicates that the nervous system is probably concerned in the phenomenon of specific dynamic action of foodstuffs.

C. R. HARRINGTON.

Determination of small quantities of bismuth in tissue, excreta, blood, and bone. J. A. SULTZBERGER (J. Amer. Pharm. Assoc., 1927, 16, 218—221).—Tissue, faeces, or urine (10—50 g.) is moistened with nitric acid, warmed overnight on a steam-heated sand-bath, and ignited until all carbon is removed. The residues are boiled with hydrochloric acid, evaporated to dryness, treated with 0.5 c.c. of hydrochloric acid and 5 c.c. of water, filtered, diluted to about 15 c.c., and compared

colorimetrically with a standard bismuth nitrate solution containing 0.05 mg. Bi per c.c. after the addition of 0.75 c.c. of 25% potassium iodide solution and 0.5 c.c. of 1% sodium hydrogen sulphite solution to the standard and unknown solutions. In the digestion of bone, the precipitation of the metal as sulphide is necessary, owing to the excessive concentration of salts. Bleaching of the bismuth potassium iodide colour occurred on the addition of sodium chloride, but the addition of hydrochloric acid restored the colour completely. If the ignition is carried out in the muffle furnace, loss of bismuth occurs.
C. O. HARVEY.

Toxicological determination of tin. P. MANICKE and H. LAUTH (Pharm. Zentr., 1927, 68, 161—163).—One treatment with potassium chlorate and hydrochloric acid does not completely destroy organic matter; subsequent treatment with hydrogen peroxide permits of precipitation of 90% of the tin present. When only small quantities of organic material are present, destruction with sulphuric acid and subsequent fusion with sodium hydroxide and nitrate allow of quantitative precipitation of the tin; if large quantities of organic material are present, it is necessary to treat with sulphuric acid, then with peroxide, and finally with nitric acid, heating each time until sulphur trioxide fumes are evolved.

S. I. LEVY.

Nitrates in biochemistry and toxicology. KOHN-ABREST and S. KAVAKIBI (Ann. Chim. anal., 1927, [ii], 9, 65—75).—An alkaline extract of the organic material is treated with basic lead acetate, the excess of lead removed from the filtrate with sodium carbonate, and the resulting solution neutralised and evaporated to dryness. The residue is treated with sulphuric acid in the cold, and, after 30 min., shaken with mercury in an apparatus so arranged that the nitric oxide evolved can be collected in a gas pipette; the first measurement of the nitric oxide is confirmed by observation of the reduction of volume on treatment with saturated ferrous sulphate. In the case of milk, preliminary treatment with sodium metaphosphate and silver nitrate is substituted for that with lead acetate. The error of the method is 2%. No nitrates were found in the common vegetables or in fresh human viscera; cow's milk contained 0—0.08, and human milk 0.145—0.19 g. of N_2O_5 per litre; normal human urine contained 0.036 g. of N_2O_5 per litre.
C. R. HARINGTON.

Effect of long-continued ingestion of zinc oxide by dogs and cats. Excretion and storage of zinc. K. R. DRINKER, P. K. THOMPSON, and M. MARSH (Amer. J. Physiol., 1927, 80, 31—64).—The administration of 0.175—1 g. of zinc oxide daily for 3—53 weeks was without clinical or other evidence of physiological damage. Figures are given for the urinary and faecal excretion of zinc and of the zinc content of the various tissues of the experimental animals. The main excretory route is the alimentary canal. Possible relations of the pancreas, adrenals, and sex glands to zinc are indicated.

R. K. CANNAN.

Effect of zinc on the reproduction and growth of the albino rat. Constant concentration of

zinc in a given species regardless of age. P. K. THOMPSON, M. MARSH, and K. R. DRINKER (Amer. J. Physiol., 1927, 80, 65—74).—The daily administration of 2—38 mg. of zinc, as oxide or as organic salt, to the albino rat before, during, and after pregnancy was without effect on the health or fertility of the mother or on the growth of the offspring. The normal zinc content of albino rats was about 0.039 mg. per g. of tissue, being independent of age. Feeding zinc leads to no significant storage of the metal by the tissues of the rat.
R. K. CANNAN.

Changes in the cation content of organs on exposure to light and at high altitudes. L. PINCUSSEN (Biochem. Z., 1927, 182, 359—365).—The potassium, calcium, and magnesium contents of the blood, lungs, brain, liver, and heart of dogs which have been irradiated or kept in the dark at different altitudes are tabulated and show that considerable displacement of the mineral content of the organism occurs both in bright light and at high altitudes.

P. W. CLUTTERBUCK.

Influencing biological reactions brought about by light. L. PINCUSSEN (Biochem. Z., 1927, 182, 366—376).—Daphnids in water and potassium iodide solutions with and without addition of certain dyes, e.g., eosin and sodium dichloroanthracenedisulphonate, are observed in the dark, in bright diffused light, in sunlight, and after irradiation with the quartz lamp. In the dark, there appears to be no difference between animals in water and in potassium iodide solution. In bright light, and still more so in sunlight and during irradiation with the lamp, the death rate is considerably increased by the presence of iodide, probably due to the setting free of iodine. This effect is enhanced by the presence also of the dyes, which have no action in themselves, waves of longer as well as shorter wavelength becoming able to set iodine free. Similar experiments with tadpoles in various salt solutions show that cations arranged in order of increasing ability to kill the animals are $Ca, Na < Al < Sr < Mg < Li < K$ and that anions similarly arranged are $Cl < Br < SO_4 < F, I$. Irradiation of tadpoles in phosphate solutions show that although $M/3$ and $M/6$ solutions are injurious, more dilute solutions have a protective action against irradiation. When tadpoles in phosphate solutions of the same concentration but of different p_H are irradiated, animals in solutions of $p_H < 6.8$ show little injurious effect, of $p_H 6.8$ all remain alive, and of $p_H 7.15—7.65$ mostly die, the death-rate increasing with the p_H .

P. W. CLUTTERBUCK.

Temperature and enzymic activity. J. R. BAKER (J. Marine Biol. Assoc., 1927, 14, 723—727).—The amylolytic activity of a fresh aqueous extract of the crystalline style of *Pecten* is at a maximum at 30° and at higher temperatures is destroyed with increasing rapidity. On keeping the extract for 1½—3 hrs. at 0—30°, the enzymic activity shows a marked increase. It is suggested that the latter may be a surface effect due to increased dispersion of the protein particles on which the enzyme is adsorbed.
C. R. HARINGTON.

Liver amylase. G. S. EADIE (Biochem. J., 1927, 21, 314—321).—The optimum p_H for liver amylase

is about 6. The previously accepted value, which is about p_H 7, is due to the presence in the liver of blood amylase. The effect of substrate concentration on the activity of liver amylase is in accordance with the theory of Michaelis and Menten (A., 1913, i, 540). The effect of sodium chloride on the activity of the liver enzyme is similar to that previously obtained with other amylases of animal origin. Langfeldt's claim that adrenaline enhances the activity of liver amylase is not confirmed (cf. A., 1921, i, 473).

S. S. ZILVA.

Gluco- and fructo-invertases. II. R. KUHN and H. MÜNCH (Z. physiol. Chem., 1927, 163, 1—72; cf. Kuhn, *ibid.*, 1925, 150, 220).—From a review of earlier work and from new determinations of the velocity of sucrose hydrolysis in presence of added cleavage products, it is concluded that (1) a glucoside or disaccharide which is unattacked by a given enzyme also shows no affinity for the enzyme, (2) affinity of an enzyme for a hexose does not necessarily involve affinity for the related hexosides or disaccharides, and (3) hydrolysis of a disaccharide by an enzyme involves affinity of the enzyme for at least one of the component sugars. Gluco-derivatives of sucrose are attacked only by fructo-invertases, fructo-derivatives by gluco-invertases. The behaviour of 11 enzyme preparations is set out in 57 tables. It is shown that the optimum p_H for the inhibitory effect of $\alpha\beta$ -dextrose depends on the β -dextrose only. For glycerol, the inhibition decreases uniformly with increasing p_H ; for α -galactose increase in p_H has no effect on the inhibition.

C. HOLLINS.

Behaviour of whole blood towards maltose in vitro. A. HYND and M. G. MACFARLANE (Biochem. J., 1927, 21, 322—326).—Using 1 c.c. of blood and determining the sugar by the Wood-Ost method, maltase could not be detected in the blood of the mouse, rat, guinea-pig, rabbit, kitten, ox, or sheep. In the case of the blood of the pig, almost a 100% hydrolysis of the maltose was recorded. If maltose counteracts the effects of insulin only after hydrolysis, the process cannot take place in the blood.

S. S. ZILVA.

Relation of the catalase system to oxidation processes in animal organs. L. STERN (Biochem. Z., 1927, 182, 139—154).—The author's catalase system is composed of catalase, anti-catalase, philo-catalase, and an activator of philo-catalase. The system is developed only in aerobic organisms, but has no direct relationship to the intensity of the oxidative processes of the organism. It exists in association with oxidases, but shows no parallelism to oxidones. By the action of oxidases, hydrogen peroxide is formed from the interaction of active hydrogen and molecular oxygen, whilst oxidones form water from the interaction of active hydrogen and active oxygen. The function of the catalase system is the decomposition of hydrogen peroxide and so it participates in the carriage of oxygen.

J. PRYDE.

Effect of temperature on catalase reaction. V. Temperature correction in catalase determinations. S. MORGULIS and M. BEBER (J. Biol. Chem., 1927, 72, 91—98).—The earlier observations

(A., 1926, 976) that the total amount of hydrogen peroxide which can be decomposed by a given amount of catalase is at a maximum at 2° are confirmed. Assuming that the enzyme is completely active at this temperature, and designating the amount of catalase required to decompose 70% of the hydrogen peroxide as one enzyme unit, a curve has been constructed showing the relationship of relative enzymic activity to temperature. The curve is regular from 0° to 24°, but at higher temperatures exhibits a deviation, which is ascribed to the increase of the rate of enzyme action relative to that of enzyme destruction.

C. R. HARRINGTON.

Mechanism of autolysis. VII. Autolysis of organs. O. STEPPUHN and Y. DURET-DELAGE (Biochem. Z., 1927, 182, 134—138).—Autolysis of organs, especially of the liver and kidney, is much more marked in the range of activity of pepsinases (p_H 3.8) than in alkaline media (p_H 7.6), but the pancreas also shows considerable autolysis at the latter reaction.

J. PRYDE.

Influence of the backward reaction in peptic hydrolysis of albumin. C. A. MORRELL, H. BORSOOK, and H. WASTENEYS (J. Gen. Physiol., 1927, 8, 601—617).—As the synthetic action of pepsin on the products of protein hydrolysis is greater within limits with increase of temperature, the optimum temperature for protein hydrolysis by pepsin would be expected to decrease as the concentration of the protein increases. The verification of this by experiment confirms the view that this synthetic action plays an important part in the dynamics of peptic hydrolysis. The retarding effects on the activity of pepsin of high concentrations of protein and of the addition of proteoses and peptones, either with the pepsin or separately, are also in accord with this view. No destruction of pepsin by heat is demonstrable at p_H 1.6 until a temperature of 40° is exceeded.

W. O. KERMACK.

Influence of thorium-X on laccase. A. MAUBERT (Compt. rend., 1927, 184, 781—783).—Measurements of the activity of laccase by Fleury's guaiacquinone method (A., 1924, i, 921, 1144) show that addition of 1—5 γ of thorium-X to a mixture of 20 c.c. of 1% aqueous guaiacol, 50 c.c. of water, and 0.5 c.c. of laccase preparation causes activation of the laccase. With larger doses, the enzyme becomes inactive.

R. BRIGHTMAN.

Influence of amino-acids on hydrolysis by pancreatic lipase. E. R. DAWSON (Biochem. J., 1927, 21, 398—403).—Amino-acids accelerate the hydrolysis, in alkaline or neutral but not in acid solutions, of ethyl butyrate and olive oil by pancreatic lipase.

S. S. ZILVA.

Enzyme action. XL. Time changes in ester-hydrolysing enzymes of extracts of whole rats of different ages. H. M. NOYES and K. G. FALK. **XLI. Extracts of mice.** K. G. FALK and H. M. NOYES. **XLII. Extracts of human uterine muscle and uterine fibroids.** H. M. NOYES and K. G. FALK. **XLIII. Extracts of rabbit tissues.** K. G. FALK and H. M. NOYES (J. Biol. Chem., 1927, 72, 449—465, 467—473, 475—488, 489—503).—**XL. On preservation under sterile conditions, for**

periods up to 23 months, extracts of whole rats show a gradual qualitative change in their capacity to hydrolyse esters, in all cases eventually approximating to the type of action exhibited by extracts of embryo rats and of a rat-carcinoma. The rate of change varied with the age of the animal from which the extract was prepared, being greatest in the case of the youngest and the oldest rats and least in that of the young adults.

XLI. Extracts of adult mice, on preservation, approximated in type of ester-hydrolysing activity to extracts of mouse-carcinoma, whilst extracts of young mice approximated to the different type of action of the mouse embryo.

XLII. Extracts of uterine fibroids fall into two types with respect to their ester-hydrolysing action; those of type I, similar in their action to embryonic extracts, showed a quantitative decrease of activity, but no change in type on preservation; those of type II, and also of uterine muscle itself, showed less decrease in total activity, but more change in type.

XLIII. Extracts of the liver, lung, kidney, and leg-muscle of rabbits show, on keeping, a change in type of ester-hydrolysing action, which becomes progressively more dissimilar to that which is characteristic of embryonic extracts. C. R. HARRINGTON.

Specific effect of salts in extraction of urease from amoebocytes of *Limulus*. L. LOEB and O. BODANSKY (J. Biol. Chem., 1927, 72, 415—431; cf. A., 1926, 434).—Urease is extracted from the amoebocytes of *Limulus* to a very small extent only by distilled water or by solutions of carbamide; sea-water, solutions of sodium and potassium chlorides isotonic with sea-water, and the protein-free serum of *Limulus* are slightly more efficient than water in extracting the enzyme; a somewhat greater power of extraction is observed with magnesium and manganese chlorides, and a very much greater power with the chlorides of calcium, strontium, and barium, which, in isotonic solution, are 20 to 100 times as effective as sodium chloride. The effect of these salts comes into play during the process of extraction, since their addition to a sodium chloride extract produces no increase in activity; the extracts prepared with their aid have a greater power of neutralising alkali, and thus keep the p_H nearer to the neutral point during the hydrolysis of the carbamide. The optimum concentration for extraction of the enzyme is greater in the case of salts with univalent than in that of those with bivalent cations. No specific effect of anions was observed. C. R. HARRINGTON.

So-called selective fermentation. A. FERNBACH, M. SCHOEN, and M. MORI (Compt. rend., 1927, 184, 551—553; cf. this vol., 279).—In continuation of the earlier work, the authors find that the difference in the rate of fermentation of optically inactive sugars, due to selectivity, varies, not only in the case of different yeasts, but also with the zymins prepared from these yeasts by the method of Albert, Buchner, and Rapp (A., 1902, ii, 521). The zymmin from beer yeast reacts at first in the same way and at the same rate as the living yeast from which it was derived, but stops before all the fermentable sugar disappears, and before the appearance of an unfermentable

reducing sugar. The same effect is found with the zymmin from Sauterne yeast. When, however, *Saccharomyces exiguus* or *Schizosaccharomyces Pombé* is used, the living yeasts render an inactive solution laevorotatory, whereas the corresponding zymins produce a dextrorotation. Similar results are obtained with invert-sugar: zymmin from beer-yeast increases the laevorotation by fermenting the dextrose, whilst the zymins from the other yeasts decrease it by fermenting preferentially the laevulose. It is suggested that selectivity depends on substances which accompany zymase, and may be modified in nature and proportion by temperature, concentration of the sugar, changes in the medium, or treatment of the yeast with acetone and ether. J. M. GULLAND.

Enzymic transformation of acetaldehyde. H. VON EULER and K. MYRBÄCK (Z. physiol. Chem., 1927, 165, 28—44).—The ability to transform acetaldehyde (this vol., 175) is restored to washed yeast by addition of boiled yeast extract or of any preparation of co-zymase, whether derived from yeast or from animal tissues; moreover, the degree of activation bears a quantitative relationship to the amount of co-zymase which is added; the identity of co-zymase and co-mutase is therefore established. Co-zymase would thus appear to be involved in a reaction of the Cannizzaro type preceding the esterification of hexose with phosphoric acid. The bearing of this on the existing theories of alcoholic fermentation is discussed. A pure sample of hexosediphosphate was not fermented by yeast free from co-zymase; the recent views of Meyerhof (Naturwiss., 1926, 1175) are therefore questioned, and it is concluded that the observed facts are in better agreement with the original equation of Harden. C. R. HARRINGTON.

Co-zymase. XI. K. MYRBÄCK and R. NILSSON (Z. physiol. Chem., 1927, 165, 140—148).—Co-zymase was not affected by trypsin, erepsin, taka-diastase, urease, catalase, or phosphatase; it was destroyed to a very small extent by esterase. It is destroyed on keeping in contact with liver- or kidney-extracts, but is stable towards strong oxidising agents such as permanganate and hydrogen peroxide; it is destroyed by bacteria. C. R. HARRINGTON.

Carbon monoxide poisoning in the absence of haemoglobin. P. F. FRANKLAND (Nature, 1927, 119, 491).—A reference to the behaviour of *Bacillus pyocyaneus*, Finkler's spirillum, and Koch's spirillum of Asiatic cholera in various gases (Proc. Roy. Soc., 1886, 45, 292). A. A. ELDRIDGE.

Bacterial production of gas containing sulphur. H. YAOI (Japan Med. World, 1926, 6, 139—144).—The principal gaseous product of the bacterial decomposition of *L*-cysteine is hydrogen sulphide; traces of a substance resembling ethyl sulphide are formed, but mercaptan is not produced except in presence of sugars. CHEMICAL ABSTRACTS.

Decomposition of hexosephosphates by *Bacillus coli communis*, Escherich. R. J. MANNING (Biochem. J., 1927, 21, 349—353).—The products of decomposition of the sodium salts of hexosemonophosphoric and hexosediphosphoric acids by *B. coli communis*, Escherich, whether the decom-

position takes place in presence or absence of oxygen, are carbon dioxide, alcohol, formic, acetic, lactic, and succinic acids. The products of decomposition are therefore the same as in the case of dextrose (cf. Grey, A., 1918, i, 143, 144; 1920, i, 699). The more rapid the bubbling of oxygen through the bacterial digest, the greater was the amount of sugar decomposed completely to carbon dioxide.

S. S. ZILVA.

Ammonium sulphate precipitation of the active principle of the culture filtrates of *C. diphtheriae*. A. F. WATSON and E. LANGSTAFF (Biochem. J., 1927, 21, 426—433).—The substance which causes the specific *in vitro* flocculation with antitoxin can be salted completely out of culture filtrates of *C. diphtheriae* adjusted to p_H 8.0 by saturation with ammonium sulphate. On the acid side of neutrality the precipitation is not complete. The presence of certain preservatives such as formaldehyde, phenol, or toluene prevents the complete removal of the active principle with ammonium sulphate. Although in general the chemical properties of the precipitates are the same, the active fraction salted out by complete saturation with ammonium sulphate is less pure than the acid precipitate obtained from the culture filtrates at the isoelectric point.

S. S. ZILVA.

Active principle of tuberculin. E. R. LONG and F. B. SEIBERT (Tubercle, 1926, 8, 111—122).—The protein-containing solution which accompanies tuberculin activity, on saturation with ammonium sulphate, yields a coagulable and a non-coagulable protein, and proteose. When the protein is destroyed by pepsin with little destruction of proteose, activity is destroyed; when the proteose alone is disintegrated by trypsin, the activity is unaffected. No non-protein has been found to be associated with tuberculin activity. Activity appears to be a function of a certain group of the protein molecule, but it is unlikely that an active group can be eliminated from the remainder of the protein molecule.

CHEMICAL ABSTRACTS.

Effect of various hydrogen-ion concentrations on the longevity of vaccine virus. R. D. DEFRIES and N. E. MCKINNON (Trans. Roy. Soc. Canada, 1926, [iii], 20, V, 359—370).—The virus, stored at 5—10° in a phosphate-buffered solution or a "universal" buffer, is resistant to minor changes in p_H , but outside the optimum range for storage (p_H 6—8) there is a distinct loss of potency. At p_H 5 and 10 the virus becomes inert in a few weeks, and at p_H values of 2, 3, 4, 11, and 12, destruction takes place within a few days.

A. WORMALL.

Relation between chemical constitution and germicidal activity of monohydric alcohols and phenols. F. W. TILLEY and J. M. SCHAFER (J. Bact., 1926, 12, 303—309).—Phenol coefficients, calculated on a g.-mol. basis, of successive members increase uniformly with an average ratio between coefficients of 3.36, 3.0, 2.7, and 3.3 for the primary, secondary, and tertiary alcohols, and phenols, respectively.

CHEMICAL ABSTRACTS.

Significance of iron, zinc, and copper for micro-organisms (with special reference to

***Aspergillus niger*).** H. BORTELS (Biochem. Z., 1927, 182, 301—358).—Adsorption by blood-charcoal removes iron, zinc, and copper from culture media. Iron and zinc are essential to the growth of *A. niger*, zinc also inhibiting fructification, whilst copper is indispensable for the formation of the black pigment of the conidia. Copper also leads to an increase in the weight of dry substance. Iron and zinc are also necessary for the growth of *B. prodigiosus* and zinc for yeast, but copper does not appear to be essential for either. Prodigiosin is produced by the action of iron on a leuco-compound formed by the bacillus.

P. W. CLUTTERBUCK.

Influence of some hormones on the excretion of dyes from the blood. H. TANGL (Biochem. Z., 1927, 182, 411—417).—The injection of extracts of thyroid, thymus, pituitary, and testis retards the excretion of dyes from the blood.

P. W. CLUTTERBUCK.

Action of extracts of spleen on the excretion of dyes from the blood. G. FARKAS and H. TANGL (Biochem. Z., 1927, 182, 399—405).—The spleen brings about the excretion of dyes injected into the blood, not only by its reticulo-endothelial cells, but probably also by means of a hormone.

P. W. CLUTTERBUCK.

Influence of extracts of spleen, thymus, and thyroid on the growth of young rats. H. TANGL (Biochem. Z., 1927, 182, 418—423).—Injection of extracts of spleen and of thyroid exerts no influence on the growth of young rats, nor does it affect the growth-assisting action of thymus extracts.

P. W. CLUTTERBUCK.

Endocrine factors in oxalic acid metabolism. G. VIALE (Rev. sud-amer. endocrinol. immunol. quimioterap., 1926, 9, 967—977).—Insulin injections do not alter the oxalic acid content of the blood of rabbits and dogs, but cause a marked decrease of its excretion in urine. Adrenaline injections and pancreatectomy cause a considerable increase in oxalaturia. Phloridzin diabetes has scarcely any effect on the excretion of oxalic acid. It is concluded that oxalic acid is an intermediate product of sugar metabolism.

CHEMICAL ABSTRACTS.

Insulin. N. R. BLATHERWICK, F. BISCHOFF, L. C. MAXWELL, J. BERGER, and M. SAHYUN (J. Biol. Chem., 1927, 72, 57—89).—Details are given of a practical combination of various known methods for the extraction and purification of insulin. Under no conditions was insulin inactivated by hydrogen sulphide. The prolonged action of cyanide causes inactivation of insulin, as does also nitrite in concentrations above 0.05*N*; diazobenzenesulphonic acid in faintly alkaline solution, and in amount considerably less than is required to combine with the tyrosine and histidine of the insulin preparation, destroys the activity. Iodine destroys the activity, but the iodine absorbed bears no relation to the unit content of the insulin. Loss of activity accompanied benzoylation, nor could activity be recovered by hydrolysis of the product. The small proportion of these inactivating agents required to destroy the insulin indicates that the actual hormone is a small fraction only of the most active preparations. That

portion of the sulphur of insulin preparations which is labile to sodium hydroxide can be largely oxidised by dilute nitrite without loss of physiological activity, whilst the activity can be destroyed with iodine without affecting the sulphur labile to sodium carbonate; the supposed connexion between activity and content of alkali-labile sulphur (cf. Abel and Geiling, A., 1925, i, 1218) must therefore be regarded as fortuitous.

C. R. HARINGTON.

Micro-methods for determination of labile and total sulphur in proteins. L. C. MAXWELL, F. BISCHOFF, and N. R. BLATHERWICK (*J. Biol. Chem.*, 1927, 72, 51—56).—The protein is heated with the selected concentration of alkali, the mixture acidified, and the hydrogen sulphide passed into a solution of hypobromite; the sulphate thus formed is precipitated with barium chloride in presence of ammonium nitrate and determined nephelometrically. Total sulphur is obtained by fusing the original material with sodium carbonate and sodium peroxide, followed by a similar nephelometric determination.

C. R. HARINGTON.

Action of sugar in the organism. II. Decomposition of dextrose by very dilute alkali. F. FISCHLER.—See this vol., 449.

Action of sugar in the organism. III. Action of degradation products of dextrose on disturbances of carbohydrate metabolism. F. FISCHLER (*Z. physiol. Chem.*, 1927, 165, 68—102).—The clinical picture of hypoglycæmia in rabbits caused by overdosage with insulin exhibits two main features, a general stimulation of the central nervous system and a local abolition of tone in the muscles which may be due to deficiency of dextrose and glycogen. All symptoms of insulin hypoglycæmia are relieved by dihydroxyacetone as efficiently as by dextrose; methylglyoxal, on the other hand, exerted a toxic effect on normal animals, and in hypoglycæmic animals increased very much the severity of the symptoms. On administration of a mixture of methylglyoxal and dihydroxyacetone to a hypoglycæmic animal, the restorative effect of the latter compound predominated. Lactic and pyruvic acids, glycerol, acetone, acetaldehyde, glycol, and glycollaldehyde had no marked effect on the symptoms of hypoglycæmia. It is suggested that the toxic effects of overdosage with insulin may be due to increased formation of methylglyoxal (cf. Kermack, Lambie, and Slater, this vol., 282).

C. R. HARINGTON.

Calcium metabolism. I. Action of the parathyroid hormone on the calcium content of the serum and on the absorption and excretion of calcium. C. P. STEWART and G. H. PERCIVAL (*Biochem. J.*, 1927, 21, 301—313).—Extensive hæmorrhage causes a lowering of the serum calcium in rabbits, but not in cats. Rabbits are less susceptible to the action of parathyroid extract than are cats. Parathyroid extract raises the serum calcium of cats when injected subcutaneously and more rapidly when injected intravenously. The action is prevented by the simultaneous injection of sodium hydrogen carbonate. Parathyroid exerts its full action on the serum calcium, even after complete removal of the alimentary canal. There is no diminution in the

excretion of calcium when the hormone is administered while the serum calcium is high. The large intestine provides the main excretory route for calcium. The liver, spleen, pancreas, pituitary, thyroid, and central nervous system seem to have no special function in connexion with the effect of parathyroid on the blood calcium. The hormone probably controls the distribution of calcium between blood and tissues by regulating the proportion of the total diffusible serum calcium.

S. S. ZILVA.

Iodine compounds of the thyroid. T. INGVALDSEN and A. T. CAMERON (*Trans. Roy. Soc. Canada*, 1926, [iii], 20, V, 297—306).—Iodothyroglobulin, from beef thyroids, shows all the characteristics of a pseudo-globulin in regard to solubility and precipitation, and from this substance an impure thyroxin preparation containing 38.5% of iodine has been obtained. The specific test for thyroxin, the formation of an orange-red colour with nitrous acid, changing to red on addition of ammonia (Kendall and Osterberg, A., 1920, i, 180), is also given by diiodotyrosine. The formation of the red colour, which appears to be specific for these two substances, is of equal intensity for molecular solutions, and appears to depend on the presence of two iodine atoms attached to the ring in a definite position. After treatment which should remove all the thyroxin from hydrolysed thyroid tissue, the above colour reaction is still markedly positive, and it is suggested that diiodotyrosine may be present, although this substance could not be isolated.

A. WORMALL.

Relative activity of thyroid fractions and derivatives. A. T. CAMERON and J. CARMICHAEL (*Trans. Roy. Soc. Canada*, 1926, [iii], 20, V, 307—319).—The method used for comparing the activities of various preparations and extracts of the thyroid is that previously described (*ibid.*, 1), the method involving calculations based on the effects on growth and on the heart, liver, and kidneys of young white rats. The full activity of the thyroid appears to reside in the thyroglobulin, but thyroxin does not represent the full activity of the thyroid gland. Aqueous extracts of the thyroid show slight activity only. Thyroid activity is not destroyed by the action of pepsin or trypsin, whilst after enzymic hydrolysis of thyroglobulin, a solution is obtained which is distinctly active, but contains only a trace of thyroxin. Diiodotyrosine has no activity alone, nor does it accentuate the effect of thyroxin when both substances are administered together.

A. WORMALL.

Isolation of thyroxin. E. C. KENDALL (*J. Biol. Chem.*, 1927, 72, 213—221).—The author has been unable successfully to apply the method of Harington (A., 1926, 644) for the isolation of thyroxin from the thyroid gland; he also finds the distribution of thyroxin among the various fractions obtained in the process of isolation to be different from that described by the latter worker. It is therefore suggested that the process of isolation may have to be varied according to the place of origin of the thyroid glands employed.

C. R. HARINGTON.

Some sterol colour reactions in their relation to vitamin-A. O. ROSENHEIM (*Biochem. J.*, 1927, 21, 386—388).—On evaporating to dryness a chloro-

form solution of cholesterol and benzoyl peroxide in equimolecular proportions, a chromogenic substance is obtained which gives with arsenious chloride a blue colour indistinguishable in appearance from that given by cod-liver oil with the same reagent. When, however, this purified chromogen is added to vegetable or animal oils which do not by themselves react with arsenious chloride, it fails to give the colour reaction. When a neutral solvent is used, the reaction is intense. The fading of the blue pigment produced by arsenious chloride with the artificial product is much slower than in the case of cod-liver oil. There is also a difference in the absorption spectrum of the two pigments. The two chromogens are therefore not identical. S. S. ZILVA.

Effect of heat and oxidation on cod-liver oil as measured by colour tests. F. WOKES and S. G. WILLIMOTT (Biochem. J., 1927, 21, 419—425).—The course of destruction of the chromogenic substance in cod-liver oil by aeration was studied at 88°, 98°, 108°, 118°, and 125°. The temperature coefficient for 10° was found to be about 1.4—1.5. The results were in agreement with those obtained by various workers on the destruction of vitamin-A in cod-liver oil as measured by the biological test. Qualitative agreement was obtained by the concentrated sulphuric acid, phosphorus pentoxide, arsenic trichloride, and antimony trichloride colour tests. The destruction of vitamin-A by aeration is probably due to volatile organic peroxides. S. S. ZILVA.

Effect of 2:6-dihydroxyquinoline obtained from the β -acid of crude oryzanin on the polyneuritis of pigeons. Y. SAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 5, 191—198).—2:6-Dihydroxyquinoline hydrochloride prepared from the β -acid of crude oryzanin (cf. A., 1926, 846) has a temporary curative effect on the spastic symptoms of polyneuritis in pigeons, but lacks the curative powers of oryzanin. It is concluded that either 2:6-dihydroxyquinoline or its tautomeric form is a nucleus of the antineuritic substance from rice-polishings, or that oryzanin possesses a growth-promoting component besides its antineuritic factor. *N*-Chloro- α -quinolone appears to possess similar antineuritic powers to 2:6-dihydroxyquinoline, and in view of the similar properties reported for 2-hydroxypyridine (Williams, A., 1916, i, 697), phloroglucinol (Iwata, J. Agric. Chem. Soc. Japan, 1926, 2, 466), and quinine, the author concludes that the active hydroxyl group of the β -acid possesses similar powers. R. BRIGHTMAN.

Precipitation of the antiscorbutic factor from lemon juice. S. S. ZILVA (Biochem. J., 1927, 21, 354—355; cf. A., 1924, i, 588, 901; 1925, i, 1220).—Most of the antiscorbutic factor in decitrated lemon juice is precipitated by lead acetate within the pH range of 5.4—7.2. An active fraction containing 0.1—0.2% of dry matter is thus quickly and conveniently obtained. S. S. ZILVA.

Vitamin-C in cow's milk. Relation to concentration, homogenisation, and sterilisation. P. LAVIALLE (Bull. Soc. Chim. biol., 1927, 9, 208—221).—An investigation to determine the influence of certain processes, particularly sterilisation, on the

vitamin-C in milk. Dogs, initially in good health, show characteristic signs of scurvy after 7—10 months if fed on a diet deficient in vitamin-C, but if concentrated homogenised and sterilised milk has been added to the diet, no signs of scurvy are evident after 16 months. The concentrated milk loses its antiscorbutic properties when heated at 120—125° for 45 min. The use of preserved milks in cases of deficiency diseases, for which these milks are suitable on account of their richness and digestibility, and the necessity of supplementing them with fresh fruit juices, are discussed. A. WORMALL.

Antirachitic substances. V. Action of ultra-violet light on ethers and esters of cholesterol. C. E. BILLS and F. G. McDONALD (J. Biol. Chem., 1927, 72, 13—19).—No cholesteryl ether acquired antirachitic properties after irradiation; cholesteryl acetate, isobutyrate, and benzoate were all activated by ultra-violet light, but not the cinnamate, in view of which it is considered that the activation of the former esters is a property of the intact molecule, and is not due to liberation and subsequent activation of cholesterol itself. C. R. HARRINGTON.

Isolation of the antirachitic fraction of cholesterol irradiated by ultra-violet rays. I. I. NITZESCU, G. POPOVICIU, and J. DENES-GOETZ (Bull. Soc. Chim. biol., 1927, 9, 126—136).—Methods involving successive recrystallisations and precipitation with digitonin have been applied to concentrate the active antirachitic fraction (vitasterol) of irradiated cholesterol. The antirachitic power of irradiated cholesterol diminishes by successive recrystallisations, but residues from the mother-liquors are about 10 times as potent as the crystalline products. The residues lose none of their activity when kept for at least three or four weeks in dark vessels. These results are opposed to the findings of Hess, Weinstock, and Sherman (A., 1926, 207). Fractions have been isolated which were active in quantities less than 0.5 mg. per 100 g. of the total diet. A. WORMALL.

Catalytic action of irradiated cod-liver oil. B. SCHLIMKUS (Arch. exp. Path. Pharm., 1927, 121, 230—237).—The lipid peroxide content of cod-liver oil irradiated by sunlight was measured by the rapid titration of the iodine liberated from potassium iodide with sodium thiosulphate; concentrations from *N*/250 to *N*/80 were obtained. The peroxide catalyses the oxidation of iodide to free iodine. E. A. LUNT.

Parent substance of vitamin-D. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1927, 21, 389—397).—Stigmasterol and sitosterol show absence of absorption bands in the spectroscopic test and cannot be antirachitically activated by irradiation. Purified cholesterol behaves similarly. Charcoal and potassium permanganate in acetone solution remove the provitamin from cholesterol. The provitamin forms a digitonide. Ergosterol shows the same characteristic absorption spectrum in the ultra-violet as unpurified cholesterol, the intensity of the absorption, however, being enormously increased. Assuming it to be ergosterol, the amount of the impurity present in ordinary cholesterol was judged

by comparative spectroscopical examination to be of the order of 1:2000. Irradiated ergosterol in daily doses of 0.0002 mg. cures and prevents rickets in rats on a rachitic diet.
S. S. ZILVA.

Search for vitamin-D in the diatom *Nitzschia closterium* (W. Sm.). J. L. LEIGH-CLARE (Biochem. J., 1927, 21, 368—372).—The diatom grown in glass and exposed to either diffused daylight or direct sunlight forms a very poor source of vitamin-D. It probably is not therefore the ultimate source of vitamin-D in cod-liver oil.
S. S. ZILVA.

Free energy of nitrogen fixation by living forms. D. BURK (J. Gen. Physiol., 1927, 10, 559—573).—From a study of free energy data, it is shown that the fixation of nitrogen from the atmosphere by living cells so as to form nitrate or ammonia is accompanied by a liberation of free energy as well as by a positive heat of reaction. The general bearing of such results on the process of nitrogen fixation by plants and bacteria is discussed in detail.
W. O. KERMACK.

Nitrogenous material in a ligneous plant during a year's growth. R. COMBES (Compt. rend., 1927, 184, 533—535).—The total and secondary percentages of nitrogenous material in the foliage, stem, and roots of a 2-year-old beech for 16 months are recorded.
J. M. GULLAND.

Light absorption by the leaves of plants and by chlorophyll solutions. P. LASAREFF (Biochem. Z., 1927, 182, 131—133).—The primary and secondary absorption maxima of a solution of chlorophyll and of the green leaf show an approximate coincidence. Only 1—2% of the incident light energy passes through the green leaf.
J. PRYDE.

Presence of sodium in plants. G. BERTRAND and J. PERIETZEANU (Compt. rend., 1927, 184, 645—649).—Direct determinations of the percentage of sodium by means of the triple acetate of uranium, magnesium, and sodium (Streng, A., 1884, 366; Blanchetière, A., 1923, ii, 579) afford values for the fresh plant ranging from 0.0006% in the case of milfoil to 0.5471% in the stem and leaves of seaweed. For the dried plants, the values found lie between 0.0017% for horse-chestnut (fruit) and 3.507% for seaweed, and for the ash the sodium content lies between the limits 0.016% (leaves of Japanese spindle-tree) and 16.78% (seaweed). Some of the plants examined had previously been reported free from sodium. Fresh leaves of the following plants gave the values indicated: lily 0.0008, pear 0.0014, mulberry 0.0007, horse-chestnut 0.0021, haricot 0.0012, iris 0.0017, maize 0.0093, plantain, 0.0464, tobacco 0.03882%.
R. BRIGHTMAN.

Relation of stored food to cambial activity in the apple. E. L. PROEBSTING (Hilgardia, 1925, 1, 81—106).—The cessation of radial increase of wood and modification of the thickness of the cell walls following defoliation of apple trees does not appear to be associated with a deficiency of stored food. Possible reasons for the cessation of growth are suggested. The concentration of reducing sugars

is much greater in the bark than in the wood of young apple trees.

CHEMICAL ABSTRACTS.

Use of the hydroquinhydrone electrode for p_{H} determination in the fluids of the organism. F. GROSSMAN (Biochem. J., 1927, 21, 267—271).—Biilmann's hydroquinhydrone electrode (A., 1921, ii, 372) yields p_{H} values identical with those obtained with the hydrogen electrode in buffer solutions with p_{H} less than 7. In more alkaline buffer solutions higher values which increase with alkalinity are recorded with the first electrode. In physiological fluids such as blood-serum, cerebrospinal fluid, and blood, consistent values are obtained with the hydroquinhydrone electrode. These figures when corrected for the alkalinity of the medium by a formula introduced by the author agree well with those obtained with the hydrogen electrode. The quinhydrone, the quinoquinhydrone, and the hydroquinhydrone electrodes cannot be used for fluids with p_{H} greater than 9. The first two electrodes are unsuitable for serum and blood.
S. S. ZILVA.

Determination of mineral matter in organic materials. A. VILA and R. ANCELLE (Bull. Soc. Chim. biol., 1927, 9, 340—342).—An apparatus is described in which organic material may be destroyed by means of fuming nitric acid, whilst any volatile products are collected in a series of absorption vessels.
W. O. KERMACK.

Determination of uric acid as ammonium urate. A. BOIVIN (Bull. Soc. Chim. biol., 1927, 9, 149—161).—The various modifications of this method are investigated, in order to find the conditions which give most accurate results for uric acid solutions. The ammonium salt is best precipitated by the addition of ammonium chloride and ammonia; the precipitate is filtered off after 24 hrs., then dissolved in sodium hydroxide, and converted into the mercuric salt, in which the uric acid-nitrogen is determined by Kjeldahl's method after removal of the ammonia present. The precipitation of the ammonium salt, under the conditions stipulated, results in a loss of less than 0.01 g. of uric acid per litre, if the concentration of uric acid is greater than 0.1 g. per litre, and if the amount of other oxypurines is not greater than the amount of uric acid present. The concentration of uric acid, for accurate work, should be at least 0.2 g. per litre, and therefore the ammonium urate methods are not directly applicable to blood.
A. WORMALL.

Micro-determination of uric acid. **Determination of a few centigrams of uric acid per litre in presence of purine bases.** A. BOIVIN (Bull. Soc. Chim. biol., 1927, 9, 162—173).—Uric acid is precipitated as the mercuric salt, the precipitate is dissolved in a small volume of potassium cyanide solution, and then the ammonium salt is precipitated. The subsequent treatment is similar to that described before (preceding abstract). In the micro-determination, an addition to the result of 3 mg. per litre is made, and then the error is of the order of 1 mg. per litre.
A. WORMALL.