## BRITISH CHEMICAL ABSTRACTS

# A.—PURE CHEMISTRY FEBRUARY, 1931.

### General, Physical, and Inorganic Chemistry.

Isotope effect on band spectrum intensities. J. L. DUNHAN (Physical Rev., 1930, [ii], 36, 1553-1559).—Theoretical. In order to discover whether the transition probability of a given line is different for two isotopic molecules, the effect of the nuclear mass on intensities is calculated on the basis of Hutchisson's expressions for the vibrational transition probability (cf A., 1930, 1331). It is shown that there is a change in the vibrational, but not in the electronic, part of the transition probability with nuclear mass. The effect of a change in nuclear mass on the population, regarded as a simple Boltzmann distribution, of the initial state is also found. Results are applied to find the magnitude of the isotope effect for certain bands which have been used to measure the abundance of the isotopes in oxygen (cf. Babcock, A., 1929, 971), nitric oxide (cf. Naudé, A., 1930, 1232), and chlorine (cf. Elliott, *ibid.*, 977). The effect is small, and generally less than 10%. N. M. BLIGH.

Change in electron coupling in rare gases. C. J. BARKER (Naturwiss., 1930, 18, 1100).—The extension to  $p^{5}s$  and  $d^{9}s$  configurations by Laporte and Inglis (A., 1930, 971) of the quantum-mechanical theory of Houston (A., 1929, 480) on the relation between the triplet interval ratio to the singlet-triplet interval for two-electron configurations in which one electron is in an s-state has been applied to the rare gases: Experimental results of Back (A., 1925, ii, 341) for the g values of the singlet and middle triplet levels of the  $2p^{5}3s$  configuration of the Ne I spectrum have been compared with calculated values. Experimental data on the Zeeman effect were used to derive g values of analogous levels of the configurations  $3p^54s$  in the A I and  $4p^55s$  in the Kr I spectra. In the spectrum of XeI only the g values of the middle triplet level of the configuration  $5p^{5}6s$ could be measured. For the spectra of Ne I, A I, Kr I, good agreement was found between calculated and experimental g values; with Xe 1 the agreement is not so good. W. R. ANGUS.

Method of applying the slitless spectrograph to the measurement of the Doppler shift. N. DEISCH (J. Opt. Soc. Amer., 1930, 20, 685-692).-Descriptive. W. Good.

Ultra-violet light theory of auroræ and magnetic storms. E. O. HULBURT (Physical Rev., 1930, [ii], 36, 1560-1569).-Various difficulties and anomalies in the recently proposed theory (cf. ibid., 1929, 33, 412; 34, 344) are removed by the application of further developments of the theory of the high atmosphere (cf. A., 1930, 392). N. M. BLIGH.

Paschen-Back effect in hyperfine structure. S. GOUDSMIT and R. F. BACKER (Z. Physik, 1930, 66, 13-30).-The method developed by Heisenberg and Jordan and by Darwin for the Paschen-Back and Zeeman effects in ordinary multiplets is applied to the interaction of nuclear spin and resultant outer electronic angular momentum, to give the Paschen-Back and Zeeman separations and component line intensities. The theory is accurate only when the Paschen-Back effect is fully developed, and lines of small hyperfine separation should, therefore, be chosen for its verification. Two rules are deduced for transition from strong to weak fields, viz., (i) the projection,  $M_{\rm F}$ , of the resultant of all angular momenta in the field direction remains unchanged; (ii) different levels with the same value of  $M_F$  do not cross over in energy value. The theoretical results are compared with Back's experimental results for bismuth (cf. this vol., 137). A. B. D. CASSIE.

Extended energy functions of the hydrogen molecule. P. M. DAVIDSON and W. C. PRICE (Proc. Roy. Soc., 1930, A, 130, 105-111).-Mathe-matical. A formula is deduced for the potential energy of a diatomic molecule which holds for all values of the internuclear distance. Previous formulæ fail either at small distances, or at large distances, or both. The present formula appears as the sum of two series, the significance of which is discussed in terms of the forces between the components L. L. BIROUMSHAW. of the molecule.

New bands in the secondary spectrum of hydrogen. III. D. B. DEODHAR (Phil. Mag., 1930, [vii], 10, 1082-1095; cf. A., 1930, 263; Finkelnburg, A., 1929, 118).-The wave numbers, estimated intensities, term values, and quantum analysis of the recently discovered group of seven bands in the violet region are tabulated and discussed.

N. M. BLIGH.

Effect of crossed electric and magnetic fields on the Balmer lines of hydrogen. W. STEUBING (Naturwiss., 1930, 18, 1098-1099).—The effect of the simultaneous action of an electric and a magnetic field has been studied. A crossed field does not produce new components, but there results a kind of displacement of Stark effect components which follows identically the intensity changes of individual components. The results on the intensity differences of components in relation to the direction of the electric field are of importance in deciding whether experimental results on the intensity distribution of Stark effect components are in harmony with the theory of

Schrödinger. Weak magnetic fields do not exert a marked influence on the intensity distribution.

W. R. ANGUS. Experimental arrangement of the H<sub>2</sub> band system into singlet and triplet systems. W. FINKELNBURG (Z. Physik, 1930, 66, 345-349).-The distinct forms of the excitation function-exciting voltage curves for singlet and triplet terms were used to distinguish H<sub>2</sub> singlet and triplet bands; A-, B-bands belong to a singlet system, and  $\alpha$ -,  $\beta$ - to a triplet system. The subsidiary maximum which appears only in the H<sub>2</sub> triplet excitation function-exciting voltage curve is in accord with Beutler and Eisenschimmel's hypothesis that during a collision process the resultant electron spin of the colliding entities must remain A. B. D. CASSIE. unchanged.

Stark effect in some helium lines in the visible spectrum. K. SJÖGREN (Z. Physik, 1930, 66, 377-388).—The Stark effect was determined quantitatively, by Stark's original method, for fields of 175-550 kilovolts per cm. The lines 2S-3P, 2S-3D, 2P-4S, 2P-4D, 2P-4F, 2P-4P, 2p-4s, 2p-4d,2p-4f, and 2p-4p were investigated.

A. B. D. CASSIE.

Change in electron coupling in the rare gases. C. J. BAKKER (Nature, 1930, 126, 955).—From experimental data on the Zeeman effect of the rare gases, the experimental g values of the analogous levels of the configuration  $3p^54s$  in A I and  $4p^55s$  in Kr I are obtained. Agreement between observed and calculated g values is satisfactory in the case of L. S. THEOBALD. No I, A I, and Kr I.

Nuclear moment of Li<sup>6</sup> and Li<sup>7</sup>. H. SCHULER (Z. Physik, 1930, 66, 431-435).-Hyperfine structure of the Li II 5485 Å. line was investigated by means of a Perot-Fabry etalon with a maximum plate separation of 3 mm. Results for Li<sup>7</sup> agree approximately with Güttinger's formulæ (cf. A., 1930, 1487) for nuclear spin of  $\frac{1}{2}$  and of  $\frac{3}{2}$  units, but do not give sufficient detail to decide between the two values. Li<sup>6</sup>, 5485 Å., has no hyperfine structure of separation greater than one fifth that of Li<sup>7</sup>.

#### A. B. D. CASSIE.

CIV lines in the visible and near ultra-violet. Term system for CIV. B. EDLÉN and J. STENMAN (Z. Physik, 1930, 66, 328-338).-The spectrum due to a carbon arc acting in a vacuum was examined. The spark lines CI, CII, CIII, and CIV were distinguished by their separate variations in intensity with variation of the self-induction of the discharge circuit. New CII and CIII lines, and the most intense CIV lines due to transitions between orbits of total quantum number 4 and 5, and 5 and 6, were observed. These lines were arranged into a term system, which includes more accurate values of terms of principal quantum number 6 than have hitherto been given. The doublet separations in  $2^2P$ ,  $3^2P$ , and  $4^2P$  fit Landé's formula. A. B. D. CASSIE.

Nuclear spin of nitrogen. W. R. VAN WIJK (Arch. Néerland., 1930, [iiiA], 13, 29-57).-The general theory of diatomic molecular spectrum structure is briefly surveyed. Measurements were made of the negative band spectrum of nitrogen due to the N<sub>2</sub><sup>+</sup>

molecule, and of the second positive group due to the neutral molecule. The value 2:1 was found for the ratio of alternating intensities of the negative bands 3914, 3884, 4278, and 4237 Å., and for the positive bands 3371, 3805, and 3755 Å. From investigation on the 3914 band, the ratio was found to be indepen-dent of the pressure. The agreement of intensity measurements with other criteria for nuclear spin value was investigated from the 3776 Å. thallium line, which showed strong absorption and confirmed the value 1 for the nuclear spin. N. M. BLIGH.

Bergmann series in the argon spectrum. E. RASMUSSEN (Naturwiss., 1930, 18, 1112-1113).-Among the inert gases Bergmann series had been observed in the spectrum of xenon only. The corresponding series has been obtained in the argon spectrum, which was photographed on negative plates, using a plane grating spectrograph (dispersion 17Å./mm.). A table of the observed series is given. The limiting terms  $3d_6$ ,  $3d_5$ ,  $3d_3$ ,  $3d_4$ ,  $3d_4$  and the term series mUand mW have been determined. Certain new combinations of principal and subsidiary series have been found and are tabulated. From these combinations the terms  $2s_2$ ,  $2s_3$ ,  $2s_4$ ,  $2s_5$ , and 3s'' were evaluated. Wave-lengths greater than 1  $\mu$  have been provisionally W. R. ANGUS. measured by extrapolation.

Structure of the iron spectrum. M. A. CATALÁN (Anal. Fis. Quim., 1930, 28, 1239-1385).-A comprehensive survey, with a bibliography, is given of previous work on the atomic structure of iron, with extensive tables of the wave-lengths and intensities of all the arc lines recorded, and of the Zeeman effect. More than 2350 lines of the Fe I spectrum are classified in 304 levels, and there are 8 series, 51 terms, and 275 multiplets. It is shown that the most intense lines originate by addition of a valency electron to the atomic residue in one or both of the spark configurations  $3d^64s$  and  $3d^7$ . H. F. GILLBE.

Intensity measurements of the multiplet  $G-e^{5}F$ . W. A. M. DEKKERS and A. A. KRUITHOF  $z^5G-e^5F.$ (Z. Physik, 1930, 66, 491–493).—Intensity relations in the  $z^5G-e^5F$  multiplet of nickel were determined from a carbon arc, one of the poles of which contained a nickel bead, or alternatively, 10% of nickel sulphate; the other pole was either of carbon or of a nickel-zinc alloy. Deviations from the summation rule always A. B. D. CASSIE. occurred.

Intensity measurements of the copper arc lines. L. S. ORNSTEIN and D. VERMEULEN (Z. Physik, 1930, 66, 490; cf. A., 1930, 1329).-Copper in a carbon arc gives the ratio of intensities of the  $1^2S$ - $2^2P$  copper doublets as 1:2, which agrees with the A. B. D. CASSIE. summation rule value.

Series of the silver arc spectrum, Ag I. H. A. BLAIR (Physical Rev., 1930, [ii], 36, 1531-1534; cf. A., 1930, 1227).—The high series members of Ag I were measured, using a Schüler tube source and helium standards. Data for the complete diffuse, sharp, and principal series are tabulated, including a few new lines, and correcting existing values. No terms of the quadruplet system nor of the  $d^9s^2 \, ^2D$  were found (cf. McLennan, A., 1928, 1167; Shenstone, ibid., 450). Ritz formulæ for the series were deduced; the value of the lowest term  $d^{10}5s^2S$  is 61104.4, giving an ionisation potential of 7.53 volts. N. M. BLIGH.

Band spectrum of silver hydride. E. BENGTS-SON (Nature, 1931, 127, 14).—The rotational structure of 14 bands belonging to  ${}^{1}\Sigma \longrightarrow {}^{1}\Sigma$  have been analysed and arranged in a vibrational scheme. The vibrational levels of the lower electronic state can be represented by the formula  $F''(v)=1723\cdot 5v'' 33\cdot 5v''^2 - 0\cdot 0094v''^3$ ; the excited electronic state shows certain irregularities which may originate from a perturbing level. The dissociation energies in both states are  $D' \sim 6300$  and  $D'' \sim 19,000$  cm.<sup>-1</sup> approximately. L. S. THEOBALD.

Effect of gases on the optically excited cadmium I spectrum. P. BENDER (Physical Rev., 1930, [ii], 36, 1535—1542).—An apparatus is described for producing intense optically-excited cadmium radiation for an investigation of the quenching effect of nitrogen, carbon monoxide, and hydrogen on the optically excited cadmium spectrum. Each gas decreases the intensity of each of the spectral lines. Nitrogen and carbon monoxide have a low quenching efficiency, the former being the less efficient, and are less effective in quenching the resonance line  $\lambda$  3261 than the remainder of the spectrum. Kinetic energy collisions of molecules of these gases with excited cadmium atoms transfer them from the  $2^{3}P_{1}$ to the metastable  $2^{3}P_{0}$  state. Hydrogen has a high quenching efficiency, collisions with the  $2^{3}P_{1}$  cadmium atoms forming cadmium hydride molecules and atomic hydrogen (cf. Bates, A., 1929, 156). The effects are compared with similar phenomena for mercury (cf. Klumb, *ibid.*, 480). N. M. BLIGH.

Optical excitation of cadmium hydride and zinc hydride bands. P. BENDER (Physical Rev., 1930, [ii], 36, 1543-1552; cf. preceding abstract).--Excitation of a cadmium-hydrogen gas mixture with light from a hydrogen-cadmium, but not from a helium-cadmium, discharge produces an intense true optical resonance of cadmium hydride bands; these are produced also through excitation of CdH molecules by collisions of the second kind between excited cadmium atoms and either normal CdH molecules or H<sub>2</sub> molecules. The mechanism of the resonance excitation is discussed. Zinc hydride bands were produced as true optical resonance radiation by hydrogen-zinc electric discharge. Mercury hydride bands were excited, using a water-cooled mercury arc, through collisions of the second kind (cf. Gaviola and Wood, A., 1929, 239) and the mechanism is discussed in relation to the foregoing results. N. M. BLIGH.

Photo-electric intensity measurements in the mercury spectrum. II. L. S. ORNSTEIN and J. F. CUSTERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 809-813).—Further measurements on the intensity of certain lines in the mercury spectrum have shown that the relations previously reported (A., 1930, 1080) hold not only for the pressure region investigated, but also at very low pressures, the measurements having been extended by the use of a more sensitive photo-electric cell. With falling pressure the peak of the curve connecting potential with current density is displaced in the direction of higher current density, but the peak potential falls at first and rises again later. The intensity, I, of the line 5461 Å, has been measured as a function of the current density i, and at all pressures the ratio I/i increases with decreasing current density.

E. S. HEDGES.

Fluorescence of excited mercury atoms. Z. ZAJAC (Compt. rend., 1930, 191, 1304-1306; cf. Pienkovski, A., 1928, 813).-Mercury vapour was excited simultaneously by an oscillating electric discharge and a low-pressure mercury arc in an evacuated sealed tube connected with a mercury reservoir, both of which could be heated independently so as to vary either the vapour pressure ( $t^{\circ}$  const.) or the density ( $p \mod 1$ ). A bluish-green luminescence appeared at 0.05 mm. in the positive region and attained a maximum intensity at 140° and 0.3 mm. Above 1 mm. pressure a continuous spectrum was obtained, the intensity of the mercury arc lines  $(\lambda 5461, 4358, and 4047)$  being greater than that obtained by electrical excitation alone. Since the intensity of the fluorescence is proportional to that of the activating light, it is concluded that a single stage of absorption precedes emission, and that the oscillating discharge produces a non-uniform distribution of the atoms in the  $2^{3}P_{012}$  state, followed by passage to the  $2^3S_1$  state consequent on absorption of certain incident radiations. The fluorescence results from the return to the normal state. J. GRANT.

Fluorescence of mercury vapour under atomic and molecular absorption. (LORD) RAYLEIGH (Nature, 1931, 127, 10).—Mercury vapour gives the green fluorescence when excited by wave-lengths as long as 3450 Å. The discontinuous nature of the fluorescence excited by wave-lengths near the resonance line 2537 Å. is confirmed by the fact that the addition of hydrogen suppresses the fluorescence arising from atomic absorption, leaving the molecular effect practically unaltered. L. S. THEOBALD.

Zeeman effect in the hyperfine structure of the thallium line, 3775 Å. E. BACK and J. WULFF (Z. Physik, 1930, 66, 31–48).—The Zeeman effect of this particularly simple line was observed for magnetic fields of 17,050, 29,700, and 43,350 gauss with a 6·3-metre Rowland grating. The results are discussed in relation to Goudsmit and Backer's theory (see this vol., 135) of the position and intensity of the Zeeman components. The presence of ordinarily forbidden transitions predicted by this theory was verified. Generally, the experimental results are in good agreement with theory if a nuclear spin momentum of  $\frac{1}{2}$  unit is assumed. A. B. D. CASSIE.

Hyperfine structure of bismuth. P. ZEEMAN, E. BACK, and S. GOUDSMIT (Z. Physik, 1930, 66, 1-12).—New experiments on the hyperfine structure of the bismuth arc lines, and their Zeeman effect, are described. The results complete earlier work, without changing the theoretical deductions. A scheme of term levels is given. The excited levels have not been sufficiently investigated to give more than their total and inner quantum numbers. The coefficient of proportionality in a Landé separation formula for interaction of nuclear spin, and resultant electronic angular momentum of the outer shell, is given for the different levels. Intensity formulæ for the hyperfine structure are also given. The different arc lines, their hyperfine structure, and Zeeman components are discussed in detail. An appendix by BACK and J. WULFF shows photographs of the 10 hyperfine Zeeman components of bismuth, agreeing with the assigned nuclear spin of 4½ units. A concave grating and a Hilger echelon were used to obtain the photographs. A. B. D. CASSIE.

Reflexion of long wave-length X-rays. J. THIBAUD (J. Phys. Radium, 1930, [vii], 1, 404).— A discussion of the results of Valouch (cf. A., 1930, 1229) in relation to the author's formulæ (cf. *ibid.*, 512). N. M. BLIGH.

Fine structure of certain X-ray emission lines. J. VALASEK (Physical Rev., 1930, [ii], **36**, 1523— 1530).—The  $K\alpha$  lines of iron, cobalt, nickel, copper, molybdenum, and silver were investigated, using two specially constructed single-crystal spectrometers. The fine structure reported by Davis and Purks (cf. A., 1928, 451, 819) was not confirmed. Photomicrographic curves from plates taken in the first and second order are reproduced, and widths of  $\alpha_1$  lines and the  $\beta_1$  line of molybdenum are tabulated.

N. M. BLIGH.

Scattering power for X-rays of the atoms in magnesium oxide and sodium fluoride. R. W. G. WYCKOFF and A. H. ARMSTRONG (Z. Krist., 1930, 72, 433—441; Chem. Zentr., 1930, ii, 353).—The intensities of the principal lines, using MoK $\alpha$  radiation, have been measured. The results for sodium fluoride agree with those of Havighurst. A. A. ELDRIDGE.

Wave-length of X-rays. T. H. LABY and R. BINGHAM (Nature, 1930, 126, 915—916).—Using Rowland's method of coincidence of lines, the K line of carbon has been photographed over a range of  $n\lambda$  from 0 to 810 Å. By comparison with the  $L\alpha$ and Ll lines of copper the wave-lengths 44.7 and 44.8 Å. have been obtained for the carbon line relative to 13.32 Å. for the copper  $L\alpha$  line. The aluminium  $K\alpha_1\alpha_2$  line is 8.315 Å. relative to copper  $K\alpha_1\alpha_2$ 1.5392 Å. L. S. THEOBALD.

Satellites of the  $K\beta_1$  line of elements from iron to zinc. S. KAWATA (Mem. Coll. Sci. Kyoto, 1930, A, 13, 383-387).—The wave-lengths of two new satellites discovered on the short wave-length sides of  $K\beta_1$  and  $K\beta_2$  of each of the elements from iron to zinc have been determined. W. GOOD.

Absorption formula of X-rays. II. M. ISHINO and S. KAWATA (Mem. Coll. Sci. Kyoto, 1930, A, 13, 375-381; cf. A., 1928, 212).—The results of experimental determination of the absorption coefficients of elements and aqueous salt solutions for various wave-lengths are given. It is shown that the true atomic absorption coefficient is not proportional to  $\lambda PZ^{q}$ , where p and q are constants independent of the wave-length,  $\lambda$ , and the atomic number, Z. p and q are nearly equal to but less than 3 and 4, respectively. W. GOOD.

X-Ray absorption in gases. W. W. COLVERT (Physical Rev., 1930, [ii], 36, 1619-1624).-Using double reflexion of X-ray spectral lines from a platinum-surfaced mirror and a calcite crystal in order to increase homogeneity of the beam, absorption measurements were made with neon, sulphur dioxide, chlorine, and argon, and mass absorption coefficients for the range of radiation wave-lengths 0.496-2.288 Å, are tabulated. N. M. BLIGH.

Glow discharge at the active electrode of an electrolytic rectifier. J. S. FORREST (Phil. Mag., 1930, [vii], 10, 1003—1014).—The luminosity appearing on the surface of the active electrode of a rectifying cell was investigated, using cells with active electrodes of aluminium, tantalum, and tungsten, through observations on the P.D.-current curves, thickness, and pressure of the gas layer on the electrode surface, spectrum of the glow, influence of magnetic fields, and comparison with the cathode glow. Evidence suggests that the glow is produced by the ionisation of oxygen molecules by collision with electrons with the ionised molecules.

N. M. BLIGH.

Photo-ionisation of cæsium vapour by absorption between the series lines. C. BOECKNER and F. L. MOILLER (Bur. Stand. J. Res., 1930, 5, 831-842).—The photo-ionisation of cæsium produced by a small continuous absorption between the series lines has been measured by the space-charge method. The relative sensitivity,  $I(\lambda)/I(3200 \text{ Å}.)$ , increases with the square root of the pressure within the range 3750-3250 Å. The values are almost independent of the temperature on the red side of 3500 Å., but on the other side the effect is reduced to about half by a rise in temperature of  $70^{\circ}$ . These results indicate that absorption between the lines is of molecular origin and that the work of dissociation of Cs<sub>2</sub> is about 0.26 electron volt (cf. A., 1930, 1079).

A. R. POWELL.

Photo-electric processes. M. STOBBE (Ann. Physik, 1930,  $[\nabla]$ , 7, 661—715).—A theoretical contribution to the quantum mechanics of photo-electric processes. W. Good.

Photo-electric effect of aluminium and aluminium amalgams. H. GERDING (Z. physikal. Chem., 1930, B, 11, 1-37).—The photo-electric current from aluminium and its amalgams with 0.06, 0.26, and 0.38% Hg has been studied in relation to the wave-length of the incident light, the time of exposure, and the condition of the illuminated surface. The quotient c/I (electron emission/intensity of light) in a vacuum is increased by scraping the surface, especially for wave-lengths near the photo-electric threshold, which is itself displaced towards the red. A scraped surface becomes fatigued in a vacuum, and more rapidly after contact with air, the photoelectric threshold in this case being displaced towards the ultra-violet. The maximum values of c/I and of the photo-electric threshold obtained by continued scraping in a vacuum are least for pure aluminium, slightly higher for the 0.06%, and highest for the 0.26% and 0.38% amalgams. This result affords support to the view that passivity is primarily attributable to differences in the metal itself. The fatigue observed on keeping is due to adsorption of air, and is caused by the negative contact potential acquired by the air film, acting as a retarding potential for the expelled electrons, increasing the work required for their expulsion. F. L. USHER.

Photo-electric emission from thin films of cæsium. L. R. Koller (Physical Rev., 1930, [ii], 36, 1639—1647; cf. Campbell, A., 1928, 1297; Zworykin, A., 1929, 1262; Olpin, A., 1930, 1230).— The photo-electric properties and methods of preparing thin films of cæsium were investigated. In one type a thin film of cæsium is adsorbed on a thin layer of oxygen previously adsorbed on the silvered bulb of the photo-electric cell. In the other, a thin film of cæsium is adsorbed on a layer of suboxides of cæsium obtained by coating a cathode with metallic cæsium and admitting traces of oxygen; the photoelectric current was recorded simultaneously. Results show that the most sensitive surfaces are obtained when a suboxide, rather than the normal oxide Cs.O. has been formed, and that their properties are due to the arrangement of molecules very near the surface. N. M. BLIGH.

Radio-frequency properties of ionised air. E. V. APPLETON and E. C. CHILDS (Phil. Mag., 1930, [vii], 10, 969-994).-The measurement of the dielectric constant of a conducting ionised medium is examined mathematically and an investigation, suggested thereby, of the high-frequency behaviour of ionised gases by measuring the dielectric constant of air is described. As ionisation increased the dielectric constant reached a minimum value from which it increased to greater than unity. This divergence from theoretical prediction was found to be due to the formation of ionic sheaths round the electrodes, thus increasing the capacity of the condenser. The variation of the thickness of the sheaths with the potential across them was examined by a wireless method, and gave results in agreement with the theory of collectors due to Langmuir and Mott-Smith. The influence of an imposed magnetic field on the radio-frequency properties of ionised air was studied, and the existence of a predicted inverse Zeeman effect confirmed. Pronounced absorption occurs at a critical frequency corresponding with a particular value of the imposed field; the ratio of the two last-named confirms the electronic nature of the electric carriers, supporting Larmor's theory of the refractive deviation of wireless waves in the upper atmosphere by free electrons.

#### N. M. BLIGH.

Internal conversion of nuclear energy. H. CASIMIR (Nature, 1930, 126, 953—954).—An expression for the coefficient of internal photo-effect has been deduced using Dirac's equation, and a comparison of the calculated photo-effects with the internal conversions measured by Ellis and Aston for radium-C (A., 1930, 1339) shows that the number of ejected electrons is larger than would be expected from the internal photo-effect. This shows that for the hard  $\gamma$ -rays of radium-C the ejection of atomic electrons is due mainly to interaction in the nuclear region. L. S. THEOBALD.

Effective cross-section of krypton towards slow electrons. J. HOLTSMARK (Z. Physik, 1930, 66, 49-59).—The data of Hartree for the atomic field of krypton, duly corrected for polarisation energy, have been used to compute the effective cross-section of krypton molecules towards electrons of energy from 0 to 7 volt<sup>-3</sup>. The agreement between the resulting values and the experimental results of Ramsauer and Kollath is satisfactory.

R. W. LUNT.

Liberation of electrons from a metal surface by positive ions. II. F. M. PENNING (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 841-857; cf. A., 1928, 681).-Measurements have been made of  $\gamma$ , the average number of electrons liberated from a metal surface by each positive ion, using positive ions of neon at different velocities. When extrapolated to zero velocity, the result  $\gamma_0 = 0.05$  is obtained, indicating that positive neon ions of zero velocity can liberate electrons. The experiments were conducted in such a way that metastable atoms, high-velocity neutral atoms, and light quanta could not strike the collecting electrodes. At higher velocities the value of  $\gamma$  depends on the material surface of the cathode and on the presence of impurities. E. S. HEDGES.

Characteristic velocities of electrons scattered from metallic surfaces. G. BERNARDINI (Atti R. Accad. Lincei, 1930, [vi], 11, 1096—1099).— Electrons having velocities of 34—50 volts emitted from a tungsten-thorium filament were allowed to impinge on brass and zinc surfaces, and the magnetic spectra of the resulting scattered electrons were photographed. The lines in these spectra correspond with characteristic electron velocities, but it is not certain whether they are really characteristic of the metallic surface, or are due to adsorbed gas.

O. J. WALKER.

Free electrons in metals and the role of reflexions according to Bragg. L. BRILLOUIN (J. Phys. Radium, 1930, [vii], 1, 377-400).-Theoretical. An investigation made of the nature of electron waves in a metal, and the conditions for selective reflexion analogous to those of Bragg for X-rays, using the Schrödinger perturbation method, leads to data on the movement of free electrons in the crystal lattice in agreement with that of Bloch (cf. A., 1929, 247; Pcierls, A., 1930, 281). The method is extended to the electronic moments, and leads to a series of surfaces, forming by their interlacing a lattice dividing the electron waves into zones, the separating planes corresponding with Bragg's conditions. Each zone corresponds with the waves obtained by the coupling of those of a certain quantum level of the ion; the condition for the numbering of the waves gives an expression for the wave-length, and agrees with the apparent numbering obtained by considering the ions as point charges. The formula for the electron energy is analogous to that of the free electrons of space, but involves an apparent mass which may become negative, and differs from the true mass. The problem is thus analogous to the numbering of the external orbits of complex atoms involving the true and the apparent quantum number of the Rydberg formula. Results deduced for a number of N. M. BLIGH. metals are tabulated.

Capture of electrons by ions. G. WATACHIN (Atti R. Accad. Lincei, 1930, [vi], 11, 993-997).--- The probability of the transition of an ion from its free state to the *n*th quantum state by the capture of electrons has been calculated from the principles of wave mechanics. The result affords an explanation of the experiments of Davis and Barnes (cf. A., 1929, 971). F. G. TRYHORN.

Energy losses of electrons in carbon monoxide and carbon dioxide. E. RUDBERG (Proc. Roy. Soc., 1930, A, 130, 182-196).-An extension of previous work (this vol., 12). In the case of carbon monoxide, the pressures used ranged from 7 to  $62 \times$ 10<sup>-3</sup> mm., and for carbon dioxide from 15 to  $24 \times$ 10-3 mm. The energy distribution of the electrons after passing through the gases showed a number of well-marked maxima which are characteristic of the energy levels of the molecules under investigation. The various maxima for carbon monoxide are correlated with transitions from the normal to excited states of the molecule, known from the analysis of the band spectra of the neutral or singly-ionised carbon monoxide molecules. In cases where a maximum is attributed to a single electronic level, an examination of the potential energy curves for the molecule shows that the position of the maximum in respect to the different possible vibrational levels is in excellent agreement with the Franck-Condon principle (A., 1927, 89). No evidence of the ionisation of soft X-ray levels has been found for either of the L. L. BIRCUMSHAW. gases.

Emission of electrons under the influence of chemical action at lower gas pressures. O. W. RICHARDSON and L. G. GRIMMETT (Proc. Roy. Soc., 1930, A, 130, 217-238; cf. Brotherton, A., 1924, ii, 377; Richardson and Brotherton, A., 1927, 713) .---Details are given of a method whereby controllable and measurable pressures of carbonyl chloride can be obtained down to 10<sup>-5</sup> mm. of mercury. The emission of electrons from an alloy of sodium and potassium (NaK) in this gas has been examined down to measured pressures of 10-5 and to extrapolated pressures of  $5 \times 10^{-7}$  mm. under various conditions. The results show that the saturation current  $i_0$  increases continuously with the partial pressure p of the gas from zero up to a critical value in the neighbourhood of  $p=10^{-3}$  mm. This critical value depends on the rate of flow of the alloy, being smaller the slower are the drops. The maximum total charge which can be emitted by any one drop appears to be a fixed quantity, proportional to the size of the drop. Evidence is adduced to show that the experimentally determined velocity distribution function among the electrons approaches a limit as the pressure is reduced. L. L. BIRCUMSHAW.

Secondary electronic emissions from metal foils and animal tissues. W. V. MAYNEORD (Proc. Roy. Soc., 1930, A, 130, 63—80).—The relative intensities of beams of X- and  $\gamma$ -radiation of different wave-lengths, when measured by the ionisation chamber method, depend on the material of the chamber. A mathematical theory is developed which shows that, neglecting certain secondary factors, small ionisation chambers artificially made sensitive by the insertion of foils of different elements show a maximum sensitivity in the region of medium wave-

lengths, when compared with an air chamber. This is confirmed by experiment. An ionisation chamber for the measurement of the intensity of  $\gamma$ -rays is described; it was found that the relative intensities of primary and secondary scattered beams of rays had different values according to the materials composing the chamber. A region of maximum sensitivity was also observed with ionisation chambers containing animal tissues. The significance of these observations is discussed. L. L. BIRCUMSHAW.

Specific charge of the electron. F. KIRCHNER (Physikal. Z., 1930, 31, 1073—1075).—The use of an oscillating circuit for determination of the specific charge of the electron (cf. *ibid.*, 1929, 30, 773) has been considerably improved, and gives for  $e/m_0$  the value  $1.7602\pm0.0025$  e.m.u. This agrees with the spectroscopic value, but deviates unaccountably from the cathode ray value. A. B. D. CASSIE.

Application of electron interference to structure analysis. E. RUPP (Physikal. Z., 1930, 31, 1076—1078).—Thomson's method for determination of the structure of a surface layer by reflexion of electrons of approximately 30 kilovolts (cf. A., 1930, 1082) is inapplicable to very thin layers. Electrons of 100 volts energy penetrate approximately 10 crystal planes, and may therefore be applied to thin layers. Reflexion from (100) planes of copper after various heat treatments was investigated by plotting intensity against electron velocity for a fixed angle of incidence. A. B. D. CASSIE.

Magnetic analysis of negative ions in mercury vapour. W. M. NIELSEN (Proc. Nat. Acad. Sci., 1930, 16, 721-727).-Ions produced by a discharge in mercury vapour at a pressure of the order of  $10^{-4}$ mm. have been analysed magnetically to determine the nature of the negative ions. The experimental method consisted in sweeping out of the path of a beam of electrons projected in the mercury vapour parallel to a magnetic field either positive or negative ions by means of a crossed electric field. The separated ions are further accelerated in a second electric field. Curves are given showing the ratio of ion to total electron current against m/e. Hg<sup>-</sup>, CO<sup>-</sup>, and C<sup>-</sup> are identified. At m/e equal to 19 and 60 two peaks (not identifiable) are observed. All the peak maxima appear in the analysis of the positive ions. The apparatus did not give trustworthy results at higher pressures because of the formation of a positive space W. GOOD. charge in the electron beam.

Pressure and high-velocity vapour jets at cathods of a mercury vacuum arc. E. KOBEL (Physical Rev., 1930, [ii], 36, 1636—1638).—Measurements on a mercury arc and fixed cathode spot gave the value  $0.017 \times 10^{-3}$  g. per amp. sec. for the amount of mercury vaporisation, and  $16-43 \times 10^5$  cm. per sec. for the vapour velocity, in good agreement with the results of Tanberg (cf. A., 1930, 832) for the vaporisation of copper from the cathode of a copper arc. N. M. BLIGH.

Distribution of rays in molecular streams. P. CLAUSING (Z. Physik, 1930, 66, 471-476).— Formulæ are deduced for the space distribution of molecules streaming through a short tube into a vessel the radius of which equals its length, the length being is small compared with the molecular free path. If diffuse scattering by the walls of the entrance tube governs this space distribution, large departures from the cosine law should occur. This is in contradiction with Mayer's experimental results (*ibid.*, 1929, 58, 373). A. B. D. CASSIE.

Relationship between electron diffraction maxima and the emission of soft X-rays. H. W. B. SKINNER (Naturwiss., 1930, 18, 1097— 1098).—An explanation of the experimental results of Rupp (A., 1930, 1493) is offered. W. R. ANGUS.

Introduction of exchange into the statistics of an electronic gas. L. GOLDSTEIN (Compt. rend., 1930, 191, 1306—1308).—The application of the statistical method (Dirac) to the atom is based on the analogy between atomic electrons and a degenerate electronic gas. Fermi's formulæ must be revised to include the energy of electronic exchange, which, together with the kinetic and potential energies, makes up the total energy of a system of electrons. It is shown mathematically that the energy of agitation of an electronic gas is made up of the energy of kinetic agitation and the energy of exchange agitation. J. GRANT.

Equations of electron theory and Dirac wave mechanics. N. R. SEN (Z. Physik, 1930, 66, 122-128).—Mathematical. A. B. D. CASSIE.

Dirac theory of protons and electrons. G. I. POKROVSKI (Z. Physik, 1930, 66, 129–136).—Theoretical. Some apparent difficulties of Dirac's theory are explained, and an upper limit for the energy of one quantum is deduced. Another result of the theory is that all motion is quantised, so that two successive transitions must have a definite time interval between them. A. B. D. CASSIE.

Graphical calculation of the magnitudes involved in an electron in motion. G. FOURNIER (Compt. rend., 1930, 191, 1302—1304).—It is shown that the relations between the lengths of the lines and angles involved in the construction of a trigonometrical circle correspond with the magnitudes of an electron in motion, e.g., the ratio of electronic velocity to that of light, the Lorentz concentration and timetransformation factors and the factors required for the calculation of the emission potential and the Broglie wave-length, and the product of H and the radius of a circle described by an electron in a field of H gauss. J. GRANT.

Properties of nuclear electrons. J. KUDAR (Physikal. Z., 1931, 32, 34-37).—Theoretical.

A. J. MEE.

Measurement of cross-section of non-inert gas molecules for slow electrons. E. BRÜCHE (Ann. Physik, 1930, [v], 7, 579-587)—Polemical against Bröse and Saayman (A., 1930, 1084). A. J. MEE.

Measurement of cross-section of non-inert gas molecules. H. L. BRÖSE and E. H. SAAYMAN (Ann. Physik, 1930, [v]. 7, 588–595).—A reply to Brüche (see above). A. J. MEE.

Measurement of cross-section of non-inert gas molecules. E. BRÜCHE (Ann. Physik, 1930, [v], 7, 596—600).—A reply to Bröse and Saayman (see above). A. J. MEE.

Measurement of magnetic susceptibilities of gases. H. BUCHNER (Ann. Physik, 1930, [v], 7, 716-730).—A method (Gouy method with torsion balance) for the measurement of magnetic susceptibilities of gases is described; it gave for carbon dioxide a value,  $(-8.6\pm0.4)\times10^{-10}$ , in good agreement with existing data. Between 0 and 600 mm. pressure the volume susceptibility is found to be directly proportional to the pressure; similarly for mixtures of carbon dioxide and oxygen (0.125-0.430% O.), the mixture law being confirmed. The Glaser pressure anomaly is apparently due to adsorption effects. Under certain conditions Glaser curves could be obtained in experiments with undried oxygen and with undried carbon dioxide. A critical review of existing researches in this field is made and it is concluded that the mass susceptibilities of carbon dioxide and mixtures of it with oxygen are independent of the pressure. W. GOOD.

Unit of at. wt. F. W. ASTON (Nature, 1930, 126, 953).—Attention is directed to the need for a reconsideration of the scale of at. wts. arising from the complexity of oxygen. L. S. THEOBALD.

At. wt. of potassium from plant ash. H. H. LOWRY (J. Amer. Chem. Soc., 1930, 52, 4332—4333). —Determinations of the potassium-chlorine ratio with potassium from cotton ash and wheat flour ash yield the at. wt.  $39.111\pm0.013$  and  $39.091\pm0.016$ (Cl=35.457), respectively, which are in good agreement with accepted values for potassium. This is evidence that plant cells do not absorb selectively the radioactive isotope of potassium from the normal mixture of isotopes (cf. Zwaardemaker, A., 1926, 554; Loring and Druce, Chem. News, 1930, 140, 34).

J. G. A. GRIFFITHS.

Revision of the at. wt. of thallium. Analysis of thallous bromide. O. HÖNIGSCHMID and H. STRIEBEL (Z. anorg. Chem., 1930, 194, 293—298).— Analysis of thallous bromide by precipitation of silver bromide yields for the at. wt. of thallium  $204\cdot390\pm$ 0.008, in agreement with that obtained previously by analysis of the chloride. The solubility of thallous bromide in water at 18°, 25.68°, and 68.5° is 423.3, 579, and 2520 mg. per litre, respectively.

H. F. GILLBE.

Separation of the isotopes of bromine. At. wt. of bromine from the ratio Ag: AgBr. P. HAR-TECK and H. STRIEBEL (Z. anorg. Chem., 1930, 194, 299-304).-The theory of the separation of isotopes by fractional sublimation is described. The most volatile fraction obtained by fractionally subliming bromine in a current of hydrogen at  $-18.5^{\circ}$ ,  $-25^{\circ}$ , and  $-36^{\circ}$  had an at. wt., determined from the ratio Ag : AgBr, of  $79.916\pm0.001$ , which is identical with that of ordinary bromine. The failure to produce any separation is ascribed to the fact that in a mixture of isotopes the vibrational energies of the individual atoms and molecules are so inter-related that the difference of the vibrational energies of two isotopes is less for a mixture than for the separated isotopes, and the magnitude of the effect is therefore reduced to less than the experimental error. H. F. GILLBE,

Relation between the emission of long-range  $\alpha$ -rays and  $\gamma$ -rays. (MME.) P. CURIE (Compt. rend., 1930, **191**, 1055—1058).—An extension and comparison with experimental results of Gamow's theory, from which it is concluded that in the cases of radium-C' and thorium-C' Gamow's formula gives approximate results. J. GRANT.

Formation of long-lived active molecules in hydrogen subjected to the action of  $\alpha$ -particles from radon. E. C. TRUESDALE (J. Physical Chem., 1930, 34, 2472—2478).—The work of Duane and Wendt (Physical Rev., 1917, 10, 117) has been repeated using certain refinements. Hydrogen sulphide could be detected in small amounts only when sulphur was present in the reaction sphere surrounding the radon, and no evidence of the existence of long-lived active hydrogen or of triatomic hydrogen was obtained. L. S. THEOBALD. Scattering of hard  $\gamma$ -rays. C. Y. CHAO (Physical

Scattering of hard  $\gamma$ -rays. C. Y. CHAO (Physical Rev., 1930, [ii], **36**, 1519—1522; cf. A., 1930, 1086).— In order to investigate the deviation of the absorption coefficient for heavy elements from that predicted by the Klein-Nishina formula measurements were made on the scattering of  $\gamma$ -rays from thorium-*C* by aluminium and lead. For lead additional scattered rays were observed; these are considered to have a nuclear origin, since their wave-length and space distribution are inconsistent with an extra-nuclear scatterer. N. M. BLIGH.

Scattering of hard γ-rays. L. LANDAU (Naturwiss., 1930, 18, 1112).—Polemical against Beck (A., 1930, 1496). W. R. ANGUS.

Artificial excitation of nuclear y-rays. W. BOTHE and H. BECKER (Z. Physik, 1930, 66, 289-306).—An apparatus for the efficient use of  $\alpha$ -rays from a polonium source in exciting nuclear levels in non-radioactive substances is described. Nitrogen, carbon, oxygen, neon, calcium, and silver showed no secondary nuclear emission within the limits of experimental error; lithium, beryllium, boron, fluorine, magnesium, and aluminium showed emission, beryllium emission being much more intense than the others. Absorption measurements of this emission from boron and beryllium showed it to be of approximately the same wave-length as the hardest y-radiation from radioactive substances, but the hard secondary radiation from lead (cf. A., 1922, ii, 13) could not be detected. A curve showing the approximate variation of intensity of the secondary radiation from beryllium with the energy of the exciting  $\alpha$ -particles was obtained, but is not sufficiently accurate for theoretical interpretation. Possible theoretical interpretations of the results, on Gamow's model of the nucleus, are discussed.

A. B. D. CASSIE. A  $\gamma$ -radiation from polonium. W. BOTHE and H. BECKER (Z. Physik, 1930, 66, 307—310).—Experiments described (cf. preceding abstract) showed that polonium emits a hitherto unobserved hard  $\gamma$ -radiation. One quantum of this radiation is emitted for every 10<sup>5</sup> atoms disintegrated, and it is therefore probably due to excitation of polonium nuclei by  $\alpha$ -particles emitted by the disintegrating atoms.

A. B. D. CASSIE.

Attempts to find a stable isotope of polonium. G. VON HEVESY and A. GUENTHER (Z. anorg. Chem., 1930, 194, 162-178).-The electrochemical be-haviour of polonium has been investigated and the best conditions for its electrolytic isolation have been determined. The  $p_{\rm H}$  of the electrolyte is of import-ance; in presence of bismuth the acid concentration should be between N and 0.33N, as at higher concentrations polonium is redissolved and at lower concentrations bismuth separates as a result of hydrolysis. In presence of tellurium electrolysis with a current density of  $10^{-3}$  amp. per cm.<sup>2</sup> from a N-acid solution yields a deposit containing only traces of tellurium; gold considerably decreases the yield. The best yield and the purest product are obtained by electrolysis with a P.D. of 1 volt and a current density of  $1-10 \times 10^{-4}$  amp. per cm.<sup>2</sup>, using a rotating molybdenum cathode. Polonium, together with tellurium, may be separated from bismuth by precipitation with a reducing agent such as stannous chloride, and from tellurium by precipitation of the hydroxide. By application of these reactions large quantities of the minerals hessite, calaverite, nagyagite, bismuth telluride, and bismuth glance, and of metallic bismuth, have been worked up with addition and final re-separation of polonium as a radioactive indicator, in order to separate a stable isotope of polonium, but X-ray analysis of the final precipitate shows that any such substance cannot be present in the minerals to a greater extent than 10<sup>-11</sup> g. per g. H. F. GILLEE.

Determination of radium by the emanation method. R. G. FULTON (J. Assoc. Off. Agric. Chem., 1930, 13, 497-503).—The Boltwood method (A., 1904, ii, 666) as modified by Sale (J. Assoc. Off. Agric. Chem., 1925, 8, 531) was used in the examination of a radioactive water sample, a water-soluble salt, and a refractory material. A few minor manipulative details were modified. The results were satisfactory and were checked against the methods of Schlundt and Moore (A., 1905, ii, 368) and of Barker (A., 1918, ii, 371). Cyrtolite ore also was examined by the procedure prescribed for a refractory substance with satisfactory results. H. J. DOWDEN.

Can lead be made radioactive? G. GUEBEN (Ann. Soc. Sci. Bruxelles, 1930, 50, B, 117-121).-Experiments have been conducted with lead of 99.95% purity; one specimen was wrapped in black paper and shielded from penetrating radiation, a second specimen was exposed to sunlight for 7 months, a third was exposed to the radiation from a mercuryvapour lamp for 580 hrs., a fourth was subjected to X-rays for 185 hrs., and a fifth was submitted to radiations from radium emanation for 7 months. None of the lead specimens became radioactive after the treatment. It is concluded that the radioactivity observed in leaden roofs is due not to the absorption of radiation, but to the accumulation of a radioactive E. S. HEDGES. deposit from the atmosphere.

Mode of working of Geiger counting chambers. C. BOSCH and H. KLOMB (Naturwiss., 1930, 18, 1098). —Geiger counters with copper, silver, gold, iron, and zinc electrodes in helium were used. The presence of electronegative impurities promoted the counts. When counters were filled with highly purified helium and the electrodes completely degassed they did not exhibit counting properties. Immersion of a counter in liquid air inhibited its counting properties for the duration of the cooling. It is suggested that the occurrence of "counts" may be due to the presence of an adsorbed layer of gas, perhaps water vapour, on the electrode. W. R. ANGUS.

Origin of the penetrating corpuscular radiation of the atmosphere. B. Rossi (Naturwiss., 1930, 18, 1096—1097).—Experiments have been made to test the results of Bothe and Kolhörster (Z. Physik, 1929, 56, 571; 1930, 59, 1). The origin of atmospheric penetrating corpuscular radiation is discussed. W. R. Angus.

Evidence for a stellar origin of the cosmic ultra-penetrating radiation. V. F. HESS (Nature, 1931, 127, 10—11).—It is concluded that the sun contributes about 0.5% to the total intensity of the cosmic ultra-radiation at 2.5 km. above sea-level, and that the penetrating power of the solar ultra-rays is at least equal to that of the total cosmic radiation.

L. S. THEOBALD. Thunderstorms and the penetrating radiation. B. F. J. SCHONLAND (Proc. Roy. Soc., 1930, A, 130, 37-63).—An ionisation electroscope capable of measuring small and rapid changes in the intensity of the penetrating rays is described. A search for beams of downward-moving "runaway" electrons in the negative fields below thunder-clouds failed to yield positive results, and it is considered that such electrons are probably stopped by direct nuclear collisions before reaching the ground. Thunderstorms at distances greater than 10 km. caused no special changes in the ionisation, but overhead storms produced a reduction in the ionisation and thus succeeded in stopping some of the ionising particles.

L. L. BIRCUMSHAW.

Quantum mechanics of dispersion and magneto-rotation on Dirac's theory of the electron. W. KROLL (Z. Physik, 1930, 66, 69-108).—Mathematical. Electron spin and the relativity correction are taken into account in deducing the dispersion and magneto-rotation due to a single electron atom.

A. B. D. CASSIE.

Atomic dimensions and quantum theory. K. C. MAZUMDER (Z. Physik, 1930, 66, 119—121).— A mean value of the radii of the atomic valency electrons is deduced on the new quantum theory by assuming these electrons moving in the field due to an effective nuclear charge. A table of the effective nuclear charge and effective total quantum number for the atoms H to Ba is given. These atomic radii show a definite periodicity, with maxima at the alkali metals. A. B. D. CASSIE.

Deduction of Planck's radiation law from the viewpoint of adsorption. A. GANGULI (Z. Physik, 1930, 66, 137-142).—Theoretical.

A. B. D. CASSIE. Values and inter-relationships of c, e, h,  $M_p$ ,  $m_0$ , G, and R. W. N. BOND (Phil. Mag., 1930, [vii], 10, 994–1003).—Theoretical. The values and significance of certain non-dimensional products of the universal constants are examined in the light of the latest available values of the latter.

N. M. BLIGH. Higher order approximations in the Born method of collision calculations. C. MøLLER (Z. Physik, 1930, 66, 513-532).—Mathematical. Higher order approximations can be comparatively simply obtained by use of Dirac impulse co-ordinates instead of ordinary space co-ordinates. The second order approximations for scattering of *a*-particles and for elastic scattering of electrons are worked out. A. B. D. CASSIE.

Para-ortho separations and mean values of the S-terms of higher quantum numbers for helium. E. A. HYLLERAAS (Z. Physik, 1930, 66, 453-470).—Mathematical. A. B. D. CASSIE.

New methods of quantitative chemical analysis by spectra. H. LUNDEGARDH (Z. Physik, 1930, 66, 109—118).—The author's previous technique for obtaining the spectra of materials in an acetylene flame has been extended by the use of a photo-cell and galvanometer to measure the intensity of the light emitted. Approximately linear curves are obtained for the galvanometer deflexion as a function of the amount of material introduced into the flame in the case of potassium, calcium, and sodium salts, the spectral lines used being 4047.2, 4226.7, and 5890.2 Å., respectively.

It has been demonstrated that by a careful choice of conditions the intensity of the carbon line  $2296\cdot 8$  Å. is proportional to the concentration of carbon dioxide in a gas through which a condensed discharge is allowed to pass between gold or palladium electrodes. R. W. LUNT.

Deformation of electron shells. II. Absorption spectrum, molecular volume, and refraction of rare-earth salts. P. W. SELWOOD (J. Amer. Chem. Soc., 1930, 52, 4308—4316; cf. A., 1930, 1235). —Observations have been extended to include neodymium nitrate and chloride at concentrations between 1N and 10N. Whilst the increase of concentration of the nitrate is associated with an increase of molecular refraction, the converse is true of the chloride solutions. For both salts, an increase of concentration leads to marked increases of molecular volume and pronounced shifts of the absorption bands towards the red. Crystals of the nitrate show a greater shift than does the concentrated solution.

A comparison of the absorption spectra of the nitrates of praseodymium, samarium, europium, gadolinium, holmium, and erbium in 0.2N and 10N aqueous solutions shows that increase of concentration leads to slight shifts of the bands towards the red in the case of the first three and definite shifts towards the blue in the case of the last two. The latter phenomenon suggests some radical difference in the atomic structure of these last rare-earth elements. Gadolinium exhibits no shift, and visible lines could not be detected (cf. Freed and Spedding, A., 1929, 1362). J. G. A. GRIFFITHS.

Validity of Beer's law for violet solutions of iodine. S. PAPP (Magyar Chem. Fol., 1929, 35, 177-189; Chem. Zentr., 1930, i, 3405).-Beer's law is valid in the greater part of the visible spectrum for 0.5-0.0005M solutions of iodine in carbon tetrachloride, carbon disulphide, and hexane, but deviations were observed in the violet and the ultra-violet. A. A. ELDRIDGE.

Absorption of ultra-violet light by some organic substances. (MLLE.) B. CHARLAMPO-WICZÓWNA and L. MARCHLEWSKA (Bull. Acad. Polonaise, 1930, A, 376–398).—Using the same method as in the previous investigation (A., 1930, 10), measurements have been made of the absorption by alcoholic solutions of 1 : 6- and 2 : 6-dimethylnaphthalene,  $\beta$ - and  $\alpha$ -naphthyl ethyl ether, indene, thionaphthene, 2 : 2'-diphenol, 2-hydroxydiphenyl, dicyclopentadiene, *iso*quinoline, acridine, carbazole, diphenylene oxide, fluorene, phloridzin, salicin, and arbutin and by aqueous solutions of amygdalin, over the wave-length range 2100–3300 Å. The positions of the absorption maxima are given and the molecular extinction coefficients are tabulated.

#### J. W. SMITH.

Absorption spectra and constitution in the deoxybenzoin series. L. Szegö and P. Ostinelli (Gazzetta, 1930, 60, 677-688).-The absorption spectra in the ultra-violet region of a number of isomeric substitution derivatives of deoxybenzoin have been measured in order to determine the effect on the absorption of the position of the carbonyl group relative to the substituent. The compounds examined were of the type  $X \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot Y$ , in which X and Y were respectively OH, H; H, OH; Me, H; H, Me; Cl, H; H, Cl; Cl, Me; Me, Cl; OH, Me; Me, OH. The proximity of the carbonyl group to the substituent in the case of the monosubstituted derivatives, or to the group having the greater absorptive effect in the case of the disubstituted derivatives, causes enhanced absorption. This behaviour is contrary to that shown by compounds F. G. TRYHORN. containing the azoxy-grouping.

Absorption of light and constitution. I. Homopolar organic compounds. A. BURAWOY (Ber., 1930, 63, [B], 3155-3172).—The absorption of light by organic homopolar compounds is referred to two types of chromophors : (1) radical-like chromophors such as the unsaturated atoms of free radicals and groups containing double linkings (R chromophors) and (2) conjugated systems (K chromophors). The bands caused by these two types of chromophor (R and K bands) are distinguished by their markedly different persistence; the maxima of the one band type are always approximately over, those of the other type under a layer of 50 mm. of a 0.000001N solution. The bathochromic action of hydrocarbon residues introduced into the R chromophors increases generally with their affinity demand, that is, saturating action; thus with aliphatic substituents it increases with the length of the carbon chain and the propinquity of the introduced methyls, whilst with the more effective aromatic substituents and other systems of double linkings increase occurs in the sequence Ph<CH:CMe2  $< C_6H_4Ph < \alpha$ -naphthyl $< CPh_3$ . Bathochromic effect is never produced by positive (auxochromic) groups on R bands; hypsochromic action is pronounced with direct substitution, feeble with union to aromatic substituents. A saturation of the R chromophor is

always observed thereby. In contrast with K bands, R bands are always displaced towards the ultra-violet approximately in accordance with the dielectric constant of the solvent. The radical character of the R chromophor is of paramount importance for the R band absorption, but in the case of groups with double linkings the second atom has a varying influence, increasing the absorption with increasing degree of polarity, *i.e.*, in the sequence C:NH<C:O< C:S or N:N, N:O. There is no parallel between degree of saturation and absorption of light. The absorption of conjugated systems of polar constitution increases with the length and with the degree of polarity.

The bathochromic action of positive (auxochromic) groups is attributable to their power of increasing the polarity of a chromophor group. Bathochromic action is observed only when they occur in conjunction with the conjugated system which causes the absorption of light, or complete such a system, that is, when they are the terminal groups of a chromophor system. In all other cases (when they are not terminal members of the chromophor groups causing the absorption bands), in substitution of R and K chromophors they have a powerful hypsochromic action in instances of direct substitution, whilst in union with aromatic substituents they have little effect. The cause of solvatochromism is found in the change of polarity of the K chromophor (of conjugated systems). The corresponding K bands are displaced towards the red approximately according to the dielectric constants (ionising power) of the solvents, the effect of the latter increasing with the degree of polarity of the K chromophor. An attempt is made to explain the hypsochromic action of positive groups by branchings in the chromophors and the ultra-violet displacement of the R bands by the action of the solvents.

H. WREN.

Residual luminescence in the infra-red of photo-luminescent crystals and micro-crystals. F. MARTIN (J. Phys. Radium, 1930, [vii], 1, 401-403).-Using filtered infra-red light from a mercuryvapour and a tungsten lamp, the residual luminescence excited in crystals of a number of phosphorescent substances which had been kept in the dark for six months was examined with a photo-electric cell as detector connected with a differential triode amplifier. Observations were made as a function of the decrease in the persistence of the phosphorescence, the intensity of which varied widely for different substances, and the results reported show a relation between the disappearance of the residual and transient luminescence and the extinction effect. N. M. BLIGH.

Infra-red region of the spectrum. I. Introductory and experimental. II. Absorption spectrum of sulphur dioxide. C. R. BAILEY, A. B. D. CASSIE, and W. R. ANGUS (Proc. Roy. Soc., 1930, A, 130, 133—141, 142—156).—I. Full details are given of a prism spectrometer (a Hilger D. 42 constant-deviation instrument fitted with quartz, fluorite, rock-salt, and sylvine prisms), by means of which a high order of accuracy may be obtained in infra-red measurements. The possibilities of experimental error due to uncertainty in (1) drum reading, (2) setting the prism at minimum deviation,

(3) value of the prism angle, and (4) temperature of the prism are discussed. The maximum possible error in any wave-length reading may be taken as that due to an error of 4 sec. of arc in the semi-minimum deviation.

II. By means of this apparatus, the infra-red absorption spectrum of sulphur dioxide has been investigated in the region  $1-22 \mu$ , and the results are compared with those obtained by Coblentz. Certain unexplained differences exist between the two sets of bands; thus, no trace has been found of Coblentz's bands at 3.18 and  $10.37 \,\mu$ , whilst in place of that at 5.68  $\mu$  there is one at 5.34  $\mu$ . The observed infra-red spectrum has been co-ordinated with the Raman spectrum of the liquid. The following values have been deduced for the molecular constants of sulphur dioxide : moments of inertia, 55, 50, and  $4.7 \times 10^{-39}$ g.-cm.<sup>2</sup>, respectively; lengths of side, S-O 4.8×10-8 cm.,  $O-O 2 \cdot 0 \times 10^{-8}$  cm., whence the angle  $OSO = 24^{\circ}$ ; fundamental vibration frequencies:  $a_1+b_1$ , 606 cm.<sup>-1</sup>;  $a_2$  1152 cm.<sup>-1</sup>;  $b_2$  0;  $a_3+b_3$  1361 cm.<sup>-1</sup> L. L. BIRCUMSHAW.

Infra-red absorption of formaldehyde vapour. E. O. SALANT and W. WEST (Physical Rev., 1929, I. [ii], 33, 640).-Ultra-violet absorption bands of the vapour of formaldehyde show rotational lines corre-sponding with quite a small moment of inertia of molecule (Henri and Schou, A., 1928, 935). Measurements extending from the visible to  $3.6 \mu$  have now been made. The strongest bands occur at [3·31, 3·38, 3·47], 218, [1·77, 1·84], 191, [144, 1·40], and  $1\cdot 25 \mu$ . The 1·4 and 1·8  $\mu$  bands appear as doublets and the  $3.4\,\mu$  band as a triplet with evidence of rotational structure. The separations of the lines in the band at  $3.4 \mu$  appear much smaller than would be indicated by the moment of inertia derived from the L. S. THEOBALD. ultra-violet lines.

Measurements of light emission by alkali halide phosphors. W. BÜNGER (Z. Physik, 1930, 66, 311-327).-An apparatus which determines the number of quanta of monochromatic light absorbed for the emission of one quantum of fluorescent or phosphorescent light is described. A crystal consisting of the ions of one alkali halide transforms absorbed radiation into chemical energy, but a mixed crystal transforms part of the absorbed radiation into fluorescent or phosphorescent radiation. The quantum efficiency of 0.015, 0.183, 0.33, 0.367, and 1.83 mol.-% TICI in potassium chloride crystals for the production of fluorescent and phosphorescent radiation was determined. Radiation absorbed at the longer wave-length band (300 mµ) of potassium chloride containing thallium chloride reappears as fluorescent, without phosphorescent, radiation with a quantum efficiency of 0.5-0.8; the shorter wavelength band (200 mµ) reappears as fluorescent radiation with a quantum efficiency of 0.22-0.4, and as phosphorescent radiation with a quantum efficiency of 0.02-0.04. The phosphorescent quantum efficiency varies with wave-length almost as the absorption coefficient. A. B. D. CASSIE.

Apparatus for investigating the Raman effect in organic compounds. S. ZIEMECKI (Bull. Acad. Polonaise, 1930, A, 309-317).-An apparatus suit-

able for investigation of the Raman effect at higher temperatures is described. The vessel to contain the substance under investigation is constructed of glass or quartz and is fitted with a plane window. It is immersed in paraffin in a metal thermostat with plane transparent windows on opposite sides.

J. W. SMITH.

Raman spectrum of dioxan. D. S. VILLARS (J. Amer. Chem. Soc., 1930, 52, 4612-4613).-The wave-numbers and intensities of the lines in the modified (Raman) radiation from dioxan in the light of the mercury arc are tabulated.

J. G. A. GRIFFITHS.

Raman effect at the critical point. G. PLACZEK (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 832-840).-Measurements at the critical point of the system methyl alcohol-hexane indicate that the intensity of the Raman lines remains unaltered, but that of the continuous Raman spectrum increases. The continuous spectrum is discussed in relation to the vibrations of molecular complexes and the È. S. Hedges. structure of liquids.

Raman spectra of pinene. G. B. BONINO and P. CELLA (Nature, 1930, 126, 915).—Eight weak lines which can be represented by the formula  $\Delta v = B \times$ (4m+4) have been observed near the line v=23,257 in the Raman spectra of d- and l-pinene. The distance between the atoms of hydrogen and carbon in the CH<sub>2</sub> group calculated from this is  $1.16 \times 10^{-8}$  cm., in good agreement with Mecke's value of  $1.13 \times 10^{-8}$  cm.

L. S. THEOBALD.

Raman lines of simple polyatomic molecules. G. B. B. M. SUTHERLAND (Nature, 1930, 126, 916-917).—The Raman spectrum of hydrazine shows three lines of approximately equal intensity at 3196, 3270, and 3344 cm.<sup>-1</sup> together with a doubtful one at 1720 cm.-1 The three lines are due to N-H vibrations. Hydrazine hydrate gives the same three lines but of weaker intensity. L. S. THEOBALD.

Raman spectra of some triatomic molecules. S. BHAGAVANTAM (Nature, 1930, 126, 995) .- The spectrum of gaseous sulphur dioxide shows a line  $1154 \text{ cm}^{-1}$  Liquid hydrogen cyanide shows a triplet giving the shifts 2076, 2097.2, and 2122 cm.-1, of which the middle component is the most intense. Krishnamurti's results for carbon disulphide (A., 1930, 1237) have been confirmed and, in addition, three new feeble bands at 4438, 4605, and 4680 Å. have been discovered in the spectrum of carbon disulphide excited by the mercury line 4358.3 Å. Assuming these to be due to Raman transitions, three new wave-numbers are given for carbon disulphide: 412, 1229, and 1577 cm.-i L. S. THEOBALD.

Raman spectrum of diamond. S. BHAGAVAN-TAM (Indian J. Physics, 1930, 5, 573-586; cf. A., 1930, 1345).-The Raman spectrum of a large clear diamond gave, on either side of the intense principal line 1332 cm.-1, feebler lines of frequency shifts 1158, 1288, 1382, 1431, 1480, and 1585, the last being the most prominent; these values correspond closely with some of the very weak infra-red absorption maxima. The optical activity of the oscillation corresponding with the 1332 line and the absorption bands, and its variation in different specimens of diamond, are discussed. Results are considered in relation to specific heat data, and are not in good agreement with the classical theories of Born and Debye. The anti-Stokes line corresponding with the principal line of frequency shift 1332 has been observed, and is shifted 1332 wave-numbers from the exciting line, in exact agreement with the shift of the Stokes line. An intensity of the principal Raman line six times that of the 992 benzene line is explained from density considerations. N. M. BLIGH.

Raman effect with cadmium arc excitation. P. KRISHNAMURTI (Indian J. Physics, 1930, 5, 587— 591).—A cadmium arc with a 50% Sn-Cd alloy has been used for the first time for exciting Raman lines. Ferrous and nickel sulphates showed no lines at about 10 $\mu$ , in agreement with previous results (cf. A., 1930, 1344). For sulphur crystals with 5086 Å. excitation all the frequencies previously reported were found (cf. *ibid.*, 1237), together with a very faint line ( $v_6$ = 183 cm.<sup>-1</sup>). The 4800 and 6439 Å. radiations excited the three strongest sulphur frequencies with moderate intensity. The use of the 6439 Å. line for orange- or red-coloured substances is considered.

#### N. M. BLIGH.

Polarisation of Raman lines: some hydrocarbons. S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 603—608; cf. A., 1930, 1236).—The polarisation of the Raman lines in benzene, cyclohexane, and pentane was investigated; relative intensities and depolarisations are tabulated, and theoretical explanations of the observed degrees of polarisation are discussed. The different components of the characteristic hydrogen frequency appear with varying degrees of polarisation. Benzene gives lines showing no detectable polarisation. N. M. BLIGH.

Origin of the continuous spectra in Raman scattering. N. N. PAL and P. N. SENGUPTA (Indian J. Physics, 1930, 5, 609-610).—Using the combined vacuum distillation system and Wood's tube, the previously proposed theory of the continuous spectrum (cf. A., 1930, 1237) was investigated for benzaldehyde. During circulation, no continuous spectrum was observed, but appeared after the circulation was stopped, and is attributed to the breaking down under the action of light of the yellow first product of photochemical action on the benzaldehyde. N. M. BLIGH.

Characteristic frequencies of radicals in different chemical combinations. N. N. PAL and P. N. SENGUPTA (Indian J. Physics, 1930, 5, 611-614).--From a consideration of the frequencies attributed to the CN radical in a number of different types of compounds it is shown that the nature of the linking, rather than the mass of the substituent radical, mainly determines the frequency. N. M. BLIGH.

Forms of oscillation of the benzene ring in Raman effect. S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 615-631).—From the theory of vibrations of an elastic solid circular ring the geometrical characteristics of the vibrations of a hexagonal ring are deduced and applied to the interpretation of the observed Raman frequencies of benzene. The properties and persistence in benzene derivatives of the 992 frequency are adequately explained. Available data on the Raman spectrum and infra-red absorption of benzene are discussed. The existence of further oscillations and corresponding lines being indicated by theory, six new Raman lines of very low intensity were observed, using long exposures, at 4163.8, 4397.2, 4438.4, 4494.2, 4505.8, and 4513.0 Å. The origin and relation of these lines to infra-red absorption data are discussed. N. M. BLIGH.

Raman spectra of inorganic crystals. I. Substances containing  $XO_3$  and  $XO_4$  groups. II. Some hydroxides, cyanides, and thiocyanates. P. KRISHNAMURTI (Indian J. Physics, 1930, 5, 633-650, 651-662; cf. A., 1930, 1237, 1344).—Using specially designed pyrex mercury arcs to obtain intense excitation, investigations were made by the powder method. All the observed frequencies of the chlorates are active, corresponding with infra-red maxima; the principal frequency  $(v_3=930 \text{ cm}^{-1})$  becomes smaller for bromates and iodates, and splits into two components in sodium bromate (770 strong; 842 weak), and into four components in potassium iodate (733, 751 strong; 784, 808 weak). The splitting is discussed in relation to group structure. Aqueous solutions gave Raman lines in the same positions as the crystals, the components of the principal fre-quency tending to disappear. Sodium and potassium perchlorates gave lines ( $v_1$ =462;  $v_2$ =633;  $v_3$ = 933 cm.<sup>-1</sup>) similar to those of sulphates; potassium periodate gave lines  $v_3$ , 794 strong, 841 weak. The periodate frequencies show considerable changes in periodate frequencies show considerable changes in solution. Ammonium molybdate gave intense lines and a doubling of the principal frequency (932 strong; 880 medium) shown also in solution. Sodium tungstate gave only one line, 928, unaltered in solution. In all cases results are discussed in relation to infra-red data.

II. The following substances were examined and data are tabulated. Sodium, barium, and strontium hydroxides, sodium and mercuric cyanides; potassium ferrocyanide; a concentrated solution of potassium silver cyanide; potassium, ammonium, and barium thiocyanates. Sodium hydroxide gave a sharp line 3630 cm.-1, due to the OH ion; strontium and barium hydroxide octahydrates gave faint lines 3484, 3417, due either to water of crystallisation or to the OH ions. Mercuric cyanide gave a strong line, 2192, due to the CN group, and a weaker line, 276, due to the Hg-CN oscillation. The CN frequency is shown to be raised by covalent linkings between the CN group and other atoms or groups. The influence of dissolution on cyanides is small. Potassium thiocyanate gave a strong line, 2050, and a weak line, 747, for the solid and in solution. The ion is shown to be S:C:N, the double linking explaining the lower frequency as compared with the C:N ion. N. M. BLIGH.

Intensities of lines in Raman spectra. S. C. SIRKAR (Indian J. Physics, 1930, 5, 593-601; cf. A., 1930, 1344).—The ratio of the absolute intensities of the displaced to the corresponding undisplaced lines was determined for Raman lines of *cyclohexane* having shifts of 2853 and 800, and of benzene having shifts of 3080 and 990. The intensities were found to be greater than is indicated by the fourth-power law, relative to the visible lines, the deviation being greater as the frequency shifts increase. The deviations for the above lines are 216, 63, 267, and 51%, respectively. N. M. BLIGH.

Relative intensities of different Raman lines due to different exciting frequencies. S. C. SIRKAR (Indian J. Physics, 1930, 5, 663—668; cf. A., 1930, 1344, and preceding abstract).—In order to obtain further evidence on deviations from the Rayleigh fourth-power law, the ratios of the absolute intensities of the two Raman lines of nitrobenzene shifted by 1342 and 1582 wave-numbers were measured for excitation by mercury 5461 and 4358.6 Å., and gave the values 6.5, 2.74, and 15.9, 3.1, respectively. The probability of abnormally great intensity of the 1342 line excited by 4358.6 Å. is discussed.

N. M. BLIGH. Modification of the fine structure of a spectral line by molecular diffusion. Influence of angle of diffusion. M. VAOHER (Compt. rend., 1930, 191, 1121—1123).—Investigations by the method previously described, but with additional precautions (cf. A., 1929, 489), of the modifications due to molecular diffusion in benzene at different angles of diffusion, 0, show that as this angle increases the broadening of the line increases, and its "centre of gravity" shifts towards the red, the edge towards shorter wavelengths remaining unchanged. The results point to the diffused radiation consisting of two lines, one undisplaced, the other displaced towards the red (cf. following abstract). C. A. SILBERRAD.

Fine structure of a spectral line in molecular diffusion. J. CABANNES (Compt. rend., 1930, 191, 1123—1125).—The theory (cf. Tamm, A., 1930, 397, and preceding abstract) that diffusion of light in a dense medium is dependent on the elastic waves produced by thermal agitation requires that the diffused radiation produced by radiation of wavelength  $\lambda$  should be replaced by two symmetrical lines of wave-lengths  $\lambda \pm d\lambda$ , where  $d = \lambda (2un/c) \sin \theta/2$ , where *u* is the velocity of sound, c/n that of light in the diffusing medium, and 0 the angle of diffusion). The experimental results, although showing values of  $d\lambda$  proportional to  $\sin \theta/2$ , do not indicate either disappearance of the original radiation or appearance of any radiation of shorter wave-length.

C. A. SILBERRAD.

Photo-electric behaviour of salts. H. ERBEL (Z. Physik, 1930, 66, 59—68).—The experiments of Werner (A., 1929, 1217) on the photo-electric sensitivity of cadmium iodide, lead chloride, and potassium nitrate have been repeated on account of a lack of the necessary precautions in the technique employed. The results of Werner have been confirmed subject to minor differences. R. W. LUNT.

Comparison of molecular ionising potentials in an alternating electric wind. W. M. THORNTON (Phil. Mag., 1930, [vii], 10, 1052—1063).—A new method of comparing ionisation in a gas in a strong electric field is described. The ions are caused to move as the field reverses, and the alternating molecular motion cools a hot wire enclosed in the gas and forming one electrode. The molecular ionisation is measured from the curves connecting the applied voltage and the galvanometer deflexions of a bridge, of which the hot wire is one arm. Results for helium, neon, and argon show that the cooling of the wire is inversely proportional to the ionising potentials. The method is extended to hydrogen, oxygen, nitrogen, air, the paraffin series, and several other gases; results are in good agreement with calculated values. The relations of oxygen and hydrogen to carbon and nitrogen are deduced and discussed. N. M. BLIGH.

Dielectric polarisation of elements. C. ZAKR-ZEWSKI and D. DOBORZYŃSKI (Bull. Acad. Polonaise, 1930, A, 300—308).—With the exception of the elements of group VII, all elements so far investigated show the same values for the dielectric polarisation in both liquid and gaseous states, and these values are independent of temperature. Hence the molecules of these elements possess no dipole moment. Chlorine, bromine, and iodine, however, are dipolar molecules, the values of the electric moment increasing with increasing at. wt. The actual values which have been deduced, however, for these dipole moments show considerable discrepancies. J. W. SMITH.

Dielectric constant of ammonia as a function of temperature and density. F. G. KEYES and J. G. KIRKWOOD (Physical Rev., 1930, [ii], 36, 1570-1575).-Using an apparatus previously described (cf. A., 1930, 1347) the dielectric constant of ammonia was measured over a range of densities at 100°, 125°, 150°, and 175°. The Clausius-Mosotti function was found to increase with increasing density, and an expression for it at low densities is deduced. The permanent electric moment of the ammonia molecule was calculated as  $1.44 \times 10^{-18}$  e.s.u. For an interpretation of the experimental facts it is shown that the assumption that the function is valid and the mean molecular polarisability increases with the density is justified. Previous results for carbon dioxide are further discussed. N. M. BLIGH.

Dependence of molecular polarisation of propyl chloride and  $\alpha\beta$ -dichloroethane on temperature, especially with regard to free rotation. R. SANGER (Physikal. Z., 1931, 32, 21-26).—The electric moment of propyl chloride has been redetermined. The value is  $2.04 \pm 0.007 \times 10^{-18}$ . The structure of propyl chloride is discussed, and it is shown that the experimental results support the assumption of completely free rotation of the end groups C.Me and C.Cl about the axis, but are not in agreement with the assumption of the existence of two forms of molecule of an approximately constant mixing ratio. The molecular polarisation of aβ-dichloroethane bears a linear relationship to the reciprocal of the temperature as required by the Debye theory. The molecule therefore possesses a constant moment, i.e., a moment independent of temperature. The actual value of the moment is not known with accuracy, but it lies between 1.2 and  $1.4 \times 10^{-18}$ . A constant electric moment is compatible only with completely free rotation or with complete rigidity. For completely free rotation, however, it has been calculated that the electric moment of the compound should be about  $2.4 \times 10^{-18}$ , assuming no deformation of the carbon tetrahedron. 148

This would have to be considerable to reduce the moment to that found experimentally. A. J. MEE.

Change of the dielectric constant of nitrobenzene with temperature. J. MAZUR (Nature, 1930, 126, 993).—The dielectric constant of nitrobenzene has been measured over the range  $-75^{\circ}$  to 30°. The value of  $\varepsilon$  steadily increases with a fall in temperature from 35.4 at 30.01° to a maximum of 35.18 [38.18?] at 9.6°, and then decreases sharply to 11.82 at 7.713°; after this the decrease is slowly asymptotic to a limiting value of 9.709 at  $-75^{\circ}$ . Irregularities in the rate of change of  $\varepsilon$  between 9.6° and 7.713° suggest possible complications in the region of the m. p. of nitrobenzene. L. S. THEOBALD.

Dielectric polarisation of some pure organic compounds in the dissolved, liquid, and solid states. S. O. MORGAN and H. H. LOWRY (J. Physical Chem., 1930, 34, 2385-2432).-The dielectric constants, densities, and refractive indices of dilute solutions of methyl chloride, bromide, or iodide, and of methylene chloride in hexane or carbon tetra chloride or both, have been measured. For the methyl halides temperature and dielectric constant can be connected by the equation  $\varepsilon = \alpha T^{-1} - \beta$ , where  $\alpha$  and  $\beta$  are constants, whilst density is a nearly linear function of temperature. For non-polar substances, the relation  $\varepsilon = \varepsilon_{m.p.} - \delta(T - T_{m.p.})$ , where  $\delta$  is the rate of change of dielectric constant with temperature, holds, and for polar substances the results can be represented by the equation  $\varepsilon =$  $\alpha' + \beta'(T - T_{m,p.}) + \gamma'(T - T_{m,p.})^2$ . Condensers have been designed for measuring the dielectric constants of liquids and solids and the use of these for direct capacity measurements is discussed.

L. S. THEOBALD. Electromechanical properties of Rochelle salt crystals. W. G. CADY (Physical Rev., 1929, [ii], 33, 278—279).—The piezo-electric strain constants,  $\delta$ , of sodium potassium tartrate are known but not those of the moduli,  $\varepsilon$ . The values  $\varepsilon_{14} 1.64 \times 10^6$ ,  $\varepsilon_{25} - 53,300$ , and  $\varepsilon_{36}$  43,400 have been computed from Pockel's values of the strain constants and Mandell's determinations of the elastic constants. The extent to which the dielectric constant is modified by the presence of piezo-electricity has also been calculated. The natural vibration frequencies of plates of the salt differently oriented with respect to the crystal axes have been measured. L. S. THEOBALD.

Dispersion [refraction] of the cyclic hydrocarbons. M. GODCHOT and (MLLE.) G. CAUQUIL (Compt. rend., 1930, 191, 1326—1328).—The specific dispersion  $\Delta n/d$  at 13.5°, where  $\Delta n$  is the difference between refractive indices determined for  $\lambda$  0.589  $\mu$ (Na yellow) and 0.436  $\mu$  (Hg violet), and d the density at the same temperature (cf. Darmois, A., 1921, ii, 1), was determined for 11 hydrocarbons with one double linking, and 12 saturated hydrocarbons belonging to the cyclo-pentane, -hexane, -heptane, and -octane series.  $\Delta n$  increases regularly with increase in mol. wt., the unsaturated hydrocarbons giving a value 20 units higher than the corresponding saturated hydrocarbon produced by hydrogenation in the presence of a platinum oxide catalyst.  $\Delta n/d$  is not strictly constant for all members of a given series and does not depend on the nature of the ring. Mean values of  $124 \times 10^{-4}$  and  $151 \times 10^{-3}$  were found for all the saturated and unsaturated hydrocarbons, respectively. In general, the conclusions of Darmois were confirmed, and the use of the additive properties of the ratio for the determination of benzene hydrocarbons ( $\Delta n/d=250 \times 10^{-4}$ ) in petrol is indicated.

J. GRANT.

Molecular refractivity of methyl alcohol. M. VELASCO (Anal. Fis. Quim., 1930, 28, 1228—1238).— The dielectric constant of benzene solutions of methyl alcohol has been measured at fractional molar concentrations from 0.0248 to 0.4981, and the molecular polarisation has been calculated. With increase of concentration  $P_{1\cdot 2}$  rises to a maximum, indicating that the solute is polar and that it is composed of associated molecules, whilst  $P_2$  is maximal at about 0.3 fractional molar concentration and falls again at higher concentrations; at infinite dilution  $P_2$  is 55.3. The molecular refractivity of methyl alcohol at 20°, calculated from measurements of the refractive index, is 8.23, and the electric moment  $\mu$  is  $1.5 \times 10^{-18}$ . The experimental results are shown to be in accordance with the Debye theory of solution.

H. F. GILLBE. Anomalous dispersion of crystalline lead chloride in the region of its first ultra-violet proper frequency. K. HECHT (Z. Physik, 1930, 66, 339—344).—The refractive index of lead chloride, vaporised and subsequently deposited on a quartz plate to give crystal layers of from 10 to  $50 \times 10^{-6}$  mm. thick, was determined from the shift of Young's interference fringes when the layer was inserted in the path of one of the interfering beams. The region investigated was that of the first ultra-violet natural frequency at 272 mµ, and the results complete the measurements of Bauer between 360 and 290 mµ.

A. B. D. CASSIE,

Magnetic rotatory power of hydrocarbons in the gaseous state. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1930, 191, 1319—1320).— The Verdet, molecular, and specific constants (reduced to 0° and 760 mm., and corrected for compressibility) of gaseous methane, ethane, propane, butane, *iso*pentane, and *iso*hexane, and of liquid butane, pentane, and hexane have been measured for  $\lambda$  578 µµ. In confirmation of calculated values, the ratios of the specific rotations obtained for the gaseous and liquid states are : butane 0.87, pentane 0.86, and hexane 0.85. Previous divergencies are attributed to foreign gases, such as hydrogen or ethylenic derivatives, in the materials which have now been eliminated. The dispersions for  $\lambda$  546 and 436 µµ are approximately 1.125 and 1.184 for all the hydrocarbons. J. GRANT.

Rotatory magnetic polarisation of organic substances liquefied by fusion. C. SALCEANU (Compt. rend., 1930, 191, 1316—1318).—Determinations with three mercury lines of the magnetic rotation of the plane of polarisation ( $\lambda$  578 mµ), of the ratio of this rotation to that of water at 20°, of Verdet's constant  $\rho$  ( $\rho$  for water at 20° 0.0136), and of the ratio of  $\rho$  to the density at 83.5—188° for naphthalene and at 34—174° for 2-methylnaphthalene gave values of the dispersion ratios at 83.5° and 49°, respectively, of  $\alpha_v/\alpha_j$  1·15 and  $\alpha_i/\alpha_j$  2·16 in both cases. The variations of these ratios with temperature are negligible. Their values calculated from measurements of birefringence, on the assumption that the dispersions for the magnetic and Kerr birefringences are approximately equal (Cotton and Mouton), are  $\alpha_v/\alpha_j$  1·13 and  $\alpha_i/\alpha_j$  1·90 for 2-methylnaphthalene, the value 1·73 for the latter being hitherto considered the maximum for aromatic substances. The magnetic P.D. used was 36,000 gauss per cm. and the field 12,000 gauss. J. GRANT.

Mutarotation in pure and in mixed solvents. J. N. RAKSHIT (J. Physical Chem., 1930, 34, 2539— 2548).—The mutarotation of solutions of morphine, codeine, and narcotine hydrochlorides in mixtures of water and ethyl alcohol have been measured at 35°. The molecular rotations of morphine and codeine hydrochlorides increase with dilution, whilst that of narcotine hydrochloride increases with dilution in pure aqueous solutions and decreases with dilution in pure alcoholic solutions and in most water-alcohol mixtures. The results obtained support the view that mutarotation is due to a reaction between solute and solvent. L. S. THEOBALD.

Optical activity and salt effect. P. A. LEVENE and A. ROTHEN (J. Physical Chem., 1930, 34, 2567-2581).—The optical rotation of aqueous solutions of mandelic acid has been measured at 25° and the calculated rotations for the undissociated acid and for the mandelate ion are  $[M]_D^{22}=237\cdot2(6)^\circ$  and  $[M^-]_D^{23}=176\cdot7^\circ\pm0.05(5)^\circ$ , respectively. The dissociation " constant " calculated from observed rotations increases with concentration from 4.2 to  $4.8 \times 10$ . The temperature coefficients of the rotation of the acid and of the mandelate ion are large and are of the same order of magnitude between 20° and 30°. The curves representing the effect of strong bases on the rotation of the mandelate ion show that for lithium, sodium, calcium, and barium, the molecular rotation has the same value at zero concentration of base and that no break occurs when I equiv. of base has been added. The mandelates of these bases are completely dissociated at a concentration 0.05N. Neutral salts increase the rotation of the mandelate ion, the influence of the ions Ca", Ba", and Sr" being especially marked. The effect decreases with an increase in the size of the ion for both uni- and bi-valent ions and the effect of the cation predominates over that of the anion. With mandelic acid the salt effect is less pronounced. Ethyl nitrite and acetic acid act similarly to the cations and alcohol to the anions. The effect of neutral salts on the rotation of  $\alpha$ -methylglucoside and of sucrose is much less than in the case of mandelic acid. L. S. THEOBALD.

Origins of stereochemistry. E. PATERNÒ (Gazzetta, 1930, 60, 910—911).—Polemical. Objection is taken to the references made by Oddo in his recent "Treatise of Organic Chemistry" to the author's paper of 1869 in that they do not give a correct account of the theory of stereochemistry put forward at that date. O. J. WALKER.

Nature of per-acids and the "acid nucleus" theory. S. HAKOMORI (Bull. Chem. Soc. Japan,

1930, 5, 333-344).—It is suggested that when a polar molecule is brought into the vicinity of an electrically neutral molecule combination may occur as a result of electrical induction. The magnitude of this " induction valency" will vary with the dielectric constant of the medium surrounding the molecules. It is supposed that in the ordinary oxy-acids the an-hydride or "acid nucleus" is held together by covalencies, but is united to water by induction valency. Similarly, the per-acids may be regarded as formed by the union of acid nuclei with hydrogen peroxide by induction valency. The intensity of the induction effect may be expected to influence the colour of the resulting compound. If the displacement due to induction is very small the acid will be colourless or yellow, and comparatively stable. The colour changes of indicators are ascribed to the inducing action of the R. CUTHILL. hydrogen ion.

Properties and applications of molecular forces. F. LONDON (Z. physikal. Chem., 1930, B, 11, 222-251).-The theory of intermolecular attractive forces due to reciprocal perturbation of electronic orbits (A., 1930, 1239) is further developed. It is shown that these forces are equivalent to a general cohesive force comparable with that of gravity and are superposable, i.e., the force between any two given molecules is practically unaffected by the presence of other molecules. The values of the forces can be deduced fairly accurately from optical dispersion data. The force between two unlike molecules in a binary mixture is in general less than the geometric mean of the forces in the two components in the pure state; the wider apart are the characteristic spectral regions of the two molecular species, the greater is this disparity. By means of the theory of the new attractive forces, the heat of sublimation of a molecular lattice may be calculated, and the values obtained for various face-centred cubic lattices are in such agreement with the experimental values as to indicate that the energy of such lattices is determined, at least as far as order of magnitude is concerned, by the attractive forces. The theory also yields the equation  $\phi/T_c = \text{constant}$ , where  $\phi$  is the heat of sublimation at 0° Abs. and  $T_c$  is the critical temperature. By applying the theory to an adsorbed gas, all the characteristics of adsorption free from such complications as the presence of chemical polar or homopolar linkings may be accounted for and the heat of adsorption,  $\phi'$ , calculated in a satisfactory manner. It is further deduced that  $\phi'/T_c^{\frac{1}{2}}$  = constant. The energies of dissociation of molecules in which the binding forces are of the van der Waals type, e.g., the compounds of mercury with argon and krypton, are also calculated. The new theory does not permit the calculation of the attractive force between two molecules as close together as, for instance, the atoms in the hydrogen R. CUTHILL. molecule.

Parachor of aliphatic acids of high mol. wt. G. B. SEMERIA and G. RIBOTTI-LISSONE (Gazzetta, 1930, 60, 862-866).—The parachor for the following acids has been determined. The values at 95° are : oleic 766.93, elaidic 764.93,  $\beta\gamma$ -oleic 763.70, stearic 778.87, erucic 938.91, brassidic 934.36, and behenic 951.36. The results indicate that oleic and erucic acids have a *cis*-configuration, whereas elaidic,  $\beta\gamma$ -oleic, and brassidic acids have a *trans*-configuration.

O. J. WALKER. Reflexion of X-rays at crystals. V. H. SEEMANN (Ann. Physik, 1930, [v], 7, 633—649).—The characteristic features of X-ray diagrams obtained by reflexion of a pencil of X-rays of wide divergence on crystals are interpreted theoretically. W. GOOD.

Fluorescence of quartz under the influence of cathode rays of low voltage. H. PETERS (Physical Rev., 1930, [ii], 36, 1631—1635).—The production of a red fluorescence by cathode rays in glass and quartz tubes was investigated. Contrary to the views of Wood (cf. A., 1930, 653), the presence of oxygen or other gases was not found to be essential. The fluorescence showed a continuous spectrum with two maxima in the red, one in the green, and one in the blue; no oxygen line was found. The disappearance of the fluorescence after bombardment for about 70 hrs. indicates that the SiO<sub>2</sub> group in the glass passes into an allotropic form. N. M. BLIGH.

Lattice constant of quartz. O. BERGQVIST (Z. Physik, 1930, 66, 494–498).—The lattice constant of quartz was determined by means of the CuK $\alpha$  and FeK $\alpha$  lines, to first and second approximations; *i.e.*, the lattice constant was first determined by neglecting the refractive index, and from this value the refractive index was calculated and used to determine the second approximation. A. B. D. CASSIE.

X-Ray investigations on rubber. E. OTT (J. Amer. Chem. Soc., 1930, 52, 4612; cf. B., 1926, 681). —Exposure of translucent rubber to X-rays results in the formation of an opaque spot defined by the diameter of the beam of X-rays. With increasing exposure, the spot becomes more opaque, due to progressive crystallisation, and the X-ray pattern becomes sharper, owing to increasing size of the particles. The opaque spot did not change during storage, but was removed by slight warming.

J. G. A. GRIFFITHS. Method for growing large crystals of the alkali halides. J. STRONG (Physical Rev., 1930, [ii], 36, 1663—1666; cf. Ramsperger, A., 1928, 351).—In addition to the conditions specified by Stöber (cf. Z. Krist., 1925, 61, 299) for growing large crystals from fused salts, two new conditions are postulated. The bottom and top of the still plastic crystal must be brought to the same temperature to avoid strains during cooling, and the crystal must be removed from the container before cooling begins, to eliminate strains due to the temperature contraction of the melting pot. Cylindrical alkali halide crystals can thus be prepared 4.5 in. long and 4.5 in. in diameter. N. M. BLIGH.

Distribution of [crystal] structure types in the periodic system. H. PERLITZ (Festschr. Jub. Ver. Estn. Chem., 1929, 10-13; Chem. Zentr., 1930, ii, 685).

Possible orientation of cubic crystals deposited on a mica plate. L. ROYER (Compt. rend., 1930, 191, 1346—1348).—All the alkali halides of cubic symmetry give an oriented deposit on a cleavage plane of mica (epitaxy) when the parameter of the

diagonal of the face of the cube is between certain limits. It is deduced that the cubic alkali phosphohexafluorides (RPF<sub>6</sub>) prepared by Lange and Müller (A., 1930, 877), which give, although with difficulty, deposits oriented similarly to those of the halides, are analogous in structure to the halides, the parameters of the a' (111) faces being for each case K 5·49, Rb 5·64, NH<sub>4</sub> 5·59, and Cs 5·80 Å. The great difficulty with which the cæsium compound is oriented and the impossibility of the orientation of cæsium chloride (parameter 6·08 Å.) are explained by the large differences between the parameter concerned and that of mica (5·12 Å.). The lower limit for orientation on mica is represented by potassium chloride (parameter 4·43 Å.). J. GRANT.

Crystal structure of para-hydrogen at liquid helium temperatures. W. H. KEESOM, J. DE SMEDT, and H. H. MOOY (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 814—819).—The X-ray spectral lines obtained from solid hydrogen at the temperature of liquid helium are in good agreement with those calculated for a hexagonal close-packed lattice having a 3.75 Å. and c/a 1.633. With 2 molecules in the elementary cell  $d_{cnlc.}$  for 2° Abs. is 0.088. Solid hydrogen is said to be isotropic at the m. p., but the X-ray data do not agree with a cubic structure. It is suggested that there may be a transformation point between 4° and 14° Abs. E. S. HEDGES.

Lattice distance and reflecting power for X-rays of bismuth according to the plane of cleavage. E. ADINOLFI (Rend. Accad. Sci. Fis. Mat. Napoli, 1930, [iii], 36, 69-75).-A new arrangement for obtaining the lattice distances of crystals by Bragg's method is described, direct comparison being made with that of calcite along the face (100), which is taken as the basis for spectrometric measurements. In this way the lattice dimension for the (111) face of bismuth crystals is found to be 3.970 Å. Comparison of the structural factors of calcite and bismuth shows that, whereas that of calcite is constant, that of bismuth, in the same frequency field, increases as the wave-length of the radiations used diminishes, so that increase in the frequency is accompanied by increase in the number of the bismuth electrons taking part in the phenomenon of reflexion.

T. H. POPE. Structure of hydrogen phosphide (PH<sub>3</sub>) and of hydrogen arsenide (AsH<sub>3</sub>). G. NATTA and E. CASAZZA (Gazzetta, 1930, 60, 851-859).—X-Ray examination of phosphine and arsine at -170° shows that these two substances are isomorphous and crystallise in the facc-centred cubic system with a cell containing 4 mols. The data are : PH<sub>3</sub>,  $a \ 6.31\pm$   $0.01 \ \text{Å}$ ,  $v \ 251 \times 10^{-24} \ \text{c.c.}$ ,  $d_{\text{calc.}} \ 0.896$ , and AsH<sub>3</sub>,  $a \ 6.40\pm0.02 \ \text{Å}$ .,  $v \ 262 \times 10^{-24} \ \text{c.c.}$ ,  $d_{\text{calc.}} \ 1.96$ . The space-group is probably  $T_h^2$  or  $O_h^4$ . O. J. WALKER.

Determination of the crystal structure of hydrogen sulphide and selenide and nitrogen dioxide at the temperature of liquid air. L. VEGARD (Naturwiss., 1930, 18, 1098, and Nature, 1930, 126, 916; cf. Natta, A., 1930, 1350).—By means of methods previously described by the author (A., 1930, 19) the crystal structures of the solid compounds at liquidair temperature have been determined. Hydrogen sulphide and selenide are isomorphous, cubic, with 4 mols. in the unit cell. The sulphur and selenium atoms are arranged in a face-centred lattice. It is concluded that the molecule is linear. The most probable space configurations are  $T^4$  for an asymmetrical and  $T_h^{\epsilon}$  for a symmetrical molecule. Hydrogen sulphide has a 5.76 Å.,  $\rho$  1.17, and the selenide 6.10 Å. and 2.34, respectively.

Solid nitrogen dioxide has also a cubic structure, but it is more complex than hydrogen sulphide or selenide; a and  $\rho$  are 7.77 Å. and 1.93, respectively, indicating 6 mols. in the unit cell. The structure is made up of space-centred lattices.  $T^5$ , the only possible space distribution, gives one parameter for nitrogen and three parameters for the oxygen atoms. With certain assumptions parameter values are found which give excellent agreement between calculated and observed intensities. W. R. ANGUS.

Structure of silicon tetrafluoride. G. NATTA (Gazzetta, 1930, 60, 911—922).—Examination of solid silicon tetrafluoride at  $-170^{\circ}$  by the powder method shows that it has a cubic-centred lattice with a cell containing 2 mols. of SiF<sub>4</sub>:  $a 5.41\pm0.01$  Å.,  $v 158 \times 10^{-24}$  c.c.,  $d_{calc}$  2.17. The tetrafluoride is a non-ionic compound and belongs to the space-group  $O^2$ . The co-ordinates of the atoms are : Si (0, 0, 0)  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , F  $(u, u, u)(u, \bar{u}, \bar{u})(\bar{u}, u, \bar{u})(\bar{u}, \bar{u}, u), (\frac{1}{2}+u)(\frac{1}{2}+u)(\frac{1}{2}+u)(\frac{1}{2}-u)(\frac{1}{2}-u)(\frac{1}{2}-u)(\frac{1}{2}-u)$ ,  $(\frac{1}{2}-u)(\frac{1}{2}-u)(\frac{1}{2}-u)$ ,  $(\frac{1}{2}-u)(\frac{1}{2}-u)(\frac{1}{2}-u)$ ,  $(\frac{1}{2}-u)(\frac{1}{2}-u)(\frac{1}{2}-u)$ , mere u=0.17. The radius of the neutral fluorine atom is 0.50 Å. O. J. WALKER.

Crystal structure of the compound Fe<sub>2</sub>B. G. HÅGG (Z. physikal. Chem., 1930, B, 11, 152—162).— A modification of the crystal structure proposed for the above compound by Wever and Müller (A., 1930, 1372) is suggested. From a consideration of the volumes of the atoms involved it seems probable that the tetrahedra which constitute the iron lattice are all very nearly equal. The boron atoms occupy a fourfold point position and are situated in the largest gaps between the tetrahedra of the iron lattice, each boron atom having 8 iron atoms equidistant from it. The value of 0.97 Å. is deduced for the radius of the boron atom. R. CUTHILL.

Structure of compounds of the type MIM'<sub>2</sub>O<sub>4</sub>. I. Cadmium and calcium indates. L. PASSERINI (Gazzetta, 1930, 60, 754-761).—By calcining mixtures of the nitrates in the required proportion at about 900° the compounds CdO,In<sub>2</sub>O<sub>3</sub> and CaO,In<sub>2</sub>O<sub>3</sub> have been prepared. An X-ray examination by the powder method shows that these substances crystallise in the tetragonal system of the hausmannite type analogous to that of the spinels. The elementary cell contains 8 mols. of the compound. CdO,In<sub>2</sub>O<sub>3</sub> has c/a 1·14,  $a 8.650 \pm 0.005$ ,  $c 9.875 \pm 0.007$  Å., v739·0×10<sup>-24</sup> c.c.,  $d_{calc}$ , 7·30; for CaO,In<sub>2</sub>O<sub>3</sub> the corresponding values are 1·12, 8·770 $\pm 0.005$ ,  $9.822\pm$ 0·007, 755·5×10<sup>-24</sup>, and 5·87. O. J. WALKER.

Crystallisation of potassium alum and the action of certain impurities on its habit. H. E. BUCKLEY (Z. Krist., 1930, 73, 443-464; Chem. Zentr., 1930, ii, 366).

Crystal structure of NiSnCl<sub>6</sub>,6H<sub>2</sub>O. L. PAUL-ING (Z. Krist., 1930, 72, 482-492; Chem. Zentr., M 1930, ii, 353).—The unit cell, a 7.09 Å.,  $\alpha$  96° 45', contains one molecule; space-group probably  $C_{di}^2$ . A. A. ELDRIDGE.

X-Ray diffraction. I. Structure of amorphous carbon. II. Some colloidal solutions and liquid mixtures. III. Some aromatic hydrocarbons in the solid and liquid states. P. KRISHNAMURTI (Indian J. Physics, 1930, 5, 473-488, 489-499, 543-558).—Using CuK radiation the diffraction patterns of various amorphous carbons showed strong scattering extending to about 7° with the primary beam. The patterns have two rings in addition to central scattering, the prominent first ring corresponding with the (002) reflexion of graphite, with spacing about 3.8 Å. compared with graphite 3.4 Å. The fainter and broader outer ring showed a spacing 2.12 Å. comparable with the (111) spacing of graphite 2.06 Å. The spacing of carbon obtained by the reaction of carbon tetrachloride and molten sodium showed it to be the most finely-divided form. Results agree with the clustering of the carbon atoms to form highly anisotropic units of about 60 atoms per unit, and are in accord with chemical evidence. Data for colloidal graphite are also reported.

II. Investigations previously reported (cf. A., 1929, 246, 751) were extended to aqueous solutions of starch, tannic acid, and gum arabic, which showed strong molecular scattering at small angles to the primary beam. The mol. wt., calculated from the extents of the coronas, were 6200, 3134, and 2810, respectively. A study of the effect of dilution on the inner ring for associated liquids like acetic acid showed disappearance of the ring even in very concentrated solutions, indicating a breaking up of association. The influence of dilution on liquids showing two prominent haloes was investigated in mesitylenecyclohexane and ethyl o-phthalate-benzene systems. These showed changes in the patterns ascribed to more random orientation of the solute molecules with increasing dilution.

III. A comparison was made of the powder and liquid X-ray diffraction patterns for seven representative aromatic hydrocarbons in addition to hexamethylbenzene previously reported (cf. A., 1930, 983). Naphthalene, phenanthrene, acenaphthene, and fluorene showed two rings in the liquid state, whilst diphenyl, dibenzyl, and stilbene show only one, this being due to the difference in arrangement of neighbouring molecules, or impedance to free rotation, or vibration introduced by o- and m-substitution in the aromatic nucleus. Stilbene shows also a faint inner ring probably due to association. The origin of the liquid patterns is discussed in relation to the dimensions of the molecules as derived from crystal structure N. M. BLIGH. data.

Crystallography of certain racemates and the corresponding optical antipodes of the asparagine group. G. CAROBBI (Rend. Accad. Sci. Fis. Mat. Napoli, 1930, [iii], **36**, 49–55).—*l*- and *d*-Chloroacetylasparagines, m. p. 150°, *d* 1.538, form monoclinic crystals, a:b:c=0.7876:1:0.4281,  $\beta$  96° 22'; *r*-chloroacetylasparagine, m. p. 105°, *d* 1.560, triclinic crystals, a:b:c=0.9068:1:0.8617,  $\alpha$  63° 29',  $\beta$  113° 20',  $\gamma$  117° 15'; *l*- and *d*-benzenesulphonyl-

asparagines, m. p. 163°, d 1·434, monoclinic crystals,  $a:b:c=0.7557:1:0.7105, \beta$  104° 42'; *r*-benzenesulphonylasparagine, m. p. 172°, d 1·559, monoclinic; *r*-benzoylasparagine, m. p. 184°, d 1·433, monoclinic crystals,  $a:b:c=0.8865:1:0.5929, \beta$  92° 12'.

T. H. POPE.

**Crystal structure of thiophen.** G. BRUNI and G. NATTA (Atti R. Accad. Lincei, 1930, [vi], **11**, 929— 934).—The X-ray spectrum of thiophen has been determined by the powder method, using a spectrograph designed for low-temperature measurements. The unit cell of thiophen (4 mols.) is tetragonal with an axial ratio a/c 0.757; at  $-170^{\circ}$  the cell constants are a 7.225, c 9.54 $\pm$ 0.01 Å., volume 498  $\times$  10<sup>-24</sup> c.c.,  $d_{calc}$ , 1.11. Considerable advantage is gained in the examination of organic compounds by using a calcium anticathode owing to the great intensity of the CaK $\alpha$ (3351.69) and  $K\alpha'$  (3354.95) lines. F. G. TRYHORN.

Crystal structure of benzene and its relations with that of thiophen. II. G. BRUNI and G. NATTA (Atti R. Accad. Lincei, 1930, [viii], **11**, 1058— 1062; cf. A., 1929, 1223, and preceding abstract).—An X-ray examination has been made by the powder method of solid benzene at  $-170^{\circ}$ . The rhombic bipyramidal elementary cell has a 7·34, b 9·52, c 6·74;  $d_{cslc.}$  1·099. There is no true isomorphism between thiophen and benzene, but there are certain analogies in the dimensions of their unit cells, which have volumes of 471 and  $498 \times 10^{-24}$  c.c., respectively. O. J. WALKER.

Crystal structure of quinonid compounds and of a molecular compound similar to quinhydrone. E. HERTEL and G. H. RÖMER (Z. physikal. Chem., 1930, B, 11, 90–96).—The unit cell of the lattice of anthraquinone has a height of 3.95 Å. and contains 8 molecules which have the planes of their rings all parallel but are at different heights. 2:7-Dinitroanthraquinone, on the other hand, has a unit cell which is 38.4 Å. high and contains 4 molecules, arranged with the planes of their rings at right angles. The crystal structure of the compound of fluorene with 2:7-dinitroanthraquinone,  $C_{13}H_{10}C_{14}H_6O_2(NO_2)_2$ , is such as to exclude the possibility of three-dimensional alternation (of. this vol., 153). R. CUTHILL.

X-Ray examination of E. Fischer's polypeptides. F. V. LENEL (Naturwiss., 1931, 19, 19).---The X-ray interference rings of certain polypeptides (dl-leucyltetraglycylglycine, l-leucyloctaglycylglycine, l-leucyltriglycyl-l-leucyloctaglycylglycine, l-leucyltriglycyl-l-leucyltriglycyl-l-leucyloctaglycylglycine) show that the high-molecular polypeptides are crystalline. F. O. HOWITT.

X-Ray study of mannitol, dulcitol, and mannose. T. C. MARWICK (Nature, 1931, 127, 11-12). The following data have been obtained for mannitol, dulcitol, and mannose, respectively: space-group  $Q_4$ ,  $C_{24}^{\circ}$ , and  $Q_4$ ; a 8.65, 8.61, and 7.62 Å.; b 16.90, 11.60, and 18.18 Å.; c 5.56, 9.05, and 5.67 Å; d1.497, 1.466, 1.501 g. per c.c.; mols. per unit cell, 4, 4, and 4; for dulcitol  $\beta$  is 113° 45′. The data suggest that in all cases the long dimension of the molecule corresponds with the a axis; in the alcohols the molecules appear to have the long-chain configuration, and in the carbohydrate, that of the mannopyranose ring with the longest dimension in the direction of the a axis. L. S. THEOBALD.

Structure of the crystal lattice of cellulose. W. T. ASTBURY and T. C. MARWICK (Nature, 1931, 127, 12—13).—From an examination of the available data for cellulose and the sugars it is concluded that the 6-atom sugar ring is associated in the crystalline state with certain linear dimensions which are approximately constant and that one dimension, at least, corresponds with one of the axial lengths of the unit cell. L. S. THEOBALD.

X-Ray diffraction in heated liquids and in solutions. V. I. VAIDYANATHAN (Indian J. Physics, 1930, 5, 501-524; cf. A., 1929, 746).-The scattering of X-rays was examined at temperatures ranging from 25° to 235° for cyclohexanone, terpineol, cyclohexene, benzene, phenol, diphenylamine, propionic acid, acetonitrile, ethyl o-phthalate, o-nitrobenzaldehyde, tetranitromethane, octane, pentane (cf. Ramasubramanyam, A., 1928, 1312), and hexoic acid. Diffuse-ness and contraction of the haloes with rise of temperature was observed, and an increase in scattering at small angles, comparable, in the case of benzene, with that observed in the scattering of light. The ratio of the intensity of the X-ray scattering at small angles to that of the primary beam, for water and benzene, is in fair agreement with the value calculated from the Einstein-Smoluchowski formula. Of the two haloes present, the inner one did not appreciably diminish in intensity with rise of temperature in the case of associated liquids, indicating that their origin depends primarily on molecular form and polarity, and not on association. The ratio of the intensity of incident to scattered radiation was examined quantitatively for dilute aqueous solutions of dextrose and sucrose and the results are compared N. M. BLIGH. with theoretical calculations.

X-Ray interpretation of the structure and elastic properties of hair keratin. W. T. AST-BURY and H. J. WOODS (Nature, 1930, 126, 913— 914).—From a consideration of the stretching properties of hair keratin and the X-ray data a skeleton of the keratin complex which gives a quantitative interpretation of the fundamental points is advanced. The skeleton consists of a peptide chain folded into a series of hexagons, each of which is in effect a diketopiperazine ring. L. S. THEOBALD.

X-Ray studies on paraffin wax and vaseline. S. TANAKA and A. TSUJI (Mem. Coll. Sci. Kyoto, 1930, A, 13, 369-374).—The influence of temperature and mechanical operations on the X-ray diffraction patterns given by paraffin wax and vaseline has been studied. Below the m. p. spectral lines characteristic of the crystalline powders are obtained, but these decrease in intensity with temperature rise and disappear on melting. The transformation occurs in a different manner for each substance. W. GOOD.

Diffraction of X-rays in liquids: effect of temperature. E. W. SKINNER (Physical Rev., 1930, [ii], 36, 1625—1630).—The effect of temperature on X-ray diffraction was examined for mesitylene, m-2- and m-4-xylenol, phenol, naphthalene, benzene, cyclohexane, di-n-propylcarbinol, heptoic acid, tert.-butyl alcohol, lauryl alcohol, octane,  $\beta \eta$ dimethyloctane, and  $\beta\beta\delta$ -trimethylpentane. The general results are in agreement with those of Vaidyanathan (cf. A., 1929, 746), and strongly support the cybotactic space-group condition in liquids. Space rearrangements within these groups with change of temperature are indicated. Anisotropic expansion within the space-groups in the liquids is indicated.

N. M. BLIGH. Structure of organic molecular compounds. E. HERTEL and H. KLEU (Z. physikal. Chem., 1930, B, 11, 59-75; cf. A., 1930, 668).-The crystal structure of the equimolecular compound of acenaphthene with 2:6-dinitro-m-xylene has been determined. A comparison of the dimensions of the unit cell of the compound with those of the constituents enables a diagram of the mode of combination to be constructed. The space-groups of the three substances, in the order named above, are  $V_h^s$ ,  $C_{2h}^{s}$ , and  $C_{2h}^{s}$ . A simple relation subsists between the corresponding dimensions: thus  $a_{AB} = \frac{1}{2}a_A + a_B$ ;  $b_{AB} =$  $b_{A}+b_{B}$ ;  $c_{AB}=c_{A}=c_{B}$ , where A denotes acenaphthene and B dinitroxylene. The structure of acenaphthene is discussed, and a criterion of a "molecular compound " is proposed. F. L. USHER.

One- and two-dimensional alternation in crystal structure of organic molecular compounds. E. HERTEL and G. H. RÖMER (Z. physikal. Chem., 1930, B, 11, 77—89).—In the lattice of an organic molecular compound it may happen as a result of the mutual saturation of residual valencies that the molecules of one of the components form a chain or net-work. Hence instead of the molecules of the components alternating with each other along all three principal axes of the crystal (cf. preceding abstract) they alternate along only two ("twodimensional alternation") if chains are present, and along only one ("one-dimensional alternation") if net-works are present. The lattice of the compound of fluorene and 1:3:5-trinitrobenzene,

 $3C_{13}H_{10}$ ,  $4C_6H_3(NO_2)_3$ , for instance, is composed of alternating net-works of fluorene and trinitrobenzene molecules. In the compound of anthracene with 1:3:5-trinitrobenzene,  $C_{14}H_{10}$ ,  $C_6H_3(NO_2)_3$ , on the other hand, the lattice is a body-centred translational lattice of the  $\Gamma m'$  class with the space-grouping  $C_{*}^{*}$ , and the trinitrobenzene molecules are arranged in chains. 1:3:5-Trinitrobenzene itself has a simple rhombic translational lattice in which the molecules form groups of four with the characteristic symmetry  $C_{10}C_{20}$ , or  $C_{20}$ . In the lattice of 2:4:6-trinitrotoluene the space-grouping is  $C_{20}^{*}$ , and here also the molecules are grouped in fours. R. CUTHILL.

Use of the rule of ferromagnetic anisotropy in calculating the properties peculiar to polycrystalline iron. N. S. AKULOV (Z. Physik, 1930, 66, 533-542).—A formula is deduced by means of which it is possible to calculate, from measurements on single crystals, the magnetisation, the magnetostriction, and the change in resistance of pure polycrystalline ferromagnetics. This formula is strict at saturation. J. FARQUHARSON.

Magnetic properties of rhenium. W. H. ALBRECHT and E. WEDEKIND (Naturwiss., 1931, 19, 20-21).—The magnetic susceptibilities of potassium perrhenate and metallic rhenium were found to be  $-0.13(\pm 0.05) \times 10^{-6}$  and  $+0.046(\pm 0.02) \times 10^{-6}$ , respectively. The value for rhenium does not lie between those of its neighbouring elements, osmium and tungsten. F. O. HowITT.

Doubling of the Curie points of nickel. R. FORRER and A. HOFFMANN (Compt. rend., 1930, 191, 1049-1049).—The difference between the para-magnetic Curie point determined from Weiss' law  $(0_p)$  and the ferromagnetic point corresponding with disappearance of permanent magnetisation  $(0_p)$  is of the order of 20°. The dependence on the previous thermal and mechanical treatments of nickel of the difference between  $0_f$  and the Curie point  $(0_h)$  of the coercive field has been investigated. It is large  $(14.5^\circ)$  for nickel which has been bent and then straightened, 1.5° for nickel ruptured by stretching, and 5-14.5° for nickel annealed under various conditions. Annealed nickel always shows a displace-ment of the Curie point, whilst variations with temperature of the mechanical constants of mechanically-treated nickels are linear, and give relatively unambiguous values. The results indicate the presence of two ferromagnetic nickels having different Curie points, which must be segregated, since solid solutions have only one Curie point. The first ferromagnetic Curie point is at 361° and is independent of the method of treatment;  $(\theta_{f_i} - \theta_{f_i})$  is of the order of  $6^{\circ}$  and is characteristic of the annealed nickel (cf. Lapp, A., 1928, 577). The difference  $(\theta_{h_i} - \theta_{f_i})$  is of the same order as  $(\theta_{h_i} - \theta_{f_i})$ , *i.e.*,  $5-14\cdot5^{\circ}$ . The ratio of the magnetisations of the two types of nickel constitutions of the two types of nickel constitution equally removed from  $\theta_f$  is unity. J. GRANT.

Magnetisation of a ferromagnetic substance under the influence of an alternating field. S. PROCOPIU (J. Phys. Radium, 1930, [vii], 1, 365— 372).—The magnetisation of iron and steel wires was studied, using a constant magnetising field, on which were superimposed in turn longitudinal and circular alternating or oscillating fields. Curves are plotted, and it was found that the magnetisation increases to a maximum when the alternating or oscillating field reaches the coercive value for the substance, after which it decreases. The variation of magnetisation is least at high frequencies of the order  $2 \times 10^6$  periods per sec. N. M. BLIGH.

Influence of internal transverse magnetism in determinations of electrical resistance of wires of iron, nickel, and of their alloys. M. MEDICI (Rend. Accad. Sci. fis. mat., 1930, 35, 248-255).-The transverse magnetism produced in a wire by the passage of an electric current affects the resistance of the wire, but the effect tends to disappear after a With iron there is an increase of certain time. resistance due to the transverse magnetic field, which decreases gradually with time and approaches that of the unmagnetised metal. Iron previously heated shows the opposite behaviour. With nickel and iron-nickel alloys, both before and after heating, the transverse magnetism produces a decrease in the resistance. Alloys containing 44% and 49% Ni lose their magnetisation in a short time; with the 36% alloy the effect of the transverse magnetic field is

the most protracted, whereas the 22% alloy, which has practically no ferromagnetism, returns rapidly to its original state. For all the alloys the variation of the resistance is proportional to the intensity of the current used to produce the transverse magnetism.

O. J. WALKER. Direction of magnetisation of single ferromagnetic crystals. F. C. POWELL (Proc. Roy. Soc., 1930, A, 130, 167-181).-Theoretical. It is shown that Mahajani's theory of ferromagnetism (cf. A., 1929, 495) fails in the case of cubic crystals. The observed deviation between the directions of magnetisation and the applied field in both cubic and noncubic crystals can be satisfactorily accounted for by taking into consideration the magnetic interaction between the effective electrons (i.e., those of which the magnetic moments contribute to the magnetisation of the crystal) and the atoms to which they belong. It is supposed that this interaction can be represented by a field b fixed in the crystal, the "crystalline field." The theory has been worked out only for cases when the applied field is great enough to produce saturation and when thermal effects can be neglected. The required magnitude of G is in agreement with that deduced from spectroscopic data, and is estimated to be 5.6, 8.2, and  $4.5 \times 10^5$  gauss for nickel, iron, and cobalt, respectively. L. L. BIRCUMSHAW.

Anomalous diamagnetism and crystal structure. V. I. VAIDYANATHAN (Indian J. Physics, 1930. 5. 559—572).—Colloids of graphite, bismuth, and antimony investigated magnetically showed a decrease of diamagnetism on colloidalisation, the effect being most marked in graphite. The anisotropy of single crystals of graphite was approximately 1:6.7 for the *c* axis perpendicular and parallel to the field, respectively. In the compounds of bismuth and antimony the ionic values are smaller than in the crystal state, and vary as deduced from different compounds.

N. M. BLIGH.

Molecular field and atomic order in ferromagnetic crystals and in hydrogenised iron. L. W. McKEEHAN (Nature, 1930, 126, 952—953).— A discussion. L. S. THEOBALD.

Magnetic isotropy of a paramagnetic alum. C. G. MONTGOMERY (Physical Rev., 1930, [ii], 36, 1661—1662; cf. A., 1930, 1354).—In order further to test, using a paramagnetic material, Forrest's theory (cf. A., 1927, 299) of variation in magnetic susceptibility with direction of the applied field for certain crystals, measurements were made on potassium chromium alum. The crystals were found to be magnetically isotropic, in opposition to Forrest's deductions. N. M. BLIGH.

Effect of internal stress on the magnetic susceptibility of metals. K. HONDA and Y. SHIMIZU (Nature, 1930, 126, 990—991).—Cold-working markedly decreases the diamagnetic susceptibility of a metal belonging to the cubic system; in the case of copper, severe cold-working changes the susceptibility of copper from diamagnetic to paramagnetic. Data for silver are also given. L. S. THEOBALD.

Magnetic forces in a crystal of the rock-salt type. J. BOUMAN (Arch. Néerland., 1930, [iiia], 13, 1-28).—Mathematical. The magnetic fields due to the lattices of elementary magnets are calculated, and the partition of the magnets in the crystal is investigated, having regard to crystal symmetry, absence of magnetisation, and the equilibrium of the magnets under the mutual influence of their magnetic fields.

N. M. BLIGH.

Magnetic properties of certain platinum- and palladium-cobalt alloys. F. W. CONSTANT (Physical Rev., 1930, [ii], 36, 1654—1660).—In order to obtain evidence on ferromagnetism, an investigation was made, using the above alloys, of the magnetic properties of ferromagnetic atoms in a state of isolation from one another intermediate between that of the pure metal and that of Gerlach and Stern's experiments. A lowering of the Curie point and a decrease in the remanent magnetisation and coercive force with decrease in the percentage of cobalt were found, in agreement with theory, in relation to which is discussed the observed increase in the magnetisation per cobalt atom. N. M. BLIGH.

High-pressure gas charging of metals. H. JELLINEK (Z. Physik, 1930, 66, 543—557).—Iron, palladium, and silver absorb hydrogen and nitrogen at high pressures after activation. The activation and purification process consisted of heating a wire of 2 mm. diameter by means of a current of 38 amp. for about 1 hr. The heating process was repeated until the electrical resistance of the metal became fixed. The absorption of gas was then measured by means of variation in electrical resistance. The resistance of iron in hydrogen showed an 8.9% increase between 0 and 35 atm. pressure, in nitrogen a decrease of 4.5% between 0 and 15 atm., and an increase of 13.3% between 15 and 20 atm. The resistance of palladium in hydrogen increased by 4.4%, and in nitrogen by 3.8%, between 0 and 20 atm. Silver in hydrogen increased its resistance by 13.1% between 0 and 35 atm. A. B. D. CASSIE.

Variable resistances and their hydrodynamic analogy. R. AUERBACH (Z. Physik, 1930, 66, 499—512).—The analogy existing between the behaviour of electrical resistances which do not obey Ohm's law and have large temperature coefficients, and the hydrodynamic behaviour of solutions of solvated colloid solutions, is noted and discussed. A. B. D. CASSIE.

Electrical conductivity of amorphous quartz. W. GNANN (Z. Physik, 1930, 66, 436-452).-The dependence of the electric current passing along a quartz cylinder, 1.2 cm. long and 1 cm. diameter, on the moisture of the surrounding atmosphere, and on the applied voltage, and its time of application, were studied. Immediately after applying the P.D. a comparatively large current passes, owing to the absence of an opposing potential. This initial current reaches a constant smaller value after a few hours. Both the final constant current and the opposing current are largely dependent on the moisture content of the surrounding atmosphere, and the surface currents are greater than the volume currents even at medium moisture content. The volume resistance of quartz is more than  $6 \times 10^{19}$  ohm per cm. The final constant current obeys approximately Ohm's law. Bakelite C also shows equally large hygroscopic effects. A. B. D. CASSIE.

Unipolarity of pressed lead sulphide. F. TREY (Naturwiss., 1930, 18, 1099).—The effect of pressure and heat treatment on the unipolarity of lead sulphide crystal detectors is discussed. The detector properties are bound up with the normal crystal structure of the sulphide. Unipolar properties are connected with the resistance of the lead sulphide. Only good-conducting lead sulphide crystals of normal crystal structure can exhibit unipolar properties. At strong pressures significant properties of lead sulphide as a detector are good conductivity and unipolarity. W. R. ANGUS.

Polymorphous organic selenium compounds. O. BEHAGHEL (Z. wiss. Phot., 1930, 29, 230-233).-No relation could be found in the appearance of polymorphous forms in sulphur and selenium compounds of similar constitution. *p*-Phenylenebisselenoglycollic acid, *p*-phenyleneselenothiodiacetic acid, and other selenoglycollic acid derivatives and certain mono- and di-selenides do not exhibit the polymorphism shown by the corresponding sulphur compounds; diselenodiglycollic acid may be obtained in three modifications, but the corresponding sulphur compound does not exhibit polymorphism (cf. A., 1930, 100). J. W. GLASSETT.

Determination of the mol. wt. of hæmocyanin by the centrifugal method. T. SVEDBERG and E. CHIRNOAGA (Bul. Chim. pura appl., Bukarest, 1929, 31, 23-52; Chem. Zentr., 1930, ii, 248-249).-The determination of hæmocyanin from Helix Pomatia in isoelectric solution of  $p_{\rm H}$  4.7 is described. The diffusion constants depend on the concentration when this exceeds a limiting value, presumably owing to the operation of intramolecular forces. The value  $5 \times 10^6$  $(\pm 5\%)$  was obtained; the hæmocyanin is regarded as a chemical individual. At  $p_{\rm H}$  7 the "molecules" are spheres of radius  $12 \cdot 1 \times 10^{-7}$  cm.; each molecule contains 300 atoms of copper. The preparation of the hæmocyanin is described. The specific volume of hamocyanin in solutions of  $p_{\rm sl} 8-3.8$  is 0.730-0.755. In agreement with Dhéré and Burdel, absorption bands were found at 610-530, 360-310, and 290-260  $\mu\mu$ . On the acid side of the isoelectric point the absorption is markedly less and is displaced towards the red. A. A. ELDRIDGE.

Magnetic susceptibility of gases. II. Temperature dependence. F. BITTER (Physical Rev., 1930, [ii], 36, 1648—1653; cf. A., 1930, 1102).—The molecular susceptibilities  $\times 10^6$  for carbon dioxide, nitrogen, and hydrogen at 25° gave the values  $-24\cdot 2$ ,  $-14\cdot 8$ , and  $-5\cdot 8$ , and at  $-185^\circ$ ,  $-14\cdot 2$  and  $-3\cdot 3$ for the two last-named gases, respectively. Results of previous investigators are tabulated for comparison, and are in fair agreement. The low-temperature result for nitrogen indicates that if a permanent moment is present it is less than 0.04 of a Bohr magneton. The anomaly of the difference in the values for hydrogen at the two temperatures is discussed.

N. M. BLIGH.

Heat of vaporisation of liquids. J. HYBL (Z. Eis- Kälte-Ind., 1930, 37, 85-86; Chem. Zentr.,

1930, ii, 208).—Kamerlingh Onnes' formula  $r^2 = a(T_{\text{crit.}} - T) - b(T_{\text{crit.}} - T)^2 + c(T_{\text{crit.}} - T)^3$  gives results in best accord with observations on water and ammonia. Values of a, b, c, and  $T_{\text{crit.}}$  for 12 organic and inorganic liquids are tabulated; the heat of vaporisation between  $-40^\circ$  and  $40^\circ$  has been calculated and expressed graphically. The curves are similar; hence the heat of vaporisation for equal values of  $T_{\text{crit.}} - T$  can be obtained by multiplication of the value for water by a constant factor.

A. A. ELDRIDGE.

Latent heats of evaporation of nitromethane and benzonitrile. J. C. PHILIP and S. C. WATER-TON (J.C.S., 1930, 2783-2784).—Redeterminations of the latent heats of evaporation of nitromethane and benzonitrile by Brown's method (J.C.S., 1903, 83, 987) give values of 135.4 and 106.5 g.-cal./g., respectively. These values are higher than those recorded in the literature. The theoretical values of the b. p. elevation constants are calculated from these values to be  $2.05^{\circ}$  and  $4.01^{\circ}$ , respectively; these are only slightly higher than the experimental values (cf. Landolt and Börnstein), which are now determined as  $1.86^{\circ}$  and  $3.87^{\circ}$ , respectively.

H. BURTON. Emissive laws of nickel. W. DEL REGNO (Atti R. Accad. Lincei, 1930, [vi], 11, 989–993; cf. A., 1929, 1353).—The method previously used for bismuth has been applied in the determination of the exponent in the Stefan-Boltzmann equation for the total emissivity of nickel. The value 4.586 was obtained from measurements over the range 60–360°.

F. G. TRYHORN.

Influence of the elastic deformation of drawing on the specific heat of metals. M. GAUDINO (Rend. Accad. Sci. fis. mat., 1930, 35, 204-207).--Permanent deformation produced in nickel, brass, and lead wires by drawing them almost to the breaking point bring about a slight increase in the specific heat of the metal. O. J. WALKER.

Necessity for adopting a standard substance for ebullioscopic and tonometric measurements. W. SWIENTOSLAWSKI (J. Chim. phys., 1930, 27, 496-502).-Attention is directed to the errors in temperature and vapour-pressure measurements and to the lack of concordance in the published data, which cannot be attributed entirely to the presence of impurities in the liquids investigated. Agreement can be reached only by the universal adoption of a comparative method of measurement, and water is suggested as a suitable standard. It is further recommended that (1) when determining the b. p. or vapour pressure of a liquid at a given temperature the b. p. and vapour pressure of the standard under the same conditions should be noted, (2) when the b. p. of the liquid differs considerably  $(30^{\circ} \text{ or } 40^{\circ})$ from that of the standard under the same pressure, comparison should be made with an auxiliary liquid, the b. p. of which is as near as possible to that of the liquid investigated, and is known in relation to the standard, (3) the coefficients dp/dt should be determined in such a way that the corresponding coefficients of the standard can be defined under the same conditions, (4) the b. p. of the liquid and of the

standard should be determined at various pressures so that the relation  $t_{subs.} = f(t_{H_{s0}})$  may be established. E. S. HEDGES.

Comparative ebullioscopic and tonometric researches with eight standard organic substances. A. ZMACZYNSKI (J. Chim. phys., 1930, 27, 503-517).-The variation of b. p. with pressure over the range 380-2000 mm. has been determined for 8 organic liquids and for water. An empirical equation for the relation between the b. p. of the substances studied and that of water at the same pressure has been established in the form  $t_{sub}$  =  $A + Bt_{n,0} + C(t_{\Pi,0})^2$  and tables of the values of the coefficients A, B, and C are given. A table of the ratio  $(dt/dp)_{subs.}$ :  $(dt/dp)_{n,o}$  is given and the coefficients dt/dp have been calculated for 760 mm. The following values of b. p./760 mm. have been determined from the data and are compared with those in the literature : ethyl bromide, 38.386°; carbon disulphide, 46.262°; acetone, 56·131°; chloroform, 61·152°; benzene, 80.122°; toluene, 110.606°; chlorobenzene, 131.687°; bromobenzene, 155.908°. E. S. HEDGES.

Thermal conductivity of liquids. J. F. D. SMITH (Ind. Eng. Chem., 1930, 22, 1246—1251).— The following results were obtained in c.g.s. units for thermal conductivities at the temperatures stated : cthyl alcohol 99.8%, 30°, 0.000435; 95%, 30°, 0.000460; water 30°, 0.00144; 75°, 0.00148; toluene 30°, 0.000357; 75°, 0.000338; isoamyl alcohol 30°, 0.000362; 75°, 0.000358; data are given for the following hydrocarbon oils : Rabbeth spindle oil, Velocite B, red oil, light heat-transfer oil. The empirical equation  $kZ^{0.12}/\rho C^{0.4} = 8.1 \times 10^{-4} (\rho C M^{1.6})^{1.15}$ gives the thermal conductivities of all non-metallic liquids at 30° and atmospheric pressure, where k is thermal conductivity in c.g.s. units,  $\rho$  is  $d_{\text{liquid}}/d_{\text{water}}$ at 30°, Z viscosity in centipoises, C sp. heat, and M mol. wt. H. INGLESON.

Specific heat charts for gases [at high temperatures]. A. C. HALFERDAHL (Chem. & Met. Eng., 1930, 37, 686-687).—The mean specific heats of hydrogen, nitrogen, oxygen, carbon monoxide and dioxide, sulphur dioxide, hydrogen sulphide, ammonia, methane, chlorine, and water and sulphur vapour were plotted up to 2500°, and a simplifying chart is given. The errors range from 1.5 to 10%.

E. A. RYDER.

Vapour pressure of chlorine monoxide. C. F. GOODEVE (J.C.S., 1930, 2733—2737).—Apparatus is described which is suitable for the determination of the vapour pressure of chlorine monoxide without undue decomposition of the gas; at temperatures below  $-10^{\circ}$  decomposition ceases. The vapour pressure p between  $-96^{\circ}$  and  $3^{\circ}$  accords with the equation log p = -1373/T + 7.87, from which the calculated latent heat of vaporisation is 6200 g.-cal./mol.; Trouton's constant, 22.5, is indicative of little association in the liquid state. The b. p. is  $2.0^{\circ}/760$  mm., and the m. p.  $-116^{\circ}\pm1^{\circ}$ . H. F. GILLBE.

Compressibility of nitrogen and hydrogen at pressures of 5000 atm. J. BASSET and R. DUPINAY (Compt. rend., 1930, 191, 1295—1297).—Data are given for the volumes occupied at 16° and pressures up to 5000 kg. per cm.<sup>2</sup> by masses of nitrogen and hydrogen occupying (a) 1 c.e. at  $16^{\circ}$  and 1000 kg. per cm.<sup>2</sup>; (b) 1 litre at 0° and 76 cm. The apparatus previously described (this vol., 59) was used and the results for hydrogen (up to 3000 kg. per cm.<sup>2</sup>) are in agreement with those of Amagat, whilst for nitrogen they are 2—3% lower. J. GRANT.

Direct connexion between equation of state and inner friction. L. SCHAMES (Physikal. Z., 1931, 32, 16-20).—Mathematical. It is possible, by means of the friction, to separate the effects of the van der Waals a and b terms, and to determine these quantities as temperature functions. A. J. MEE.

Measurements with the aid of liquid helium. XII. Plasticity of metal crystals at the lowest temperatures. W. MEISSNER, M. PÓLÁNYI, and E. SCHMID (Z. Physik, 1930, 66, 477–489).—Stressstrain curves for the extension of zine and cadmium crystals at temperatures in the liquid helium range are given. The form of these curves does not change as the temperature is lowered. Plasticity is separated into two parts; one, apparent only in crystals, is independent of temperature, and the other, which may be associated with the self-diffusion of amorphous substances, is dependent on temperature. The first is termed "athermic," the second "thermic," plasticity. The experimental method, and a means of transporting liquid helium, are described in detail.

A. B. D. CASSIE.

Determination of molecular velocities and proof of the cosine law. P. CLAUSING (Ann. Physik, 1930, [v], 7, 569-578).-An expression derived for the mean time taken by a molecule in its zig-zag path down a long capillary tube (cf. this vol., 34) is tested experimentally for argon and neon at the ordinary temperature. It is necessary to assume that during its passage down the tube the molecule does not collide with another, and that the adsorption time of the molecules on the glass walls of the tube is so small that the time of travel down the tube is independent of it. From the experiments it is shown that the cosine law for diffuse scattering of molecules is correct for argon and neon at glass at the ordinary temperature, and that the mean molecular velocity agrees with the Maxwell velocity distribution.

A. J. MEE.

Critical constants of carbon dioxide-oxygen mixtures. H. S. BOOTH and J. M. CARTER (J. Physical Chem., 1930, 34, 2801-2825).-The maximum temperatures of condensation, the critical temperatures, and the corresponding pressures have been determined for the following volume mixtures of oxygen and carbon dioxide : 1:1, 3:2, 7:3, 4:1, and 9:1, respectively, in an apparatus specially designed for the study of critical phenomena at low temperatures. Mixtures containing 50% or less of carbon dioxide should not lose their uniformity under the ordinary conditions of transport or storage. The mixture containing 50% CO<sub>2</sub> cannot be liquefied at all above  $-8.4^{\circ}$  and cannot be completely liquefied above  $-35.7^{\circ}$ . With less carbon dioxide even lower temperatures are required. A discontinuity in the critical curve of the mixtures is shown by those which contain from 62% to 97% O2. The curve representing the maximum temperatures of condensation also shows a discontinuity for mixtures containing 88-98% O<sub>2</sub>. Solid carbon dioxide is soluble to about 3% in liquid oxygen near its critical temperature. The retrograde phenomena are explained.

L. S. THEOBALD. Changes in volume and temperature that accompany the mixing of organic liquids. I. E. R. WASHBURN and A. LIGHTBODY (J. Physical Chem., 1930, 34, 2701—2710).—The changes in temperature and volume which accompany the mixing of methyl, ethyl, and *iso*propyl alcohols with benzene and with toluene, respectively, have been determined. The maximum temperature changes become greater as the homologous series is ascended and the volume changes appear to vary in a regular manner, but no simple relation exists between the temperature and volume changes for a given mixture. The presence of water in the system ethyl alcohol-benzene increases the magnitude of both changes. L. S. THEOBALD.

Application of the Debye dipole theory to binary liquid mixtures. III. Derivatives of ammonia. J. M. FOGELBERG and J. W. WILLIAMS (Physikal. Z., 1931, 32, 27-31; cf. A., 1928, 578, 1180).—The structure of the ammonium group is discussed. The ammonium model, consisting of a pyramid in which the nitrogen atom is situated at the point of the pyramid, is in agreement with stereochemical observations, and also with the dipole moment data. The dipole moments of a number of aromatic and aliphatic amines have been determined to ascertain whether they can be classed as ammonium derivatives. The binary mixture method, previously developed, was used. Values for the dielectric constants and densities are given. The conditions under which the dipole moments can be calculated are stated.

A. J. MEE.

Theory of orderly structure of solid solutions. C. WAGNER and W. SCHOTTKY (Z. physikal. Chem., 1930, B, 11, 163-210).-The array of the particles in the lattice of a solid binary compound will be disturbed if an excess of one component is introduced so as to form a solid solution, and some of the particles will be wrongly placed as compared with the original lattice, either through the formation of a solid solution of the interstitial or substitutional type, or by the appearance of empty places in one of the partial lattices. By a combination of thermodynamical and statistical methods it has been possible to determine the number of such points of disarray and the activities and chemical potentials in solid solutions of the various types as functions of the composition. In solid solutions with metallic lattices the relationship between electrical resistance and composition is dependent on the number of points of disarray. It is considered that even when the composition of the solid solution corresponds with a simple stoicheiometric ratio some points of disarray are present, and the ratio of the number of points of disarray to the total number of lattice points in the crystal is termed the "degree of disarray." Various examples of the calculation of this quantity from experimental data are given. R. CUTHILL.

Isomorphism between oxides of quadrivalent metals. Systems CeO<sub>2</sub>-ThO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub>, and

CeO<sub>2</sub>-HfO<sub>2</sub>. L. PASSERINI (Gazzetta, 1930, 60, 762-776).—An X-ray examination by the powder method has been made of the various binary solid solutions of the above oxides obtained by calcination at about 800° of the solid solutions of the corresponding hydroxides, which were prepared by precipitation with potassium hydroxide of solutions containing the required amounts of the metallic nitrates or sulphates. The binary solid solutions of the dioxides, like the dioxides of cerium and of thorium, crystallise in the cubic system with a lattice of the fluorite type. In the system CeO<sub>2</sub>-ThO<sub>2</sub> the components are soluble in one another in all proportions and the lattice constants and densities vary regularly with the composition of the solid solution. In the other two systems the solubility is only partial, the maximum solubilities being approximately 27% of zirconium oxide in cerium oxide, 23% of cerium oxide in zirconium oxide, 25% of cerium oxide in hafnium oxide, and 32% of hafnium oxide in cerium oxide. By extrapolation from the data for the solid solutions the following lattice dimensions have been obtained for the cubic form of zirconium dioxide and for the probable cubic form of hafnium dioxide:  $ZrO_2$ ,  $a \ 5.065 \pm 0.01$  Å.,  $v \ 129.94 \times 10^{-24}$  c.c.,  $d \ 6.27$ ; HfO<sub>2</sub>,  $a \ 5.115 \pm 0.01$  Å.,  $v \ 133.82 \times 10^{-24}$  c.c.,  $d \ 10.43$ . These two oxides have a fluorite type lattice. The calculated diameter of the  $Hf^{++++}$  ion is 1.79 Å. For the binary systems investigated the solubility in the solid state depends on the difference between the diameters of the metallic ions. O. J. WALKER.

Thermal conductivity of copper alloys. II. Copper-tin. III. Copper-phosphorus. C. S. SMITH (Amer. Inst. Min. Met. Eng. Tech. Pub., 1930, No. 360, 11 pp.).—The addition of tin rapidly reduces the thermal conductivity of copper (0.941 g.-cal. per cm.<sup>2</sup> per cm. per sec. per 1°) until with 10.41% Sn it is only 0.121 at 20°; 0.93% of phosphorus reduces the value to 0.129. The electrical conductivity decreases more rapidly on alloying than does the thermal conductivity. The Wiedemann–Franz–Lorenz ratio increases rapidly at first, but beyond 2.0% Sn or 0.15% P it remains nearly constant.

CHEMICAL ABSTRACTS.

X-Ray investigation of the system cadmiummagnesium. U. DEHLINGER (Z. anorg. Chem., 1930, 194, 223—238).—X-Ray diagrams of cadmiummagnesium alloys show the existence of two series of mixed crystals,  $\alpha$  and  $\beta$ , of which the axial ratios are 1.89 and 1.62, respectively, at all concentrations; no phase having a different lattice type appears to exist. Powder diagrams of the compound CdMg<sub>3</sub>, which has the  $\beta$  structure, resemble closely those of pure magnesium and indicate a regular distribution of cadmium in the magnesium lattice without appreciable distortion. The cell constants a and c of the compound are 3.13 and 5.07 Å., as compared with 3.19 and 5.16 Å. for magnesium; the observed density of the compound is 3.49, whilst that calculated on an assumption of atomic substitution is 3.45. The compound Cd<sub>3</sub>Mg, which is of the  $\alpha$  type, is formed in the analogous manner by substitution of magnesium atoms in the cadmium lattice, of which the lattice constants a and c diminish from 2.96 and 5.63 Å. to 2.93 and 5.53 Å. The transformation experienced by cadmium when subjected to pressure (3000 atm.) appears to be reversible, but by hammering a cadmium-magnesium mixed crystal containing 50 at.-% of magnesium a permanent change from the cadmium to the magnesium type of lattice takes place; the presence of magnesium thus lowers the pressure necessary to cause the cadmium transformation. This phenomenon is thermodynamically in accordance with the smaller cell volume of the magnesium type of mixed crystal. H. F. GILLBE.

Electrical conductivity and thermal expansion of magnesium-cadmium alloys. G. GRUBE and E. SCHIEDT (Z. anorg. Chem., 1930, 194, 190-222).-The variation with composition of the conductivity and thermal expansion of magnesium-cadmium alloys has been determined between 50° and the m. p. The conductivity-composition isotherms at 50° exhibit three sharp peaks corresponding with the compound MgCd and the compounds Mg3Cd and MgCd3; at higher temperatures the maxima become flatter, since the compounds are stable only at relatively low temperatures. MgCd<sub>3</sub> separates at 89° on cooling the cadmium-rich a-mixed crystals, and Mg<sub>3</sub>Cd at 150° from the magnesium-rich  $\beta$ -mixed crystals; MgCd decomposes at temperatures above 251°. Cadmium and MgCd<sub>3</sub>, as well as MgCd<sub>3</sub> and MgCd, form continuous series of mixed crystals at the ordinary temperature, whereas MgCd and Mg<sub>3</sub>Cd have only limited mutual solubility. The  $\alpha$ -mixed crystals, stable at the ordinary temperature, contain from 0% to 65% of magnesium, whilst the  $\beta'$ -mixed crystals contain from 100% to about 60% of magnesium. The heterogeneous region at  $61{-}67\%$  magnesium vanishes at  $150^\circ,$  but at 100° a second heterogeneous region appears at 28-33% magnesium. The transformation of the  $\alpha'$ - and  $\beta'$ -mixed crystals into the  $\alpha$ - and  $\beta$ -types, stable at higher temperatures, has been investigated, and the limits of co-existence of the various phases have been determined. For alloys containing 40-60% and 70-80% of magnesium the temperature coefficients of the conductivity and thermal expansion are at first constant, and then, at 70-80° below the transition interval, increase slowly; in the transition range the increase becomes abrupt, and finally, after the transition has been completed, the coefficients fall to a small constant value. The transitions thus appear to take place in two stages, of which the first involves the gradually accelerated breakdown of the regular orientation of the atoms and the second the rearrangement of the still partly oriented atoms into the structure of the mixed crystals stable at the higher tem-H. F. GILLBE. perature.

Equilibrium relations in aluminium-magnesium silicide alloys of high purity. E. H. DIX, jun., F. KELLER, and R. W. GRAHAM (Amer. Inst. Min. Met. Eng. Tech. Pub., 1930, No. 357, 15 pp.).— Aluminium containing 0.14-2.37% of Mg<sub>2</sub>Si was investigated. At the eutectic temperature, 595°, the solid-solubility of Mg<sub>2</sub>Si is 1.85%; it decreases with falling temperature, being less than 0.27% at 200°. The mechanical properties of the alloys were studied. CHEMICAL ABSTRACTS. Equilibrium relations in aluminium-antimony alloys of high purity. E. H. DIX, jun., F. KELLER, and L. A. WILLEY (Amer. Inst. Min. Eng. Tech. Pub., 1930, No. 356, 9 pp.).—The solid-solubility of antimony is less than 0.10% at 645°. The cutectic lies at 1.1% Sb and 657°. CHEMICAL ABSTRACTS.

Constituents of aluminium-iron-silicon alloys. W. L. FINK and K. R. VAN HORN (Amer. Inst. Min. Met. Eng. Tech. Pub., 1930, No. 351, 11 pp.).—X-Ray examination of the annealed alloys confirms Dix and Heath's results. The  $\alpha$  ternary constituent appears to be a solid solution of silicon in the compound FeAl<sub>3</sub>. The  $\beta$  constituent is a ternary compound which may contain excess of aluminium in solid solution. CHEMICAL ABSTRACTS.

Strontium amalgams. G. DEVOTO and E. RECCHIA (Gazzetta, 1930, 60, 688—692).—A thermal analysis has been made of strontium amalgams containing up to approximately 20 at.-% Sr. A compound, SrHg<sub>8</sub>, is formed by a transition which occurs at 262°. A slight arrest is found at 39°, which may be due to the compound SrHg<sub>12</sub>, and a cutectic point occurs at -43°, with approximately 1.1 at.-% Sr. The initial b. p. of mercury in these amalgams is 390°, compared with 337° for calcium amalgams.

F. G. TRYHORN.

Multicomponent systems containing iron. III. System iron-phosphorus-silicon. W. HUMMITZSCH and F. SAUERWALD (Z. anorg. Chem., 1930, 194, 113-138).-The system Fe-Fe<sub>2</sub>P-FeSi has been investigated thermally and microscopically. Fe<sub>2</sub>P and FeSi form a quasi-binary system, the components being completely miscible when fused and immiscible when solid; the cutectic mixture formed at 1185° contains Si 15.0, P 12.05%. Fc<sub>3</sub>P and FeSi do not form a quasi-binary system; Fe<sub>3</sub>P melts incon-gruently at 1165—1173°, and the liquidus curve which commences at this point rises to a maximum, but there is no evidence for the existence of a compound such as  $2Fe_3P$ , FeSi; the eutectic formed at 1180° contains P 8.95%, Si 14.42%. Mixtures containing 8% P exhibit two binary eutectics, viz., with mixed crystals and Fe<sub>3</sub>P (1027°) and with mixed crystals and FeSi (1147°) as solid phases, whilst at a slightly lower phosphorus content (7.45%) a ternary eutectic mixture containing Si 6.35% separates at 1018°, the phases being ternary saturated mixed crystals of unknown composition, Fe<sub>3</sub>P, and FeSi. An invariant point exists at 1110°, corresponding with the trans-formation liquid +  $Fe_2P = Fe_3P + FeSi$ ; the liquid phase contains P 6%, Si 13.55%. There is no evidence of a thermal effect due to the compound H. F. GILLBE. Fe<sub>3</sub>Si<sub>2</sub>.

Peaks in the isotherms of the electrical conductivity of metallic mixed crystals. G. GRUBE and J. HILLE (Z. anorg. Chem., 1930, 194, 179–189). —The application of measurements of electrical conductivity to the investigation of changes in metallic systems which cannot be studied by thermal methods is described; a particular case is that of transformations in solid alloys, which often take place with extreme slowness. The types of isotherm to be expected when the two components form an undissociated compound which yields mixed crystals with

each component, and when transformations take place in the solid state, are described for the three cases in which the transformation temperature is (1) lowered by each component, (2) raised by each component, (3) raised by one component and lowered by the other. In case (1) the maximum in the conductivity isotherms does not vary with temperature; in the second case, as the temperature falls, secondary, flattened maxima appear at concentrations above and below that of the peak due to separation of the compound, and at low temperatures the isotherm becomes a smooth curve with a pronounced minimum; in case (3) a flattening and displacement of the peak takes place, and flattened secondaries appear. The maximum may be displaced in case (1) if the compound undergoes partial dissociation. Since the conductivity of an alloy is a function of the volume and not of the mass, the composition by volume should, theoretically, be employed; nevertheless, the ordinary weight composition-conductivity curves exhibit the displacement of the maxima, and for the investigation of the limits of existence of the various phases temperature-resistance curves are satisfactory.

H. F. GILLBE.

X-Ray study of the A3 point of iron and some iron-nickel alloys. O. L. ROBERTS and W. P. DAVEY (Met. and Alloys, 1930, 1, 648-654).—The lattice parameters at the ordinary temperature for alloys containing 0, 0.87, 1.04, 2.78, 4.27, 11.73, and 13.21% Ni are, respectively, 2.858, 2.864, 2.866, 2.851, 2.849, 2.848, and 2.846 Å., indicating that the first 1-2% Ni stretches, whilst 3% or more contracts, the iron lattice. The transition temperature for the change body-centred  $\longrightarrow$  face-centred iron lies between 907±3° and 910±3°. The Ac3 points for alloys of iron and nickel containing 1.04, 2.78, 4.27, 11.73, and 13.21% Ni lie, respectively, between the limits 820-815, 720-715, 660-655, 525-520, and 520-515°, all ±3°. The Ac3 and Ar3 points do not coincide. The fractional lowering of the Ac3 point is greater for the first 10% Ni than for larger percentages. CHEMICAL ABSTRACTS.

Transformation of austenite at constant subcritical temperatures. E. S. DAVENPORT and E. C. BAIN (Amer. Inst. Min. Met. Eng. Tech. Pub., 1930, No. 348, 30 pp.).—In all the carbon steels examined, the transformation was most rapid at about 540°. In the range from Acl to 500° the transformation time decreases with either increasing or decreasing carbon content as the eutectoid recedes. Manganese retards markedly the transformation. At lower temperatures both carbon and manganese decrease the rate of transformation. The small amount of chromium (0.26%) in a low alloy steel retards the reaction of the austenite. Two methods for determining the rate of transformation, suitable respectively for temperatures above 300° and for low temperatures, are described.

#### CHEMICAL ABSTRACTS.

Systems of four immiscible liquid layers. E. L. SMITH (Nature, 1931, 127, 91).—A four-phase system can be produced at the ordinary temperature by mixing hexane (or light petroleum) 12 c.c., aniline 7 c.c., and oleic acid 0.5 c.c., and adding 10 c.c. of 0.8N-aqueous sodium hydroxide to saponify the fatty acid and salt out the soap. The addition of 1.5 c.c. of alcohol, although not essential to the system, greatly reduces the time required for separation into layers. A rise in temperature or an increase in concentration of electrolyte favours the miscibility of the hexane (first layer) and the aniline (third layer) which then form the top layer. L. S. THEOBALD.

Variation with temperature of the solubility of the rare gases in liquids. G. TAMMANN (Z. anorg. Chem., 1930, 194, 159-161).-The function  $(1/\log l)[d(\log l)/dT]$ , where l is the solubility of a gas in a liquid at  $T^{\circ}$  Abs., has been calculated for solutions of helium, neon, and argon in a number of nonaqueous solvents at temperatures between 18° and 37°, and is shown to assume an average value equal to -1/T, a condition theoretically necessary if the heat change Q corresponding with a chemical reaction between the gas and the solvent molecules is zero. The experimental error in the determination of l is, however, too great to permit a decision as to the actual value of Q in any particular case. The temperature variation of the solubility of argon and neon in water, as determined by a number of observers, indicates that in this solvent Q is not zero.

H. F. GILLBE. Solubility effects. VII. Thiocarbamide antipyrine, caffeine-antipyrine. E. OLIVERI-MANDALA and L. IRRERA (Gazzetta, 1930, 60, 872-877; cf. A., 1927, 303).-The solubility of thiocarbamide and of caffeine in water is considerably increased by the addition of antipyrine. Two supposed criteria for the recognition of complex formation in solution are discussed, viz., (a) determination of the temperature coefficient of solubility, and (b) determination of f.-p. depressions. The former method does not constitute a sure basis for deciding what molecular complexes are present in a solution, and the two methods often give different results. In the case of thiocarbamide and antipyrine the former method suggests that no compounds are formed in solution, whereas for solutions of caffeine and antipyrine both methods indicate the formation of a caffeine-antipyrine compound. O. J. WALKER.

Is there an intermediate horizontal portion between two eutectic points in the fusion curves of binary systems? N. A. PUSHIN and I. I. RIKOVSKI (Z. physikal. Chem., 1930, 151, 257—268; cf. Kremann and Pogantsch, A., 1924, i, 52).—Thermal analysis of the systems *m*-dinitrobenzene-o-phenylenediamine, *m*-dinitrobenzene – *m*-phenylenediamine, benzamide-*m*-nitrophenol, benzamide-*p*-nitrosodimethylaniline, and benzophenone-picric acid affords no indication in any of the existence of a horizontal portion joining two eutectic points, and the molecular compounds assumed by Kremann to account for it do not exist. An equimolecular compound is formed between *m*-dinitrobenzene and naphthalene, but the diagram is of normal type. F. L. USHER.

System thorium nitrate ether-water between  $0^{\circ}$  and  $20^{\circ}$ . P. MISCIATTELLI (Gazzetta, 1930, 60, 833-838).—The solubility of thorium nitrate in water between  $0^{\circ}$  and  $20^{\circ}$  has been determined, and

BRITISH CHEMICAL ABSTRACTS.-A.

solubility data and triangular diagrams are given for the ternary system with ether at 0° and 20°. O. J. WALKER.

System uranyl nitrate-ether-water between 0° and 20°. P. MISCIATTELLI (Gazzetta, 1930, 60, 839-842; cf. preceding abstract).—Solubility data and triangular diagrams are given for the system at 0° and 20°. O. J. WALKER.

Extraction of phenols from alkaline solution with ether. G. VAVON and J. PAIRA (Ann. Off. Nat. Combust. liq., 1929, 4, 997-1013; Chem. Zentr., 1930, ii, 234-235).-The following phenols were prepared by the Fries displacement from tolyl acetates : o-methyl-p-ethyl-, b. p. 218-220° (p-nitrobenzoate, m. p. 70-71°; dinitrobenzoate, m. p. 137-138°; arylglycollic acid, m. p. 125-126°); m-methyl-o-ethyl-, b. p. 215-219°, m. p. 44-45° (as above, m. p. 88—89°; m. p. 115—116°; m. p. 94—95°); m-methyl-p-ethyl-, b. p. 230—233°, m. p. 26—27° (as above, m. p. 116°; m. p. 128°; m. p. 131—132°); p-methyl-o-ethyl-, b. p. 215—219° (as above, m. p. 95—96°; m. p. 136—137°; m. p. 132—133°). The extraction coefficients of the phenols for other are, respectively, 65, 66, 43, 74. The hydrolysis of phenoxides and the extractability by ether are not completely parallel. m-Cresol and thymol are readily, phenol and o-cresol fairly readily, and m- and o-cresol with difficulty separable by fractional extraction with sodium hydroxide; p- and m-cresol are not thus separable. With o-cresol and a-naphthol separation can be effected with 20% sodium hydroxide and ether, but not by 4% sodium hydroxide. Butyl ether is ineffective; benzene gives slight, and carbon tetrachloride partial, separation. Various phenols were isolated from a crude Saar tar and identified.

A. A. ELDRIDGE.

Sorption of water vapour at low pressures by activated charcoals. I. A. J. ALLMAND and R. B. KING (Proc. Roy. Soc., 1930, A, 130, 210-217).-The sorption of water vapour by six specimens of activated charcoal has been measured at 25° over the pressure range 10<sup>-1</sup> to 10<sup>-3</sup> mm., the experimental method used being very similar to that described by Chaplin (cf. A., 1929, 133). The final isothermals obtained are apparently reversible. The influence of traces of residual gas present in the charcoal surface on the nature of the isothermal is discussed. It is found that the heat of adsorption of water vapour rises with decrease in the quantity adsorbed, as in the case of carbon tetrachloride (following abstract). Adsorbed water vapour appears to be less effective than other vapours in freeing a charcoal surface from its residual layer of bound oxygen or adsorbed carbon L. L. BIRCUMSHAW. dioxide.

Sorption of carbon tetrachloride at low pressures by activated charcoals. IV. A. J. ALL-MAND and A. PUTTICK (Proc. Roy. Soc., 1930, A, 130, 197—209; cf. A., 1930, 1513).—Experiments have been carried out which indicate that the effect of hightemperature degassing can be much greater than was previously found, but support the views already advanced on the part played by adsorbed oxygen (loc. cit.). In the case of a chemically-activated charcoal and carbon tetrachloride, a charging pressure of about 0.1 mm. at  $25^{\circ}$  is insufficient to clean up adsorbed oxygen from the charcoal surface, but this can be effected in practice by a charging pressure of 1.0 mm. An isothermal has been determined over a large pressure range ( $3\cdot3 \times 10^{-2}$  to 70.45 mm.) in a single experiment, the higher pressures being read by a mercury manometer and the lower by the Pirani gauge; the results indicate that the readings of the latter instrument are valid. Further evidence of the discontinuous nature of these isothermals has been obtained. L. BIRCUMSHAW.

Swelling of charcoal. I. Preliminary experiments with water vapour, carbon dioxide, ammonia, and sulphur dioxide. D. H. BANGHAM and N. FARHOURY (Proc. Roy. Soc., 1930, A, 130, 81-89).-A form of extensometer is described by means of which simultaneous measurements can be made of the percentage linear expansion (x) of a rod of wood charcoal and the weight (s) of gas taken up per unit weight of the adsorbent. In the case of ammonia, carbon dioxide, and sulphur dioxide the swelling is given by equations of the type x = k[s/(S-s)], where k and S are constants characteristic of each gas. An additional term is necessary to represent the behaviour of water vapour. The values of the constant S represent nearly equal volumes of the normal liquids at the experimental temperature. It is found that for any given value of s the corresponding x is slightly greater at higher temperatures. It is suggested that the expansion is caused by the pressure exerted by the adsorbed molecules at sharp re-entrant angles in the L. L. BIRCUMSHAW. surface of the adsorbent.

Adsorption from solution by ash-free, adsorbent charcoal. VI. Adsorption of invertase. E. J. MILLER and S. L. BANDEMER (J. Physical Chem., 1930, 34, 2666-2692; cf. A., 1928, 831).-The adsorption of invertase by blood-charcoal purified as previously described (A., 1927, 821) and the effect of adsorption on the inverting power of the enzyme have been investigated. As is the case with acids adsorbed by charcoal, large amounts of invertase can be adsorbed with complete loss of the power to invert sucrose. Adsorption of still larger amounts results in the retention of some activity by the invertase. Purification of the invertase results in a large decrease in adsorption. Ash-free charcoals from other sources show inactivation, but with unpurified charcoals some activity is retained by the enzyme. Displacement or reactivation of the adsorbed invertase was without success, suggesting that the invertase complex undergoes decomposition when adsorbed on charcoal. The presence of acetic, benzoic, or hydrochloric acid in the invertase solution or of acid adsorbed on the charcoal increases the adsorption of invertase by the latter, but, under these conditions, an inverting activity up to 50% is retained by the enzyme.. The age, concentration, and method of preparation of the invertase, time of contact with adsorbent, the presence of acids, and previous treatment of the charcoal are the main factors controlling adsorptions. Freshly-ignited charcoal adsorbs much larger amounts of invertase and the inactivation after adsorption is less complete. The addition of gum arabic to an invertase solution of low

yeast gum content causes the invertase to show a behaviour on adsorption which is the same as that of an invertase of high yeast gum content. Yeast gum and gum arabic are both considered to function as protective colloids for the invertase. The present work favours the view that the active group of the invertase is of colloidal dimensions.

L. S. THEOBALD. Adsorbed moisture in Kanbara clay. H. ISOBE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 229-274).-Acid, neutral, and alkaline Kanbara clays are found together at different levels, the acid clay being uppermost. The acidity or alkalinity of the clay is due to the presence of soluble acids or alkalis which can readily be washed out, leaving a neutral clay. Measurements of the adsorption coefficient for water by the dried clay give values between the extremes 8.2 and 25.8%; the adsorptive power is not affected by heat treatment below 275°, but decreases as the baking temperature rises above 400°. Neutral clay has the highest adsorbing power. The acidic, neutral, and alkaline clays have different water vapour pressures, but the vapour-pressure curve of neutral clay is the same whether naturally neutral, or neutralised with acid or alkali, or by washing with water. The various ways in which water may be taken up by the dried clay are discussed in relation to the experimental results. The amount of water retained in relatively large crevices depends on the porosity of the sample and varies between 20% and 50%. The water adsorbed by capillary action varies from 20% to 35% and the vapour-pressure curve of this part can be expressed by the equation  $a = \alpha P^n$ . About 2% to 18% of the water can be ascribed to true adsorption at the surface of the clay, and the vapour-pressure curve is represented by the formula  $a = k P^{1/n}$ , where 1/n has a value between 0.46 and 0.58. When the clay is heated between 600° and 800° a molecule of water of crystallisation is expelled and X-ray investigation shows that the crystal structure of the clay changes from hexagonal to cubic. At the m. p., 1300°, Kanbara clay expels water vapour, which must be water internally combined in the clay. The chemical reactions of Kanbara clay are consistent with the proposed formula, viz., [Al(SiO<sub>4</sub>SiO<sub>2</sub>)<sub>3</sub>]H<sub>4</sub>AlMgH<sub>2</sub>O.

E. S. HEDGES. Rigidity of adsorption layers. D. TALMUD, S. SUCHOWOLSKAJA, and N. LUBMAN (Z. physikal. Chem., 1930, 151, 401-412) .- The force required to rupture the adsorption layer formed at a solution-air interface has been determined for various capillaryactive substances, both soluble and insoluble. The substances studied were palmitic, oleic, heptoic, and octoic acids, cetyl alcohol, ethyl oleate, aniline, and saponin. In every case a well-defined maximum of rigidity was found for a surface concentration lower than that corresponding with a close-packed unimolecular layer. The surface concentrations corresponding with maximum rigidity coincide with those at which air bubbles blown with the respective solutions exhibit their maximum stability. These results support Talmud's theory, according to which the molecules in an unsaturated adsorption layer are only partly oriented and behave as a two-dimensional liquid crystal. F. L. USHER.

Adsorption time and its measurement by streaming methods. P. CLAUSING (Ann. Physik, 1930, [v], 7, 521-568).—The apparatus used in the determination is described (cf. this vol., 34), together with the construction of the ionisation manometer employed. The results of the experiments with argon, neon, and nitrogen, with glass as adsorbent, are discussed. It seems that the experiments with argon and nitrogen are not readily reproducible, in spite of the fact that the streaming tube was perfectly cleaned each time. It was found possible, however, to reproduce the temperature coefficient of the adsorption time, and this is determined exactly for the adsorption of argon on glass. The experiments with nitrogen were not so conclusive, and all that can be said is that the adsorption time for the same temperature interval is of the same order as that for argon. These values are also in agreement with those found by Langmuir. For neon and glass between the same temperature interval (78–90° Abs.) the adsorption time is less than  $2 \times 10^{-7}$  sec. The use of the method for similar determinations with different materials is discussed. A. J. MEE.

Atomic theoretical explanation of adsorptive power. F. LONDON and M. POLANYI (Naturwiss., 1930, 18, 1099-1100).-Previous theories of adsorption are briefly discussed and a new theory, based on London's conception (A., 1930, 1239) of molecular

bondon's conception (A., 1950, 1259) of molecular forces, is put forward to explain adsorptive power. W. R. ANGUS. Boedeker's adsorption equation. L. WÖHLER and W. WENZEL (Kolloid-Z., 1930, 53, 273-288).— The adsorption of acetic, propionic, butyric, and valeric acids by charcoal has been studied between 20° with risk to prove the studied between 20° and 80°. With rising temperature the exponent n of the adsorption isotherm rises and the constant a falls proportionally. By extrapolating to the b. p. the value of n for acetic acid becomes 1. In the presence of large amounts of carbon the distribution law holds for all four acids when dilute. The adsorption of paraffin from light petroleum by carbon is less, the higher is the b. p. of the petroleum ; the exponent is 0.4 for pentane, 0.74 for petroleum of b. p. 143°, and tends asymptotically towards 1.0 with rising b. p. of the solvent. The variation of the adsorption with temperature is small. Ether as a solvent behaves as a saturated hydrocarbon having the same b. p. At high dilutions the adsorption of chloride, thiocyanate, and iodate ions from electrolyte solutions gives the exponent n=1, but with increasing concentration the value rapidly falls to a fraction. In very dilute ammonium thiocyanate solution, when the amount of adsorbent is sufficient, solvent and solute are adsorbed in equal amounts and the concentration of the solution does not change. With smaller amounts of carbon the adsorption curve passes through a maximum, which is followed by a minimum, and the maximum of adsorption corresponds with the maximum turbidity of the suspension after shaking. The distribution law, with n=1, holds over a wide concentration range for the adsorption of carbon dioxide from aqueous solution by carbon. The tendency of the exponent towards 1 in so many cases leads to the view that adsorption is a modified distribution influenced in velocity and equilibrium

by the solid phase. The factors determining the adsorption exponent are considered to be the structure of the adsorbent surface, and polar properties, degree of solvation, and thermal agitation of the molecules of solute. Saturation of the adsorption layer occurs the more quickly the smaller is the adsorption exponent. The rise of the exponent and fall of the constant with rising temperature are due to the inhibition of the adsorptive force through thermal agitation. The fundamental difference between distribution and adsorption is in the ease of solvation of the solute in the two phases. E. S. HEDGES.

Drop method of measuring surface and boundary tensions. J. TRAUBE (Kolloid-Z., 1930, 53, 300-303).—A reply to Junker (A., 1930, 1109). The paper cited is said to lead to false ideas of the accuracy of the drop method. E. S. HEDGES.

Electrocapillarity. III. Surface tensions of solutions containing two surface-active solutes. J. A. V. BUTLER and C. OCKRENT (J. Physical Chem., 1930, 34, 2841-2859; cf. A., 1930, 1514).-Lang-muir's adsorption theory has been applied to the simultaneous adsorption of two solutes from solution and the surface tension effects have been evaluated. In the absence of interaction between molecules in the surface layer, the lowering of surface tension produced in the presence of a surface-active substance at a concentration  $c_1$  by a second at concentration  $c_2$  is given by the equation  $\Delta \gamma_2 = b_2 \log [1 + c_2/a_2(1 + c_1/a_1)]$ , where the lowering of  $\gamma$  of the first substance alone is given by Szyszkowski's equation  $\Delta \gamma_1 = b_1 \log (1 + c_2) \log (1 + c_2)$  $c_1/a_1$ ). Measurements of the surface tensions at the air interface of aqueous solutions of ethyl and propyl alcohols, and of propyl alcohol and phenol, made by the capillary rise method at 20°, are in good agreement with these equations. Electrocapillarity curves have been derived for solutions of caffeine and phenol in 0.5M-sodium sulphate over wide ranges of concentration and the lowerings of surface tension obtained are in satisfactory agreement with a form of Szyszkowski's equation modified to fit the case of highly active solutes. Similar measurements have been made for mixtures of sodium cinnamate and sodium o-toluate in 0.5M-sodium sulphate. The effect of the o-toluate on the surface tension of solutions of the cinnamate is less than that predicted by theory, and the deviations are ascribed to the effect of the electric charges of the adsorbed cinnamate ions which tend to prevent the adsorption of further ions of the same sign.

L. S. THEOBALD. Surface tension of soap solutions and its relation to the thickness of adsorbed films. R. BULKLEY and F. G. BITNER (Bur. Stand. J. Res., 1930, 5, 951—956).—The sharp minimum which has been observed in the surface tension-time curves of certain soap solutions by earlier workers is shown to be due to the action of the carbon dioxide in the air on the dissolved soap and does not occur when the measurements are made in purified air. A. R. POWELL.

Change of the temperature of maximum density of aqueous solutions and of the surface tension in relation to the concentration. G. TAMMANN and A. ROHMANN (Z. anorg. Chem., 1930, 194, 273-277).—The temperature of maximum density  $T_m$  has been calculated for aqueous solutions of a number of volatile liquids which cause  $T_m$  to vary with concentration according to a parabolic law. Since in all cases the values obtained are smaller than the observed values, the internal pressure of the solution is diminished by the solute, and by assuming that  $T_m$  is influenced to the same extent by a change of internal pressure as by a change of external pressure, the magnitude of the effect has been calculated. At low concentrations the reduction of the internal pressure  $\delta \kappa$  produced by the aliphatic alcohols is proportional to the concentration. Although on account of interfacial adsorption and of the influence of the size and form of the molecules the surface tension of a solution is not proportional to the internal pressure, for capillary-inactive solutes such as sodium chloride the lowering of the surface tension  $\delta\sigma$  is proportional to the fractional molar concentration of the solute and  $\delta\sigma/\delta\kappa$  varies from 13 to 72, whereas for active substances such as propyl alcohol  $\delta\sigma/\delta\kappa$  lies H. F. GILLBE. between 5000 and 70,000.

Adherence of quartz powder in electrolyte mixtures. A. von Buzagh, H. FREUNDLICH, and J. TAMCHYNA (Kolloid-Z., 1930, 53, 294-300).-Parallelisms between the adherence of microscopic quartz particles to a quartz plate in the presence of electrolyte solutions, as determined by the angle of tilt method, and the coagulation of hydrophobic sols are pointed out. In mixtures of electrolytes an antagonism of cations has been observed, especially between lithium chloride and aluminium or magnesium chloride. The effect is smaller when the lithium salt is replaced by salts of sodium or potassium. The order of adding the electrolytes has no influence in this case. The angle of tilt in pure electrolyte solutions containing the same cation varies considerably with the nature of the anion, the anion effect being greater for potassium than for lithium salts. With increasing concentration the increase in the angle of tilt becomes less as the valency of the anion increases. The experiments confirm the view that ion-antagonism, coagulation, and the adherence of particles depend mainly on the oppositely charged ion, and not only on its discharging effect, but also on the alteration in the thickness of the boundary layer. The similarly charged ion has also an influence, which is confined mainly to its effect on the properties of the adsorption layer.

E. S. HEDGES.

Reflexion and duration of sojourn of metal atoms at an oil surface. G. VESZI (Z. physikal. Chem., 1930, B, 11, 211–221).—From observations of the displacement on reflexion of atoms incident normally on the surface of a rapidly flowing stream of oil, it appears that atoms of zinc, cadmium, and bismuth show a period of the order of  $10^{-5}$  to  $10^{-4}$  sec. between incidence and reflexion. In the case of thallium and lead, however, no definite evidence of sojourn on the oil surface was obtained.

R. CUTHILL.

Movement of xylene drops on the surface of an aqueous solution of *n*-propyl alcohol. G. G. KANDILAROV (Kolloid-Z., 1930, 53, 304—306).— When drops of *n*-propyl alcohol are added to water on the surface of which a few drops of xylene have

spread, the xylene collects at the sides of the containing vessel and finally gathers into drops, which execute movements similar to those of camphor particles on a water surface. An explanation in terms of surface tension alterations is given.

E. S. HEDGES.

Structure of thin films formed from solutions of crystallisable and non-crystallisable substances. G. TAMMANN and H. E. VON GRONOW (Z. anorg. Chem., 1930, 194, 268-272).-The question is discussed as to whether substances such as gums, which do not crystallise from aqueous solution, are capable of forming unimolecular layers composed of oriented molecules when the solutions are slowly evaporated, and experiments are described showing the changes which take place when films of sodium oleate and other soap solutions are slowly evaporated. The thickness of a sodium oleate film assumes values which are multiples of  $4.2 \ \mu\mu$ , in agreement with Perrin's value for the thickness of unimolecular films of sodium oleate; for potassium undecoate the films are 25% thinner. By study of the changes which occur as crystallisation takes place it appears that the films are strongly supersaturated liquid layers in which the soap molecules are already partly oriented. The power of orientation is restricted to those molecules which are able, under the conditions of the experiment, to undergo crystallisation.

H. F. GILLBE. Dialysis of solutions of sodium hydrogen carbonate. E. CANALS and J. DAUBIAN-DELISLE (Bull. Soc. Chim. biol., 1930, 12, 1158—1161).—The dialysis of aqueous solutions of sodium hydrogen carbonate of various concentrations through parchment membranes has been investigated. The ions Na<sup>•</sup> and  $CO_3''$  do not pass through the membrane in equivalent amounts except at a concentration of approximately 0.5N; solutions more dilute or more concentrated than this have accordingly an excess of one ion. This inequality has a maximum in 0.25N-solution.

#### F. O. HOWITT.

Stationary states at non-living membranes. J. STRAUB (Chem. Weekblad, 1930, 27, 672-674).-The hypothesis previously stated (A., 1929, 264), viz., that the steady concentration differences at living membranes are maintained by electrical forces resulting from metabolism, has been demonstrated by the maintenance of similar conditions in solutions of electrolytes at cellophane membranes and at porous porcelain surfaces by the action of electrical energy. The term "harmony" is proposed to describe conditions of dynamic equilibrium in which constant differences of mechanical and osmotic pressure, electric potential, and concentration are in harmony with constant velocities of chemical reaction, diffusion, and current intensity. H. F. GILLBE.

Equilibria in osmotic systems in which forces act. I. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 820—826).— A membrane is said to be "inactive" when there are no forces acting in it capable of driving one or more of the substances in some direction or other. Where such forces do occur, as in living membranes, the membrane is said to be "active." A theoretical treatment is given of osmotic systems with an "active" membrane permeable to one substance only. E. S. HEDGES.

Reaction equilibrium in the cation-exchange of permutits. R. W. BELING (Z. Pflanz. Düng., 1930, 18A, 292—308).—The course of ionic exchange in permutit is affected by temperature changes which determine the degree of dissociation of the reacting salt solution and of the permutit, both before and after the exchange of ions. Ionic exchange proceeds to completion when the anion of the reacting solution and the cation displaced from the permutit form an insoluble compound. The mathematical formulæ of Jenny and Nageler (A., 1927, 415) are not supported by experimental results. A. G. POLLARD.

Dependence of base-exchange in permutits on the nature of the anions. E. UNGERER (Z. Pflanz. Düng., 1930, 18A, 342—346).—The exchange of bases between calcium permutit and the chlorides and sulphates of lithium, sodium, potassium, and magnesium is examined. In all cases the displacement of calcium from permutit is greater with the sulphates than with the corresponding chlorides, the divergence increasing with the concentration of the displacing ion. The effect is ascribed to the dehydrating action of the highly hydrated sulphate ion. A. G. POLLARD.

X-Ray study of the dehydration of heulandite. J. WYART (Compt. rend., 1930, 191, 1343-1346).-X-Ray study using copper  $K\alpha$  radiation shows that up to 210° the evolution and absorption of water by heulandite is completely reversible, the water molecules being distributed between the recticular (010) planes aperiodically, and the crystal lattice showing the normal Laue diagrams with a relative contraction in one direction of 2%. Above 210° the diagrams show a complete change corresponding with the production of crystalline planes oriented in various directions, although the capacity to reabsorb water and to revert to the original form is not destroyed so long as the heating has not been too prolonged or at too high a temperature (e.g., 24 hrs. at 350°). The recticular intervals of the planes are 8.88 before and 8.00 A. after dehydration. J. GRANT.

Relation between the change in the refractive index of a solution of varying concentration and the changes of aggregation which the dissolved substance undergoes. M. FRANKEL (Biochem. Z., 1930, 227, 304-318).—The magnitude of the refractive index of a solution is strictly proportional to the concentration of the dissolved substance provided that no change occurs in its state of aggregation. If association takes place the value of the index falls below that which would have corresponded with proportionality : conversely, if dissociation occurs, the index increases. Investigation of the way in which the refractive index of a solution changes with its concentration affords a simple, accurate, and rapid method of discovering the state of aggregation of the dissolved substance or substances. Only a few W. MCCARTNEY. drops of solution are required.

Boric acid problem. W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1930, 34, 2479-2507).-The influence of boric acid on the rotatory power of tartaric acid and that of glycerol or mannitol in the titration of solutions of boric acid are discussed. In neither case does compound formation afford a satisfactory explanation. The phenomena are attributed to solvent effects involving increased dissociation of the boric acid and to an abnormal influence of the boric acid solutions on the optical properties of the hydroxy-compounds. L. S. THEOBALD.

Viscosity of electrolytes. W. E. Jov and J. H. WOLFENDEN (Nature, 1930, 126, 994—995).—The relative viscosities of dilute aqueous solutions of potassium chloride have been determined at 18° in silica and glass viscosimeters of the Washburn-Williams type. In both cases, the viscosities are greater than that of water for concentrations up to 0.025N. The limiting slope predicted by the Dole-Falkenhagen equation (A., 1929, 1389) is tangential to the extrapolated curve drawn through the experimental points. A linear curve is obtained by plotting  $(\phi-1)/c^{\frac{1}{2}}$  against  $c^{\frac{1}{2}}$ . L. S. THEOBALD.

Measurement of polarisation of the Tyndall beam of aqueous suspensions as an aid in determining particle size. T. HATCH and S. P. CHOATE (J. Franklin Inst., 1930, 210, 793-804).-The tedious process of microscopical measurement of individual particles may be supplanted by determination of the degree of polarisation of the Tyndall beam. The relation between the degree of polaris-ation and particle size has been examined for suspensions of silica, granite, and calcite, having particles ranging from 1 to  $50\,\mu$ . The degree of polarisation was found to be a function of the arithmetic mean diameter of the particles. Birefringence is another determining factor, the quantitative effect of which has not been studied. By combining the equation expressing the relation between particle size and strength of Tyndall beam with the mathematical relation between degree of polarisation and particle size, an indirect method of obtaining a complete definition of particle size is given. The values obtained in this manner agree to within about 10% with those obtained by direct measurement.

E. S. HEDGES. Dispersoid synthesis of gold by means of alkaline formaldehyde solutions. II. P. P. von WEIMARN (Kolloid-Z., 1930, 53, 352—370; cf. A., 1929, 1142).—A summary of many years' published work on the preparation of colloidal gold solutions. The subjects discussed are the influence of the purity of all the reagents used, especially the water, the influence of the form and material of the reaction vessel and the method of heating, preparation of sols most suitable for accurate quantitative investigation, structure of the dispersed gold particles, the ammonia test, and causes of the stability of gold sols prepared by the formaldehyde method.

#### E. S. HEDGES.

Rate of formation of gold sols by reduction with dextrose or *d*-galactose. A. L. BERNOULLI, M. SCHENK, and R. PINCZUK (Helv. Chim. Acta, 1930, 13, 1236—1254).—The reduction of chloroauric acid by dextrose or *d*-galactose in aqueous solution at 83° is a unimolecular reaction, the velocity being independent of the concentration of the acid. Galactose

has a much more powerful reducing action than dextrose. R. CUTHILL.

Polyatomic hydroxy-compounds formed during the synthesis of electronegative hydrosols. V. Hydroxy-acids. A. DUMANSKI and A. G. JAKOVLEV (Bull. Soc. chim., 1930, [iv], 47, 1211— 1216, and J. Russ. Phys. Chem. Soc., 1930, 62, 1665— 1670; cf. A., 1930, 1370).—The system 0·1N-ferric chloride–0·1N-sodium hydroxide-sodium salt of acid (0·1N) has been studied, using the Gibbs method of triangular co-ordinates. Diagrams are given showing the regions of stability for positive and negative sols, N-solutions, and regions of precipitation. Increase in the number of hydroxyl groups decreases the peptising efficiency of the acids studied, in the order tartaric>glycollic>malie>citric. The ammonium ion favours peptising action to a greater extent than the sodium ion. J. R. I. HEPBURN.

Benzene dispersions of basic soaps of nickel and iron. B. C. SOYENKOFF (J. Physical Chem., 1930, 34, 2419—2538).—The preparation and properties of dispersions of basic ferric and nickel stearates in benzene are described. Basic ferric stearates are polymerised in benzene, whilst those of nickel form aggregates with the properties of colloids and remain dispersed only when free stearic acid is present. These dispersions of stearates and stearic acid in benzene do not conduct electricity.

L. S. THEOBALD.

Liquid ammonia as a lyophilic dispersion medium. R. TAFT (J. Physical Chem., 1930, 34, 2792—2800).—The dispersibility of more than 100 substances in liquid ammonia has been qualitatively examined. Good dispersion is obtained with dextrin, cellulose acetate, nitro-cotton, dyes of high mol. wt., and a few proteins such as zein, gliadin, nucleic acid, bactopeptone, and proteose peptone. Gums, resins, most proteins, and soaps are not dispersed.

L. S. THEOBALD.

Influence of hydrolysis temperature on some properties of colloidal ferric oxide. III. Vis-cosity and hydration. G. H. Avres and C. H. SORUM (J. Physical Chem., 1930, 34, 2826-2840; this vol., 37).—The viscosities of ferric oxide sols prepared at different temperatures have been determined at 25°+0.02°. Viscosity decreases with a rise in the temperature of preparation. When heated to different temperatures samples of stock sols show viscosity and flocculation values which diminish as the temperature to which they are heated rises. Complete precipitation occurs between 170° and 190°. The addition of alcohol or acctone to the sols lowers the relative viscosity and flocculation value to a similar extent. The results show that hydration is a stability factor in the ferric oxide sols studied and the effects observed can be correlated with corresponding changes in E-potential and dielectric constant. L. S. THEOBALD.

Photometric measurement of concentration and dispersity in colloidal solutions. I. Measurement of light weakening. T. TEORELL (Kolloid-Z., 1930, 53, 322-338).—A study of the diminution of intensity of light as a result of adsorption and scattering has been undertaken with reference

to the thickness of the layer of sol, the concentration, the wave-length of the light, and the particle size. The variation with thickness of the layer is in accordance with Lambert's law between wide limits and the discontinuous variation of the absorption constant with thickness (Soos, A., 1927, 625) has not been confirmed. Beer's law holds for the variation with concentration up to high values, but at higher concentrations the absorption constant per unit of concentration decreases. Rayleigh's law holds only for very highly disperse sols of small extinction; in most cases the wave-length must be raised to a power less than 4. The diminution in intensity of light is greatest at a medium degree of dispersion of the colloid, and the position of the maximum is displaced in the direction of greater particle sizes with increase in wave-length of the light. Beer's law does not hold for hydrophilic colloids, because the degree of hydration varies with the concentration.

E. S. HEDGES. Spectrophotometric investigations of effect of light on nuclear silver sol. A. GALECKI and R. SPYCHALSKI (Kolloid-Z., 1930, 53, 338-352).-The changes taking place in silver sols prepared by the nuclear method when irradiated with ultra-violet light have been investigated by optical, viscosity, and electrical conductivity measurements. The first effect of the radiation is on the aqueous dispersion medium, producing hydrogen peroxide, which undergoes oxidation reactions with the silver particles, particularly when the sol is highly dispersed. The sol then loses its colour, silver ions going into solution, and an increase in conductivity and a decrease in viscosity are observed. On further exposure to ultra-violet light the silver ions are partly reduced, the sol again acquires its colour, and the electrical conductivity diminishes. The colour change involved has been observed quantitatively by a spectrophotometric method, which has established that the reaction is of the first order. The temperature coefficient of the reaction involving decolorisation has a mean value of 1.3. E. S. HEDGES,

Method for following the variation in the number of particles during the evolution of a colloidal solution. Application to blood-serum. A. BOUTARIC (Compt. rend., 1930, 191, 1332-1334).--Rayleigh's expression for the coefficient of absorption (h) of light by a suspension is applied (a) to simple agglomeration of the particles without participation of the suspending medium (the volume of an aggregate of particles being equal to the sum of the volumes of the particles), and (b) to the increase in size of an aggregate of particles by removal of liquid from the medium, the number of particles remaining constant. The law of mixtures is applied to the resulting expression, and it is shown that h may be taken as proportional to the mean volume of the individual particles for suspensions in which these two phenomena occur simultaneously. Since, further, the processes (a) and (b) result in unchanged and increased viscosities  $(\eta)$ , respectively, a comparison of h and  $\eta$ gives an indication of the variation of the number (N) of suspended particles. The method applied to the serum of horse-blood at various temperatures

confirms the conclusions reached by other methods, namely, that N does not change with change in temperature, *i.e.*, that the molecules of serum swell by fixation of water. J. GRANT.

Experiments with precipitated and colloidal manganese dioxide. J. MUKHERJEE, S. R. CHOUD-HURY, and M. R. S. RAO (J. Indian Chem. Soc., 1930, 13, 803-813).—Contrary to the statement of Ghosh and Dhar (A., 1927, 617), a negatively-charged manganese dioxide sol is similar to arsenious sulphide, since, on dilution, it is stabilised against potassium ions and sensitised against barium and aluminium ions; the expected "ionic antagonism" (cf. loc. cit.) is completely absent. Cations are adsorbed to a greater extent than anions; the ratio probably remains constant on dilution. The conclusions of Dhar and others (A., 1927, 305, 617, 827) are criticised. A positively-charged manganese dioxide sol obeys the Schulze-Hardy law and the coagulating concentrations for anions are in the order nitrate>chloride> sulphate. oxalate, phosphate>ferrocyanide. The order for the nitrate and chloride is the reverse of that of Ghosh and Dhar (A., 1927, 305). The ratio of adsorption of barium and chloride ions does not alter with dilution. With copper chloride solutions, only copper ions are adsorbed. The ratio of adsorption of barium and chloride ions by precipitated manganese dioxide (negatively charged) also remains constant. For another specimen of precipitated oxide (also negatively charged) the ratio copper: chloride decreased with diminution in the amount of oxide used; this is also contrary to the results of Dhar and others (loc. cit.). H. BURTON.

Lyophilic colloids. I. Hydration of lyophobic colloids. II. Theory of macro- and micro-syneresis. S. LIEPATOV and L. KOROBOVA (Z. anorg. Chem., 1930, 194, 369-376, 377-382).-I. Although in aqueous solutions of geranin the solute is in a condition of molecular dispersion, gelatinisation takes place on cooling to 0°. Cryoscopic measurements indicate an increase of mol. wt. as the concentration of the solution increases, and although the solute molecule is smaller than, e.g., that of Congo-red, it cannot be dialysed. Measurements of viscosity and of osmotic pressure show that the geranin particles are very considerably hydrated both in the true solutions and in sols prepared by addition of salts or of alcohol to the solutions; the hydration envelope is of multimolecular thickness. The dehydration of lyophilic colloids may be reversible or irreversible. The first is observed when the dehydrating agent acts only on the aqueous envelope and does not alter the composition of the colloidal nucleus; irreversible dehydration, which takes place when, e.g., tannin is added to a geranin sol, involves a change of the chemical nature of the disperse phase. The viscosity of a geranin sol falls rapidly with increase of the tannin concentration, whilst the osmotic pressure falls rapidly to a minimum and thereafter rises slowly.

II. Aqueous geranin sols, prepared in presence of 0.1N-sodium chloride, exhibit complete syneresis even at a concentration of 0.1%. The conductivity of these sols is very small and is independent of the concentration of the associated phase, whereas the

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conductivity of geranin sols in 10-25% alcohol increases with the concentration; thus the associated phase carries a charge, and correspondingly syneresis in these sols takes place to only a slight extent. It appears that in both lyophilic and lyophobic systems stability is a function only of the charge on the particles and is independent of hydration. Charged lyophilic and lyophobic colloids differ only in the velocity of the changes which terminate in syneresis, and the differences of velocity are a result of variations of viscosity and of the mobility of the particles. Experiments with geranin are described which demonstrate the four principal characteristics of syneresis: (1) the attractive force between the particles is equal in all directions, -(2) the velocity of syneresis is governed by the distance between the particles and the magnitude of the force of attraction, (3) the liquid which separates contains molecules of the colloid at a concentration which is independent of the concentration in the gel, (4) the upper limit of the gel concentration at which syneresis can occur is that at which the particles are in contact, i.e., at which the volume of the disperse phase is equal to the total H. F. GILLBE. volume of the system.

Coagulation of hydrophobic sols by electrolyte mixtures. H. FREUNDLICH and J. TAMCHYNA (Kolloid-Z., 1930, 53, 288-294).-No anion antagonism was observed in the coagulation of sols of ferric hydroxide, cupric oxide, and titanium dioxide by mixtures of electrolytes. Antagonism of anions was observed with a sol of arsenious sulphide, positively charged by adsorption of malachite-green, especially between chloride and sulphate ions when the chloride ions were added to the sol first. The ion of similar charge to the colloid also exerts an influence, decreasing in the order K'>Na'>Li', and the antagonism is not observed when the ion with the higher valency is added first. Cation-antagonism has been observed in the coagulation of negatively-charged arsenious sulphide sols, the order of influence of the cations being the reverse of that given above. In this case the anion also has some effect; antagonism is not observed when a cation of higher valency is added first. E. S. HEDGES.

Hofmeister series and hydrogen-ion concentration. E. H. BUCHNER (Rec. trav. chim., 1930, 49, 1150—1160; cf. A., 1927, 825).—The saltingout capacity of the sodium salts of various acids for gelatin sols at 40° has been studied in relation to the  $p_{\rm H}$  of the liquid. The salts fall into two groups, in one of which (univalent anions) the effect increases, whilst in the other (phosphate, citrate, tartrate) it decreases, with increasing acidity. Sulphate occupies an intermediate position and shows only a small variation over a large  $p_{\rm H}$  range. The reversal of the Hofmeister series in acid solution is not general. The results are discussed theoretically. F. L. USHER.

Vapour pressure of gels. E. H. BUCHNER (Compt. rend., 1930, 191, 1323—1324).—Two small glass tubes, one open at both ends and one closed at the top only, were filled with gelatin gel and partly immersed in water for 1 month. The gelatin contents determined by desiccation in a vacuum had then fallen from 21% to  $14\cdot5\%$  for the lower (immersed) portion, and 18% for the upper portions of the contents of both tubes. The fact that the (upper) portion of the gel in the closed tube cannot have lost water vapour is considered to contradict the theory of Bary based on a similar experiment (cf. A., 1930, 858, and following abstract). J. GRANT.

Vapour tension of gels. P. BARY (Compt. rend., 1930, 191, 1325—1326).—Polemical against Buchner (cf. preceding abstract). The author's original experiment (A., 1930, 858) was intended to show that continuous distillation of water does not occur through the gelatin, and not to confirm the reality of the swelling of gels in a saturated vapour. J. GRANT.

Hysteresis in sol-gel transitions. S. N. BANERJI and S. GHOSH (Z. anorg. Chem., 1930, 194, 305-315).-The time required for the complete solidification and re-melting of sols of sodium palmitate and stearate in methyl, ethyl, propyl, and butyl alcohols has been determined as a function of the temperature. The hysteresis H in degrees is defined as the difference between the solidification and melting temperatures for a specified time interval (12 min.). With increase of concentration H passes first through a minimum and then through a maximum; methyl alcohol sols form an exception. Stirring, inoculation with gel, or addition of free alkali or of sodium or potassium chloride causes a diminution of H; electrolytes at low concentration cause peptisation, but at higher concentrations produce coagulation, their efficiency falling in the order Li', Na', K', NH4', which, probably as a result of solubility relationships, is the reverse of that which would be anticipated. Gelatin sols behave in a manner similar to that of the soap sols. The experimental results are shown to be in accordance with the view that in sols of this type there exists an equilibrium between single and complex molecules H. F. GILLBE. and colloidal micelles.

State of biochemical substances in anhydrous solutions. J. LOISELEUR (Compt. rend., 1930, 191, 1391—1392).—Biochemical substances, particularly proteins, dissolve in certain aliphatic acids, either alone or with the addition of compounds such as amino-acids, phenol, aniline, etc., to form true solutions which become colloidal on the addition of water. P. G. MARSHALL.

Properties of biochemical substances, especially proteins, in anhydrous solutions. J. LOISE-LEUR (Compt. rend., 1930, 191, 1477—1479).— Solutions of proteins in aliphatic organic solvents such as formic acid exhibit no specific colloidal properties, are not flocculated by the addition of high concentrations of metallic ions (in the same solvent) or by heat, and are readily nitrated in such media. The specific colloidal properties are restored on simple dilution of the solution with water.

J. W. BAKER.

Action of short-wave irradiation on proteins. I. B. RAJEWSKY. II. Dependence of the behaviour of protein on the intensity of the ultraviolet irradiation. W. GENTNER and K. SCHWERIN (Biochem. Z., 1930, 227, 272–285, 286–303).—I. The effect produced in very dilute aqueous solutions of paraglobulin by exposure to short-wave radiation has been studied by a modification of the method of Nakashima (Strahlenther., 1926, 24), whose observations on the latent period previous to coagulation and on the rhythmical course of this process have been confirmed. With the shorter wave-lengths the extent of the latent period decreases, but otherwise all the short-wave radiations used have the same effect, the sensitivity of the solutions being parallel to the course of the absorption. The behaviour of the protein towards ultra-violet light is fundamentally independent of temperature, but the effect of Röntgen rays is modified so that an increase in the velocity of the reaction takes place.

II. From the results of the ultramicroscopical examination of 0.01% aqueous paraglobulin solutions which had been exposed to ultra-violet radiation curves have been drawn which show a direct relation between the number of the particles and the energy of the incident radiation. An equation which expresses the relation between this effect and the intensity of irradiation is given. W. McCARTNEY.

Swelling of cellulose in perchloric acid. K. ANDRESS and L. REINHARDT (Z. physikal. Chem., 1930, 151, 425-432; cf. A., 1928, 1226).-The absorption of perchloric acid by ramie fibre has been measured at various concentrations of the acid. When the normality exceeds 9.3 an additive compound, 2C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>, HClO<sub>4</sub>, is formed, and on washing out the acid, mercerised fibre remains, whereas with lower concentrations of acid the fibre is recovered unchanged. X-Ray analysis, in agreement with absorption experiments, shows a diagram differing from that of cellulose for acid more concentrated than 9.3N, and a third diagram, obtained with very concentrated acid, is said to be probably due to a perchloric ester. The unit cell of the additive compound has a 16.5, b 10.3, c 10.7 Å., β 93°. F. L. USHER.

Preparation of cellulose membranes containing proteins. J. LOISELEUR and L. VELLUZ (Compt. rend., 1931, **192**, 43–45).—Solutions (10%) of gelatin and cellulose in cold glacial acetic acid are shaken together in the requisite proportions. The membranes are then prepared by desiccation in the usual way, and are transparent for 5% and opalescent for 25% gelatin. For other proteins (casein, ovalbumin, gliadin, serum-proteins, etc.) the solutions are made in warm or cold formic acid. Earlier investigations (this vol., 166) indicate that these "proteocellulosic" membranes are true solid solutions, the structure of which is dependent on the protein/ cellulose ratio. J. GRANT.

Structure of celluloid and the swelling function of gelatinising agents for cellulose nitrate. II. X-Ray diagrams of camphor-celluloid with varying content of camphor. J. R. KATZ, J. C. DERKSEN, C. A. KRAMERS, K. HESS, and C. TROGUS. III. Celluloids containing cyclic ketones other than camphor as gelatinising agents. IV. Acid amides and esters as gelatinising agents. J. R. KATZ, J. C. DERKSEN, K. HESS, and C. TROGUS (Z. physikal. Chem., 1930, 151, 145-162, 163-171, N 172—189; cf. B., 1930, 984).—II. The apparently "amorphous" character of X-ray diagrams of celluloid prepared without camphor is due to the fusion of a group of contiguous crystal interference rings. By the gradual addition of camphor the interference pattern undergoes a radical alteration and a diagram characteristic of a compound (or compounds) of cellulose nitrate with camphor is obtained. The interference rings become split into segments when the celluloid is stretched, indicating a parallel arrangement of fibrous units in the compound as in the original cellulose nitrate. The experiments support the conclusions based on the optical anisotropy of stretched celluloid.

III. An alteration of the X-ray diagram of celluloso nitrate similar to that produced by camphor has been observed with fenchone, menthone, carvone, cyclopentanone, cyclohexanone, and cyclohexanol. It is concluded that compounds are formed with each of these substances.

IV. Both unsymmetrical diphenyldiethylcarbamide and acetethylanilide produce an alteration of the X-ray diagram of celluloid resembling that due to ketones and similarly attributable to compound formation. A large number of esters possess the same property, although here the ability to form compounds appears to depend on the size of the alcoholic constituent. Thus methyl phthalate and isoamyl phosphate combine with cellulose nitrate, whilst isobutyl phthalate and tolyl phosphate do not. It is probable that all good gelatinising agents form compounds, and that combination is effected by the residual valencies of the carbonyl oxygen atom.

F. L. USHER.

Diffusion and distribution in a solvent of graded composition. G. S. HARTLEY (Trans. Faraday Soc., 1931, 27, 10-29) .- The distribution of a molecular solute in a solvent in which the concentration of a second solute varies from point to point has been studied for several types of gradient. Measurements have been made of the movement of a solute (iodine) in two mutually diffusing solvents, using alcohol-carbon disulphide and benzene-carbon tetrachloride as the solvent pairs. The results indicate that the viscosity effect is included in the solubility effect. Measurements of the diffusion of ethyl ether through an aqueous ferric hydroxide sol show that the gradient of activity in the static component is relatively very much greater in the colloid and therefore depends on the size of the molecules. To determine how far the distribution theory is applicable in a ternary molecular solution where one component is diffusing through the system, the behaviour of ammonium oxalate, lithium carbonate, potassium chlorate, and of succinic acid with respect to a concentration gradient of acetone in water, and of acetone with respect to a gradient of sodium chloride in water, has been studied. There is no evidence that the distribution of a solute free to move in a maintained gradient is influenced by other forces than those internal ones which determine solubility and the dynamic effect of the diffusing components. It seems, therefore, that the statistical effect examined theoretically by Chapman (A., 1928, 588) must be automatically included in the solubility effect, and

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that the factors leading to increase of diffusion velocity must also tend to decrease solubility. O. J. WALKER.

Theories of the Soret effect. G. S. HARTLEY (Trans. Faraday Soc., 1931, 27, 1-10).-Various kinetic theories of the Soret effect are reviewed and the error common to them is pointed out. The mechanism of the phenomenon is considered to be too complicated for the kinetic theory to be a useful method of approach. The phenomenon is also incapable of treatment by use of the ordinary thermodynamic functions, for the temperature gradient is characterised by the freedom of both components and the distinction between solvent and solute is a purely arbitrary one. In fact, the common error of the theories discussed is that they attribute to the solvent no other role than that of vehicle or carrier of the solute. Actually, however, the solvent molecules have a tendency to migrate from the warmer to the colder region also, and the Soret effect is the result of a balance between the two tendencies. Eastman's theory (cf. A., 1928, 365) which connects the "homogeneous effect" in electrolytic thermo-couples with the Soret effect in electrolytes is discussed, and the relation between the Soret effect and the homogeneous thermal E.M.F. in electrolytes is derived from more general considerations, thus providing independent support for the conclusions of Eastman's O. J. WALKER. theory.

Spectrometric determinations of the effect of a neutral salt on the dissociation of acetic acid. N. V. SIDGWICK and L. A. WOODWARD (Proc. Roy. Soc., 1930, A, 130, 1-16; cf. Sidgwick, Worboys, and Woodward, this vol., 39).-Using solutions containing N/40,000-methyl-orange, N/500-sodium acetate, and a range of concentrations of acetic acid, determinations have been made of  $c_1$  (the ratio of the acid to the alkaline colour), from which the values of  $[\mathbf{H}_{\text{free}}]$ ,  $[\mathbf{H}_{\text{bound}}]$ , [OAc], [HOAc], and  $K_{\text{HOAc}}$  have been calculated. The mean value of the last-named is  $1.83 \times 10^{-5}$  at 18°, in agreement with the value obtained from conductivity measurements. In the presence of 2N-potassium bromide a mean value of  $1.92 \times 10^{-5}$ is found for the same constant. Using N/40,000methyl-orange and various concentrations of hydrochloric acid, measurements were made by the wedgeshift method and an improved "flicker" photometer to test the Tizard equation for wave-lengths from 4500 to 5625 A. The values of K (the apparent dissociation constant of the indicator acid) calculated from this equation show fair agreement, but point to a higher value than that previously obtained with the simpler apparatus. The optimum wave-length is that showing the greatest difference of absorption between the two forms, and for further measurements the wave-length 5125 Å. was selected. Under these conditions the value of K is found to be  $3.34 \times 10^{-4}$ at 18°, in good agreement with that obtained by Güntelberg and Schiödt (A., 1928, 1093). In the presence of varying concentrations of potassium bromide (0.0916-1.832N) both K and  $K_{HOAC}$  pass through a maximum with increasing salt concentration. The results are discussed from a thermodynamic point of view.

L. L. BIRCUMSHAW.

Formation of complexes of ferric ion and acetate ion in aqueous solution. W. D. TREAD-WELL and W. FISCH (Helv. Chim. Acta, 1930, 13, 1209-1218).-In the potentiometric titration of ferric chloride solution with sodium acetate the potential of the indicator electrode undergoes an abrupt change when the mol. ratio of acetate to chloride is 8:3, corresponding with the reaction  $3Fe^{-} + 2H_2O + 8AcO' \implies [Fe_3(OAc)_6(OH)_2] + 2AcOH;$  the liberation of 2 mols, of acetic acid has been demonstrated by a distribution method. The colour of the mixture is also deepest when the composition corresponds with the above ratio. Acetic acid does not affect the titration, but if a mineral acid is present the acetate reacts with this completely before any complex ion is formed. R. CUTHILL.

Formation of complexes of aliphatic monoand di-carboxylic acids with ferric chloride. II. W. D. TREADWELL and W. FISCH (Helv. Chim. Acta, 1930, 13, 1219—1227).—The formation of the following complex ions in aqueous solution has been detected by potentiometric titration of ferric chloride with the sodium salts of the corresponding organic acids (cf. preceding abstract):  $[Fe_3(HCO_9)_6(OH)_2]$ ,

" ITTON (OD TTOID) AT	THE (THOO) (OTT) T
$[\text{re}_{3}(\text{UICH}_{2}^{\circ}\text{UU}_{2})_{6}(\text{UH})_{2}],$	$[re_3(LUU_2)_6(UH)_2],$
$[\mathrm{Fe}_{3}(\mathrm{PrCO}_{2})_{6}(\mathrm{OH})_{2}]^{*},$	$[Fe(O \cdot CH_2 \cdot CO_2)_3]''',$
$[Fe(CO_2 \cdot CH_2 \cdot CO_2)_2]',$	$[Fe(CO_2 \cdot CH_2 \cdot CO_2)_3]'''$
$[Fe(C_2O_4)_2]', [Fe(C_2O_4)_3]',$	and
$[\operatorname{Fe}_3(\operatorname{CO}_2 \cdot \operatorname{C}_2 \operatorname{H}_4 \cdot \operatorname{CO}_2)_3(\operatorname{OH})_2]^{\bullet}$ .	R. CUTHILL

Electrometric determinations of dissociation of glycine and simple peptides. P. H. MITCHELL and J. P. GREENSTEIN (J. Gen. Physiol., 1930, 14, 255—275).—The apparent acid and basic dissociation constants of glycine and several peptides, measured potentiometrically by hydrolysis and titration methods with and without potassium chloride and potassium sulphate, show that dissociation decreases as the length of the carbon chain between the basic and acidic groups increases. The constants vary with the hydrogen-ion activity and the ionic strength of the solutions, and exhibit deviations from the Debye-Hückel theory. Specific ion effects are suggested as a possible explanation. A. COHEN.

Effect of salts on ionisation of gelatin. K. V. THIMANN (J. Gen. Physiol., 1930, 14, 215—222).— Ionised complex salt formation between gelatin and sodium chloride on the basis of the zwitterion theory is demonstrated by applying the Donnan relationship to previously published data on the system. Ionisation is at a maximum at 0.001*M*-salt concentration. The valency of gelatin in complex positive ion formation is deduced from similar behaviour with calcium and copper chlorides. The bearing of the zwitterion theory on solubility phenomena of proteins in salt solutions is discussed. A. COHEN.

Debye-Hückel theory and its experimental testing. II. H. VAN VELDHUIZEN (Chem. Weekblad, 1930, 27, 681-685; cf. A., 1930, 1372).--Methods available for the experimental investigation of the validity of the expression for the activity coefficient are reviewed, prominence being given to solubility determinations. A survey is given of the results obtained by a number of workers for solutions of various types of salts. H. F. GILLBE. Specific character of the osmotic coefficients of alkali halides. G. KARAGUNIS, A. HAWKINSON, and G. DAMKÖHLER (Z. physikal. Chem., 1930, 151, 433-466).—F. p. of aqueous solutions of the fluorides and chlorides of potassium, rubidium, and cæsium, lithium and sodium fluorides, and sodium iodide have been determined at concentrations between 0.002N and 3N by a differential method using thermoelectric junctions. The largest fluctuation in the f. p., for solutions more dilute than 0.1N, was  $0.0002^{\circ}$ . Concentrations were determined interferometrically. Details of the technique, and tables showing the osmotic coefficient at different concentrations for each of the salts, are given.

F. L. USHER. Thermodynamic action and reaction. W. JAZYNA (JACYNO) (Z. Physik, 1930, 65, 571-573).--From the fact that the energy equation of a reaction is independent of the initial distribution of energy between the reactants it is possible to deduce the law of thermodynamic equilibrium. J. W. SMITH.

Graphical demonstration of a theory of Roozeboom. A. MAZZUCCHELLI (Gazzetta, 1930, 60, 719-721).—Le Chatelier's principle is applied to show that the phase change which takes place in a one-component system in the vicinity of an invariant point is that which is associated with the maximum absorption of heat. F. G. TRYHORN.

Heats of distillation. M. BARTHEL (J. Phys. Radium, 1930, [vii], 1, 411—415).—Theoretical. The equilibrium between binary liquid and vapour mixtures circulating in opposite directions is considered, and an expression is derived for the flow of heat which involves only the initial and final compositions of the vapour. C. W. GIBBY.

Automatic maintenance of solid-liquid equilibrium in a metal. P. A. ANDERSON (Rev. Sci. Instr., 1930, [ii], 1, 764—767).—A method is described for automatically maintaining a bath of zinc in twophase equilibrium by making use of the abrupt increase in specific resistance which accompanies isothermal fusion. Applications of the method and its extension to other metals are indicated.

N. M. BLIGH.

System Li<sub>2</sub>O-SiO<sub>2</sub>. F. C. KRACEK (J. Physical Chem., 1930, 34, 2641-2650).-This system has been investigated by the heating curve and quenching methods. The system contains the three compounds  $Li_4SiO_4$ ,  $Li_2SiO_3$ , and  $Li_2Si_2O_5$ . The orthosilicate decomposes at 1255° before its m. p. is reached; the composition of the liquid phase is  $50.9 \text{ wt.-}\% \text{ SiO}_2$ . The eutectic between the ortho- and meta-silicates corresponds with  $1024\pm1^{\circ}$  and  $55\cdot3\pm0\cdot1$  wt.-% SiO<sub>2</sub>, and that between tridymite and the disilicate with  $1028\pm$  $0.5^{\circ}$  and  $82.2\pm0.1$  wt.-% SiO<sub>2</sub>. The m. p. of the metasilicate is  $1201\pm1^{\circ}$ , and its liquidus curve meets the incongruent m. p. of the disilicate at  $1033^{\circ}$  and  $80.1 \text{ wt.-}\% \text{ SiO}_2$ . The composition of the liquid at the tridymite-cristobalite inversion at  $1470\pm10^{\circ}$  is 91.0 wt.-% SiO<sub>2</sub>. The author's results are incorporated with those of others in a complete phase diagram for the system. The optical properties of the lithium silicates (by H. E. MERWIN) are as follow : disilicate, apparently orthorhombic with three cleavages at 90°,

one micaceous and two perfect; optical character positive with  $2V 50^{\circ}$ — $60^{\circ}$ ;  $\alpha 1.547$ ,  $\beta 1.550$ ,  $\gamma 1.558$ : metasilicate, uniaxial apparently with  $\omega 1.591$  and  $\varepsilon 1.611$ ; orthosilicate, rounded grains with two lamellar twinnings oblique to extinction directions,  $\alpha 1.602$ ,  $\gamma 1.610$ , but the optical character and  $\beta$  could not be determined. L. S. THEOBALD.

Fusion diagram of the systems  $HgBr_2-HgSO_4$ and  $HgCl_2-HgSO_4$ . M. PAIĆ (Compt. rend., 1930, 191, 1337—1339; cf. this vol., 50).—The system  $HgBr_2-HgSO_4$  shows a cutectic at 236° which corresponds with less than 1 mol.-% of the latter, the exact concentration being outside the limits of accuracy of the method. Above this concentration the curve mounts rapidly to 506° for 30 mol.-%. The X-ray diagram shows no evidence of combination. The system  $HgCl_2-HgSO_4$  shows a cutectic at 240°, the sulphate being less miscible with the chloride than with the bromide. For 10 mol.-% of mercuric sulphate the m. p. is 512°, and there is no evidence of combination. J. GRANT.

Equilibrium  $FeS_{,} \Longrightarrow FeS + S$ . F. DE RUDDER (Bull. Soc. chim., 1930, [iv], 47, 1225-1254).-An experimental investigation of the thermal decomposition of pyrites shows that there is no intermediate stage corresponding with the formation of compounds of the type  $Fe_n S_{n+1}$  as suggested by earlier workers. Such substances must be regarded as crystalline forms of ill-defined mixtures of the disulphide, ferrous sulphide, and sulphur. The whole of the arsenic present in natural pyrites is expelled as sulphide at the beginning of the decomposition, and the hygroscopic water is evolved as sulphur dioxide and hydrogen sulphide. The reversibility of the reaction has been shown directly by experiment. According to the thermal method employed in studying the dissociation, a sharp break occurs in the timetemperature curve with rising temperature, which corresponds with the point of decomposition at the particular pressure employed. Following this method the dissociation curve has been constructed for pressures from 9 to 768 mm.; the corresponding temperatures are 600° and 689°. The heat of dissociation at atmospheric pressure is calculated as 18.513 g.-cal. The bearing of these results on the industrial roasting of pyrites is discussed, and it is shown that ferrous sulphide is an intermediate product J. R. I. HEPBURN. in this process also.

Affinity of metals for sulphur. I. Thermal equilibria between hydrogen and the sulphides of iron, tin, cadmium, bismuth, and antimony. E. V. BRITZKE and A. F. KAPUSTINSKI [with L. G. TSCHENZOVA and R. A. NEISCHUL] (Z. anorg. Chem., 1930, 194, 323—350).—The thermal equilibria have been determined at temperatures between 400° and 1000°, and the following data are recorded : affinity (g.-cal.) of sulphur for cadmium 65,380, tin 60,420, iron 58,220, antimony 57,860, bismuth 56,240; heat of formation (g.-cal.) from metal and diatomic sulphur, and heat of dissociation (kg.-cal. per g.-mol.) of CdS 69,140, 19·80, SnS 70,520, 20·51, FeS 65,460, 17·98, Sb<sub>2</sub>S<sub>3</sub> 57,860, 42·50 (black), and of Bi<sub>2</sub>S<sub>3</sub> 74,360, 67·20, respectively; normal potential (volts) of

Sb"+0.1, Bi""+0.2, Fe"-0.43, Sn"-0.10, and of Cd"-0.40. H. F. GILBE.

Carbides of high m. p. and the problem of the fusion of carbon. C. AGTE and H. ALTERTHUM (Z. tech. Physik, 1930, 11, 182—191; Chem. Zentr., 1930, ii, 700).—The following m. p. (° Abs.) have been determined : ZrC 3805°, NbC 3770°, Mo<sub>2</sub>C 2960°, MoC 2965°, HfC 4160°, TaC 4150°, W<sub>2</sub>C 3130°, WC 3140° Abs. The pairs  $W_2$ C-TaC and  $W_2$ C-NbC exhibit continuous mixed crystal formation;  $W_2$ C-ZrC does not. The systems ZrC-TaC and HfC-TaC exhibit m. p. maxima at the ratio 4TaC : 1Zr(Hf)C, these maxima being 4205° Abs. and 4215° Abs., respectively. Indications of superficial fusion of graphite were obtained. A. A. ELDRIDGE.

Iron-iron carbide-oxygen equilibrium. P. PINGAULT (Compt. rend., 1931, 192, 45-47).—The equilibrium curve for the reaction  $CO_2 + Fe_3C \Longrightarrow$ 3Fe+2CO has been determined at atmospheric pressure both by carburation and decarburation, and concordant results have been obtained. The curve cuts those for the reactions  $CO_2+C \rightleftharpoons 2CO$  and  $CO_2+Fe \rightleftharpoons FeO+CO$  at 740° and 700°, corresponding with concentrations of 28 and 42% CO2, respectively. The resulting diagrams provide an interpretation of carburising comentation (temperature above 740° and 0-28%  $CO_2$  in the gas phase), oxidising cementation (740-700° and 28-42% CO2), and degraphitisation of castings containing both graphite and cementite (oxidation of carbon without decomposition of iron carbide). The calculated heat of reaction for the first equilibrium at 700-1000° is -14.5 g.-cal., whence that of the reaction  $3Fe+C=Fe_2C$  is -27.5 g.-cal.

#### J. GRANT.

Dissociation pressure of anhydrous uranyl nitrate and of anhydrous thorium nitrate. P. MISCIATTELLI (Gazzetta, 1930, 60, 883–885).—The pressures corresponding with  $2UO_2(NO_3)_2 = 2UO_3 +$  $4NO_2+O_2$  and  $Th(NO_3)_4 = ThO_2+4NO_2+O_2$  have been determined by the dynamic method of Centnerszwer and Krustinson (A., 1927, 21) between 87° and 161°. The results indicate that basic salts are not formed and that only two solid phases are present, viz., anhydrous nitrate and oxide. From the data the heats of dissociation 39,442 and 81,828 g.-cal. are derived for the uranyl and thorium salts, respectively. O. J. WALKER.

Ternary system  $Na_2SiO_3$ -Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. N. L. BOWEN, J. E. SCHAIRER, and H. W. V. WILLEMS (Amer. J. Sci., 1930, [v], 20, 405-455; cf. A., 1930, 36).—Equilibria in the system  $Na_2SiO_3$ -Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> have been determined by microscopic examination of mixtures quenched from definite temperatures, and the results are expressed graphically. No binary compounds are formed between hæmatite and silica, and the two compounds are almost completely immiscible in the fused state; ferric oxide has probably a higher m. p. than silica. Two ternary compounds exist within the equilibrium triangle, viz., acmite, m. p. 990° (incongruent), and a *compound*,

 $5Na_{2}O_{7}Fe_{2}O_{3},8SiO_{2}$ , which forms optically positive hexagonal prisms having  $n_{a}$  1.609 and m. p. (congruent) 838°; a third ternary compound,  $8Na_{2}O_{7}4Fe_{2}O_{3},5SiO_{2}$ , lying outside the equilibrium

triangle, forms rounded grains having  $n_{\beta}$  1.96, m. p. 1091° (congruent). As in all systems containing silica which have so far been investigated, the lowest eutectic (760°) lies at a high silica content (above 72%), and silica is one of the components of the mixture. The geological significance of the results is discussed. Since the felspars normally associated with acmite in rocks enter only into the liquid phase, acmite can be formed only at temperatures below 990°. The view that the presence of volatile constituents is necessary for the formation of quartz cannot be maintained. The course of crystallisation of mixtures rich in acmite involves an initial separation of hæmatite, followed by its reabsorption by the liquid and ultimate redeposition; alternative courses of crystallisation from one liquid phase are possible as a result of this phenomenon. H. F. GILLBE.

Purification of disodium phosphate. M. LEMARCHANDS and C. TRANCHAT (Compt. rend., 1931, 192, 50-51).—The equilibrium constants for the reaction  $BaHPO_4 + Na_2SO_4 \implies Na_2HPO_4 + BaSO_4$  are  $8\cdot36$  (100°) and 100 (18°). The heat of reaction is thus found to be 6528 g.-cal. (calc. 6200 g.-cals). Since the use at 18° of a saturated solution of disodium phosphate (47.8%) yields a mixture containing 0.478% of sodium sulphate, the reaction may be used for the purification of the former salt prepared commercially from sodium carbonate and natural tricaleium phosphate. J. GRANT.

Stability of complex cobalt and chromium salts as precipitates. II. A. BENRATH and H. STEINRATH. III. A. BENRATH and H. PITZLER (Z. anorg. Chem., 1930, 194, 351-357, 358-368; cf. A., 1929, 256).-II. The nature of the solid phase which is stable in contact with solution has been determined by shaking a number of complex chromium salts with solutions of ammonia, ethylenediamine, and nitric, hydrochloric, and hydrobromic acids. The salts investigated include bromoaquo-, chloroaquo-, hydroxyaquo-, and diaquo-tetramminochromic chlorides and bromides, nitratoaquo- and diaquo-tetramminochromic nitrate, triethylenediamincchromic chloride, 1:2and 1:6-dichlorodiethylenediaminechromic chloride, and oxalatotetramminochromic nitrate.

III. The system  $[Co(NH_3)_5Cl]Cl_2 + 2HBr \Longrightarrow$ [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Br+2HCl has been investigated at 25° and constant pressure and the phase model has been constructed. Determinations of the equilibria between various hexa-, penta-, tetra-, and tri-amminocobaltic salts and aqueous solutions of ammonia show that the solubility of the complexes in all cases increases with increase of the ammonia concentration. For all except the hexamino-complex the solubility curve rises to a maximum and then falls rapidly, and since the curves do not intersect and lie above that of the hexammine, the latter is the only stable compound, the others being metastable forms. In presence of dilute acids the stability of the complexes increases with increase of the number of ammonia groups in the molecule, whilst the only stable phase is the simple cobalt salt. H. GILLBE.

Heat of formation of water. F. D. ROSSINI (Proc. Nat. Acad. Sci., 1930, 16, 694-699).—This has been redetermined by finding the amount of electrical
energy required to produce the same rise in temperature of the calorimeter as that produced in the formation of a measured mass of water from combustion of oxygen and hydrogen. Sources of error and their correction are mentioned. The value obtained for the heat of formation of liquid water at  $25^{\circ}$  and a constant pressure of 1 atm. is  $285,890\pm40$ absolute joules. The best values already existing for this quantity are attended by an uncertainty of about  $\pm 240$  absolute joules. W. Good.

Reversible oxidisability of organic substances; thermochemistry of the oxidation of rubrene. C. DUFRAISSE and L. ENDERLIN (Compt. rend., 1930, 191, 1321-1323).—The heats of formation of rubrene, oxyrubrene, isooxyrubrene, and metrubene or rubrene monoxide are -131, -108.4, -50.4, and -92.4 g.-cal./mol., respectively (cf. Moureu, Dufraisse, and others, A., 1928, 594, 628, 1127). The difference between the values for rubrene and oxyrubrene is less than that which would correspond with the normal introduction of two oxygen atoms into an organic molecule, and less than the differences for the two other oxides. There is therefore no essential difference between the reversible oxidation of rubrene and of respiratory pigments (e.g., hæmoglobin), since the oxidation of the former is catalytic in nature and may be carried out through the agency of light (i.e., photochemically) or of other appropriate catalysts. J. GRANT.

Connexion between ionic mobility and rate of diffusion in solid salts. C. WAGNER (Z. physikal. Chem., 1930, B, 11, 139—151).—Theoretical. Equations have been obtained by a thermodynamic method which permit diffusion coefficients in a binary solid solution composed of two salts with a common ion to be calculated from ionic mobilities. The relationships observed by Tubandt (A., 1929, 255) and by von Hevesy (*ibid.*, 638) may be deduced from these equations. The thermodynamic derivation depends on the assumption that the ions migrate independently of each other. R. CUTHILL.

Electrical conductivity of sulphur dioxidewater mixtures between 8 and 22% SO<sub>2</sub> and from 0° to 40°. M. DE K. THOMPSON and N. PROMISEL (Trans. Amer. Electrochem. Soc., 1930, 58, 101-108).—At 20° the conductivity increases continuously from 0.046 to 0.076 mho/cm. over the concentration range specified. At higher concentrations a two-phase system is formed. For a solution of given concentration the conductivity increases with rise of temperature, reaches a maximum, and then decreases again. This maximum occurs at 30-32° for an 8% solution, but moves to lower temperatures with increasing concentration, reaching 20° for a 20% solution. H. J. T. ELLINGHAM.

[Polarity of] alkali alkyls. F. HEIN and H. SOHRAMM (Z. physikal. Chem., 1930, 151, 234-256; cf. A., 1925, ii, 217; 1927, 138).—Lithium ethyl, whilst differing from all other alkali alkyls in not possessing the character of a salt, is definitely polar, with an association factor of about 6 in benzene, as calculated from the f.-p. depression. Addition of zinc ethyl causes first depolymerisation, and afterwards combination to form a solvate which in benzene is present in the form of double molecules (MEt,ZnEt<sub>2</sub>)<sub>2</sub>. Sodium, potassium, and rubidium ethyl behave similarly. The molecular conductivity of the sodium ethyl-zinc ethyl complex in benzene decreases with dilution, as expected. The electrolytic nature of rubidium ethyl is confirmed by a study of its conductivity in zinc ethyl solution. Its "salt" character is more pronounced than that of the other alkali alkyls. F. L. USHER.

Determination of electrolytic resistance by the barretter method. J. SCHIELE and M. WIEN (Ann. Physik, 1930, [v], 7, 624-632).—The method is described. It gives more accurate results than the usual Kohlrausch telephone method with platinised electrodes. A. J. MEE.

Gas electrodes. A. C. KRUEGER and L. KAHLEN-BERG (Trans. Amer. Electrochem. Soc., 1930, 58, 341-383; cf. A., 1928, 1330).--A systematic investigation has been made of the potentials of gasmetal electrodes consisting of the gases hydrogen, oxygen, nitrogen, helium, and argon in conjunction with more than 20 different metals and a few nonmetals such as carbon and silicon in N-solutions of hydrochloric acid, potassium chloride, and potassium hydroxide at the ordinary temperature. Nitrogen, helium, and argon, which are normally regarded as electromotively inactive, are reported to give potentials as characteristic as those of hydrogen or oxygen, and these potentials often vary with the nature of the electrolyte in a manner similar to the latter. All the potentials are greatly dependent on the nature of the metal as well as on the electrolyte, and the effects of these factors are largely specific. Thus, although with a given metal and electrolyte the potentials produced by the gases often become increasingly positive in the sequence hydrogen, argon, nitrogen, helium, oxygen, this order is by no means general, and for a given metal may be changed by using a different electrolyte. There are even cases where oxygen gives a more negative potential than hydrogen in a given electrolyte, e.g., with aluminium, electrolytic iron, or graphite electrodes in N-potassium chloride, and with cadmium, mercury, iridium, or tungsten electrodes in N-hydrochloric acid. The E.M.F. of a hydrogen-oxygen cell set up with platinum electrodes in a given solution is far greater than that of a similar cell set up with electrodes of any other metal. All the results are tabulated in various ways so as to indicate the effects due to gas, metal, and electrolyte, and are H. J. T. ELLINGHAM. discussed at length.

Poisoning of hydrogen electrodes. A. H. W. ATEN and (MISS) M. ZIEREN (Trans. Amer. Electrochem. Soc., 1930, 58, 109—132; cf. A., 1929, 1246).— The effect of oxygen on the potential of a platinumblack or palladium-black hydrogen electrode in a pure sodium hydroxide solution or pure dilute sulphuric acid remains quite small until the partial pressure of oxygen in the gas approaches  $\frac{1}{3}$  atm. With a pure hydrogen electrode of this type addition of arsenious oxide to the electrolyte causes the potential to assume somewhat more positive values (2 mg. per litre makes the potential about 2.3 millivolts more positive), but this effect eventually decreases with time. If, however, a small percentage of oxygen be now admitted with the hydrogen to the poisoned electrode, the potential gradually changes to very positive values (above 800 millivolts more positive with 2% of oxygen) during a period of days. With smooth platinum or palladium electrodes this change occurs much more rapidly, and is even observed in solutions of commercially pure sodium hydroxide or sulphuric acid to which no arsenious oxide has been added. Since preliminary treatment of the solution with platinumblack prevents this action of oxygen, it is concluded that these solutions normally contain traces of some poisoning impurity. This would account for the slightly positive values often given by pure hydrogen electrodes in which smooth platinum plates are used. The effects of varying the proportions of hydrogen and oxygen (0-100%) in the gas supplied to a palladiumblack electrode in pure sulphuric acid and sodium hydroxide solutions and in these solutions with various additions of arsenious oxide are shown by a series of curves. In experiments with smooth electrodes it is shown that appreciable poisoning is produced by a quantity of arsenious oxide much less than would be necessary to form a unimolecular layer on the electrode, but the fact that anodic treatment restores the true hydrogen potential indicates that poisoning is due to the deposition of a substance on the electrode surface. The theoretical interpretation of the results is discussed, but a satisfactory quantitative explanation is not yet forthcoming. H. J. T. ELLINGHAM.

Electrode potentials in air-free electrolyte. A. L. MCAULAY, G. L. WHITE, and E. C. R. SPOONER (Nature, 1930, 126, 914—915; cf. A., 1930, 423).— A summary of the authors' work on the potential assumed by a metal immersed in a salt solution with no sensible concentration of its own ions. When this is the case and when the electrode is not covered by an oxide film, its potential is determined by  $p_{\rm H}$  if the hydrogen overvoltage is positive to the deposition potential which it would have in a solution about 0.001N with respect to its own ions. When this is not the case, the potential is controlled by the anion concentration probably arising from a film of electrolyte in contact with the metal with a concentration of the electrode metallic ions of the order 0.0001N.

### L. S. THEOBALD.

Electrode properties of stainless steel. E. NEWBERY (Trans. Amer. Electrochem. Soc., 1930, 58, 335-340).—The single potential of a sample of stainless steel (containing about 13% of chromium) in N-ferrous sulpliate solution is much more positive than that of pure iron in the same solution and approximates to the potential exhibited by a sample of chromium in this electrolyte. On the other hand, the hydrogen overpotential of the stainless steel in N-sulphuric acid, measured by the commutator method, is practically identical with that of pure iron under the same conditions and is much less than that of chromium. The use of stainless steel as cathode in the controlled electrolytic reduction of certain organic substances is suggested and preliminary experiments on these lines are referred to. The oxygen overpotential of stainless steel at low current densities in N-sulpburic acid is comparable with that of chromium, but when the current density exceeds a certain value the overpotential increases suddenly to a value which is intermediate between those of iron and chromium. Partial dissolution of the stainless steel with formation of chromic acid then takes place. A tentative explanation of the phenomena is advanced.

### H. J. T. ELLINGHAM.

Electrochemistry of aluminium and aluminium amalgams. H. GERDING (Z. physikal. Chem., 1930, 151, 190-218).—The potentials of aluminium amalgams of varying composition have been determined in a solution of aluminium acetylacetonate in acetylacetone. There is no indication of compound formation. The mutual solubility of the metals is very small, and a two-phase system with constant potential extends from 0.8 to 99.97 at.-% Hg. A P.D. of 0.130 volt exists between the two-phase system and "theoretical" (active) aluminium, which is due to a difference of free energy between the pure metal and the amalgam and is independent of the liquid. It follows that the potential of active aluminium in a 1N-solution of aluminium chloride in water is -1.47 volt (H=0). Pure aluminium does not dissolve in the liquid used, but when the content of mercury exceeds 0.2% aluminium acetylacetonate is formed with evolution of hydrogen, which latter causes the potential to become more negative. Oxygen has the opposite effect. The behaviour of aluminium and its amalgams in acetylacetone cannot be explained by assuming the existence of a film of oxide, but is ascribed to a real difference in the metal. F. L. USHER.

Potential of the iridi-irido-chloride electrode. H. TERREY and H. C. BAKER (J.C.S., 1930, 2583— 2586).—Potentiometric measurements with the cell Hg|Hg<sub>2</sub>Cl<sub>2</sub> + N-NaCl|N-NaCl + Na<sub>2</sub>IrCl<sub>6</sub> + Na<sub>3</sub>IrCl<sub>6</sub>|Ir show that the *E.M.F.* of the concentration cell at 25° is given  $E_0 = (RT/F) \log (i/o)$ , where *i* and *o* are the concentrations of the iridi- and irido-salts, and that the electrode reaction is  $IrCl_6''+e \longrightarrow IrCl_6'''$ ; for values of *i/o* between 2·166 and 8·900 and an iridised iridium electrode  $E_0$  lies between 0·976 and 0·983, and for values of *i/o* from 0·105 to 11·06 and an iridised glass electrode between 0·968 and 0·970. The *E.M.F.* is a linear function of the temperature, and has a temperature coefficient of about -0.001 volt per 1°; the calculated heat effect of the cell reaction is 25,400—26,100 g.-cal., and regarding the reaction as Hg+Cl'+IrCl<sub>6</sub>''  $\longrightarrow$  HgCl+IrCl<sub>6</sub>''' the heat of formation of the iridi- from the irido-chloride (Q') is 5600 g.-cal./mol. H. F. GILLBE.

Potentials of unstable oxidation-reduction systems. L. F. FIESER (J. Amer. Chem. Soc., 1930, 52, 4915—4940).—A "discontinuous titration" method is used which involves the addition of varying amounts of potassium molybdicyanide (0.03M-solution) to a fixed amount of a well-buffered reductant (0.0003M) whereby varying quantities of the oxidant become available. The ratio oxidant : reductant is fixed momentarily in each case and the potentials of the solutions are determined after varying intervals. The initial potentials are fixed by extrapolation of the first straight portion of the potential-time curves. A composite titration curve is constructed from the results and the normal oxidation-reduction potentials are calculated from it. The method is applicable to systems which are so unstable that the half-life period for the decomposition of the oxidant is 0.1-0.5 min. The variation of potential with the hydrogen-ion concentration over the range of  $p_{11}$  1--8 was determined for the systems *p*-benzylaminophenol-*N*-benzyl-*p*benzoquinoneimine, *p*-methylaminophenol-*N*-benzyl-*p*benzoquinoneimine, and *p*-aminophenol-*p*-benzoquinoneimine. The following systems were also studied : *p* - phenylenediamine-*p* - benzoquinonediimine, methyl - *p* - phenylenediamine-*N* - methyl - *p*benzoquinonedi-imine, 4:4'-dihydroxystilbene-stilbene-4:4'-quinone, and 4:4'-dihydroxydiphenyl-diphenoquinone.

Application of the method to the following substances was unsuccessful owing to the instability of the oxidised solutions : *o*-aminophenol, *o*-phenylenediamine, pyrocatechol, nitroquinol, and 2 : 6-dihydroxynaphthalene. H. BURTON.

Indirect method of studying the oxidationreduction potentials of unstable systems, including those from phenols and amines. L. F. FIESER (J. Amer. Chem. Soc., 1930, 52, 5204-5241). —A method is described for determining the potential at which the velocity of the reaction between an oxidisable substance (e.g.,  $\alpha$ -naphthol) and an oxidising system (e.g., ferricyanide-ferrocyanide) reaches a small, limiting value. This is called the "critical oxidation potential." For the two examples quoted, oxidation occurs only when the potential exceeds 0.790-0.800 volt. A series of ferricyanide-ferrocyanide solutions is prepared in which the total concentration of the cyanides is the same, whilst the ratio of oxidant to reductant is varied. Following the determination of the potentials of these solutions,  $\alpha$ -naphthol (equivalent to the ferricyanide) is added, and the potential changes are noted during 5 min.; the solutions are usually made up in 37% alcohol containing neutral buffer salts (phosphates). The percentage oxidation of the naphthol can be calculated from the results and is found to be a linear function of the initial potential of the solution. Extrapolation of the percentage oxidation-potential curve gives the "critical oxidation potential." The "critical oxidation potentials" of 71 substances (mainly phenols and amines) are recorded, and their relationship to the normal oxidation-reduction potentials and the structural formulæ of the reducing agents are discussed. H. BURTON.

Reduction cells containing alkali chlorites. G. R. LEVI and D. GHIRON (Atti R. Accad. Lincei, 1930, [vi], 11, 1104—1107).—The E.M.F. of cells in which the reduction of potassium chlorite is effected by various substances have been measured at 20° in cells of the type Pt+ $|0\cdot1N$ -KClO<sub>2</sub>|X|Pt<sup>-</sup>, in which X represents the reducing solution. The observed E.M.F. in volts are :  $0\cdot2M$ -K<sub>2</sub>S, 1·119;  $0\cdot1N$ -KNO<sub>2</sub>,  $0\cdot3905$ ;  $0\cdot025M$ -K<sub>4</sub>Fe(CN)<sub>6</sub>,  $0\cdot476$ ;  $0\cdot1M$ -Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>,  $0\cdot437$ ;  $0\cdot1N$ -KI,  $0\cdot285$ ;  $0\cdot1M$ -N<sub>2</sub>H<sub>4</sub>,H<sub>2</sub>SO<sub>4</sub>,  $0\cdot370$ ;  $0\cdot1N$ -(NH<sub>2</sub>·OH)<sub>2</sub>,H<sub>2</sub>SO<sub>4</sub>,  $0\cdot350$ . The E.M.F. of the cell Pt<sup>+</sup> $|0\cdot1N$ -KClO<sub>2</sub> $|0\cdot1N$ -KCl+Hg<sub>2</sub>Cl<sub>2</sub>|Hg<sup>-</sup> is  $0\cdot363$ volt. O. J. WALKER.

Variations of the E.M.F. during the formation of alloys in the wet way. E. PACE (Gazzetta, 1930, **60**, 811-818).—Measurements have been made of the E.M.F. of voltaic couples of the type A|solution of A<sup>+</sup>|B during the whole process of dissolution of the more electropositive metal A and the deposition on the metal B to form an alloy of the type  $A_nB$ . The following systems have been investigated : coppertin, copper-antimony, antimony-tin, gold-cadmium, silver-cadmium, gold-tin, and silver-tin. Values of the E.M.F. at the ordinary temperature and at 100° are given with closed and open circuit.

O. J. WALKER.

High-voltage anodic layer on aluminium. J. E. LILIENFELD, L. W. APPLETON, and W. M. SMITH (Trans. Amer. Electrochem. Soc., 1930, 58, 285-331). -Anode layers were formed on aluminium sheets by electrolysis in borax-boric acid solutions of various concentrations at various current densities and temperatures, the current being kept constant and the voltage allowed to rise until sparking commenced, at which stage the voltage was kept constant and the current allowed to fall. From calculations based on the estimated thickness of the layer and from direct observation of the amount of oxygen gas evolved, it is concluded that the oxygen which enters into the formation of the layer is only a very small fraction of the total amount released by the current. The behaviour of the formed plates, set up in the electrolyte, as condensers was examined particularly with regard to the variation of leakage current. The condenser was charged to 380 volts and, when the leakage current had decreased to a steady value, it was completely or partly discharged. After being kept idle in this condition for a time it was re-charged to the original voltage and the leakage current redetermined. From these data the extent of the deterioration which had occurred during idleness under various conditions was estimated. The results are not in harmony with the views that deterioration is due to dissolution of aluminium oxide from the layer or to escape of oxygen imprisoned in the layer, but can be explained on the assumption that changes occur in the spatial orientation of particles of oxide in the layer without any loss of material from the layer. The layer behaves as a dielectric containing a large number of polar molecules which are oriented by the electric field during formation, but tend to become disorganised by thermal motion during idle periods. Conduction through the layer is believed to occur by the passage of electrons from molecule to molecule, the resistance depending on the state of organisation. H. J. T. ELLINGHAM.

Passivity of chromium. I. E. MÜLLER and O. ESSIN (Z. Elektrochem., 1930, 36, 963—972).— The potential of chromium, deposited electrolytically on copper, in contact with solutions of different acids has been determined as a function of time and of temperature. The results indicate that at 0° the metal is passive towards N-hydrofluoric, -hydrochloric, -hydrobromic, -sulphuric, -perchloric, -phosphoric, and -nitric acids, but that on warming to a temperature which is characteristic for each acid and increases with the diameter of the anion, the metal becomes active towards the first four acids; in phosphoric, perchloric, and nitric acids it remains inactive at 100°. Treatment such as immersion in chromic acid solution or heating in a vacuum, which tends to remove hydrogen from the chromium film, reduces its (negative) potential; in contact with non-activating acids the potential increases with time to values greater than the reversible hydrogen potential without the metal losing its passivity. Cathodic polarisation in perchloric and nitric acids causes sudden activation when a certain potential is attained. The activating influence of anions follows the same order as their power of producing cathodic reduction of chromic acid; the influence of hydrochloric acid is hindered by the presence of other acids. It is suggested that the passive metal is covered with a superficial oriented film of oxide molecules through which the anions must penetrate in order to produce activation.

H. F. GILLBE.

Colloidal diaphragm for the electrolysis of water. G. F. JAUBERT (Compt. rend., 1930, 191, 1447-1449).-If a 25% solution of potassium hydroxide holding in colloidal suspension a hydrogel, e.g., calcium magnesium silicate (colloidal asbestos) or ferric hydroxide, is electrolysed with a nickel anode and an iron cathode, a uniform layer of the colloidal substance, several millimetres thick, is deposited on the anode in the course of some hours or days, according to the fineness of the suspension. If a sheet of iron wire gauze is placed between the electrodes a similar deposit accumulates thereon, and this after about 50 hrs. is absolutely impermeable to the free gases. A diaphragm thus prepared is very cheap, possesses a very low resistance, and enables hydrogen of 100% and oxygen of 99.5% (0.5% hydrogen) purity to be readily prepared. C. A. SILBERRAD.

Thermal transformation of para-hydrogen. A. FARKAS (Z. physikal. Chem., 1930, B, 10, 419-433). -The conversion of para-hydrogen into ortho-hydrogen when heated in a quartz vessel is a homogeneous reaction, although traces of such impurities as dust or metals exert a powerful catalytic effect. Measurements of the velocity, made chiefly at 600-750° and under pressures of 50-400 mm., show the reaction to be of the order 1.5, which is taken as pointing to the mechanism  $H^{e}_{+}+H = H + H^{o}_{+}$ , the hydrogen atom being of thermal origin. If this reaction is regarded as the exchange of a bound hydrogen atom for a free atom, leading to the formation of para- and orthomolecules in the equilibrium ratio 1:3, it does not contravene the principles of quantum mechanics. The effect of rise in temperature on the velocity is due far more to increase in the number of free atoms than to increase in the proportion of effective collisions. The Arrhenius equation gives 4200 g.-cal. per g.-mol. for the heat of activation, whereas the value of 11,000 g.-cal. is deduced from the absolute velocity.

## R. CUTHILL.

Ignition of electrolytic gas by electric sparks. A. KOVALSKY (Z. physikal. Chem., 1930, B, 11, 56— 58; cf. A., 1930, 299).—The limiting pressures at which electrolytic gas can be ignited by a single spark have been determined in relation to the "strength" of the spark, the latter being measured by the capacity of a condenser charged to a constant potential, from which the spark was obtained. The limiting pressure decreases with increasing strength of spark down to 17 mm. for 2 microfarads. The limiting pressure of ignition by a spark at 450° coincides with the lower limit for propagation of ignition in the mixture. F. L. USHER.

Thermal decomposition of nitrous oxide between 1 and 10 atm. N. NAGASAKO and M. VOLMER (Z. physikal. Chem., 1930, B, 10, 414—418; cf. A., 1930, 1255; Hinshelwood, *ibid.*, 1528).—The above reaction has been measured at 830—940° Abs., and found to be unimolecular. The heat of activation, 53,000 g.-cal. per g.-mol., is practically independent of the pressure. R. CUTHILL.

Atomic reactions possessing inertia. H. von HARTEL and M. PÓLÁNYI (Z. physikal. Chem., 1930, B, 11, 97-138).-In seeking to account for the apparent absence of inertia in many of the reactions in which free atoms or free radicals participate, it must be noticed that a reaction with a heat of activation below about 15,000 g.-cal. will occur so rapidly as to seem instantaneous. London's theory of chemical reactions (A., 1929, 1397), indeed, indicates that the upper limit of the heat of activation of reactions involving free atoms or radicals corresponds approximately with this figure. The reaction of methyl iodide with sodium vapour at 240° is free from inertia, but the reactions with the bromide, chloride, and fluoride possess inertia, the magnitude of which increases in this order. From the ratio of the number of effective collisions to the total number of collisions it is calculated that in the reaction with methyl bromide the heat of activation is 3200 g.-cal., and in that with the chloride S800 g.-cal.; similar values are also deduced from the temperature coefficient of the reaction velocity. With the fluoride, the heat of activation must exceed 25,000 g.-cal., and this is the only reaction which would occur at a measurable speed at the ordinary temperature. The order of the reactivities of the halides is what would be expected from London's theory. The reaction of sodium vapour with cyanogen exhibits considerable inertia, which appears, however, to be due, not to the smallness of the heat of activation, but to some steric factor, probably to the shielding of the sensitive region of the C·C linking by the nitrogen atoms. This effect does not vary with the temperature. In the reaction of sodium vapour with cyanogen chloride the proportion of sodium chloride to sodium cyanide formed depends on the temperature, which may be explained by supposing that the inertia of the reaction Na+CNCl=NaCl+CN depends on a low heat of activation and therefore varies with the temperature, whereas the inertia of the reaction Na+CNCl= NaCN+Cl is independent of the temperature. The reactions of a variety of other organic halogen compounds with sodium have been studied. From kinetical considerations and examination of the energy changes involved it may be demonstrated that in all such reactions the primary result of the formation of a molecule of sodium halide is the liberation of the free radical previously combined with the halogen. When sodium reacts with a methyl halide in presence of hydrogen, methane is formed by the reaction  $CH_3+H_2=CH_4+H$ , the heat of activation of which is about 8000 g.-cal. From this figure it is deduced that the heat of the reaction  $CH_3+H=CH_4$  is 98— 110 kg.-cal. R. CUTHILL.

Decomposition of ethylamine. Unimolecular reaction. H. A. TAYLOR (J. Physical Chem., 1930, 34, 2761—2770).—The decomposition of ethylamine has been investigated over the range  $500-540^{\circ}$  and at pressures between 50 and 400 mm. The decomposition is a homogeneous, unimolecular reaction with an energy of activation of 43,400 g.-cal.; E/RT is 28.9. The addition of hydrogen, nitrogen, or ammonia has no effect. L. S. THEOBALD.

Effect of neutral salts on the velocity of reaction of ions in low total ionic concentration. A. PARTS (Festschr. Jub. Ver. Estn. Chem., 1929, 44—50; Chem. Zentr., 1930, ii, 687).—When potassium persulphate (0.00625M) and iodide (0.0250M) react in presence of neutral salt (0.0500N) the velocity coefficient (0.317) attains values as follows : potassium chloride, 0.459, sodium chloride 0.374, ammonium chloride 0.417, barium chloride 0.682, calcium chloride 0.485. Values for the reaction (CHBr·CO<sub>2</sub>)<sub>2</sub>''+OH' (each 0.01813M)— $\rightarrow$ (CO<sub>2</sub>·CH:CBr·CO<sub>2</sub>)''+Br'+H<sub>2</sub>O are (1.70), sodium nitrate 2.09, lithium nitrate 2.33, barium chloride 4.83, calcium nitrate 9.61. The results are interpreted by means of Debye and Hückel's theory. A. A. ELDRIDGE.

Hydrolysis of acetamide. T. W. J. TAYLOR (J.C.S., 1930, 2741-2749).-The velocity coefficients K of the hydrolysis of acetamide by 3N-, 4N-, and 5N-hydrochloric acid and 4N- and 5N-hydrobromic and sulphuric acids at 25°, and by 4N- and 5N-hydrochloric acid at 40° and 41°, respectively, have been determined and the influence of the alkali metal halides has been investigated. With increase of the concentration of hydrochloric or hydrobromic acid up to about 3N, K increases to a maximum and thereafter diminishes, but with sulphuric acid K is smaller in 4N than in 5N solution. It appears that at the higher concentrations undissociated molecules of hydrochloric and hydrobromic acids form with the amide complexes which are not capable of undergoing hydrolysis; this view is supported by calculations of the uncombined fraction of the amide based on the assumption that the complexes formed are of the type 2NH,Ac,HCl. In 4N-hydrochloric acid solution N-sodium or -potassium chloride accelerates the hydrolysis, but lithium chloride is without effect, whilst in hydrobromic acid solution potassium bromide acts as a positive catalyst, sodium bromide is apparently without effect, and lithium bromide retards the reaction. The salt effect is of the same nature if the hydrolysis be carried out in alkaline (N-sodium or -potassium hydroxide) solution. On account of the specific nature of the salt effect it is suggested that acetamide is able to form with certain salts complexes which are stable in solution.

H. F. GILLBE. Reactions of zero order. A. PARTS (Festchr. Jub. Ver. Estn. Chem., 1929, 23—30; Chem. Zentr., 1930, ii, 687).—A discussion of the hydration of pinene. A. A. ELDRIDGE.

Velocity of dissolution of oxygen in water. III. S. MIYAMOTO and T. KAYA (Bull. Chem. Soc. Japan, 1930, 5, 321-325; cf. A., 1930, 1379).—The relationship of the rate of oxidation of sodium sulphite in aqueous solution when air is bubbled through it to the radius of the bubbles has been found to conform to the theoretical considerations previously advanced (*ibid.*, 866). R. CUTHILL.

Passivity phenomena with aluminium in still, dilute acids and alkalis. L. W. HAASE (Hausz. V.A.W. Erftw. Aluminium, 1930, 2, 53-60; Chem. Zentr., 1930, ii, 976).—Interaction of aluminium with solutions of acids, bases, and salts in concentration corresponding with natural water leads to the gradual formation, not of passivating films, but of a homogeneous protective layer of aluminium oxide or hydroxide of low water content. A. A. ELDRIDGE.

Influence of the azide ion on the catalysis of [the decomposition of] hydrogen peroxide by colloidal platinum. II. E. OLIVERI-MANDALA (Gazzetta, 1930, 60, 878-82; cf. A., 1930, 170).— The decomposition of hydrogen peroxide by colloidal platinum is also a first-order reaction in presence of azoimide, which acts as a negative catalyst, although there is not a strict proportionality between the values of K and the concentration of the azoimide, which reduces the value of K from 0.0029 to 0.00078. The temperature coefficient of the velocity coefficient for  $10^{\circ}$  is 1.66. O. J. WALKER.

Slow and induced oxidation of potassium oxalate, sodium nitrite, and sodium sulphite by air. S. N. CHAKRAVARTI and N. R. DHAR (J. Physical Chem., 1930, 34, 2749-2760; cf. Palit and Dhar, A., 1926, 822) .- In the presence of cerous hydroxide, potassium oxalate or sodium nitrite is not oxidised by the passage of air through their solutions at the ordinary temperature, but in the presence of ferrous hydroxide or sodium sulphite oxidation occurs. Oxidation increases with an increase in concentration of inductor and acceptor and with the time of passage of the air. In all the above cases a compound of the peroxide type, liberating iodine from acidified potassium iodide, is formed. Sodium phosphite is oxidised by air in the presence of sodium sulphite, but no peroxide is formed in this case. L. S. THEOBALD.

Autocatalysis in oxidation. IV. Mechanism of antioxygenic action. G. DUPONT and J. ALLARD (Bull. Soc. chim., 1930, [iv], 47, 1216-1225; cf. A., 1930, 1003).-The proportion of quinol required to prevent the autoxidation of abietic acid in xylene solution increases as the oxidation advances; whilst 1 part in 5000 parts is sufficient at the start, 5 parts are required if the quinol is added when oxidation has already occurred. Similarly, in presence of 1% of cobalt as cobalt abietate addition of 1% of quinol at the start prevents oxidation, but if added when the oxidation has attained its maximum velocity 1.4-1.6% of quinol is required. In presence of 0.5% of cobalt abietate the proportion of quinol necessary is halved. On addition of quinol to a solution of cobalt abietate in abietic acid and of oxidised cobalt abietate in abietic acid the characteristic complementary absorption band at 500 µµ disappears and the solutions give the absorption spectrum of neutral cobalt abietate. Accordingly, it is concluded that the dark absorption band below 500 µµ is due to the formation

positive catalyst of the oxidation, and the constituent of oxidised abietic acid which forms this complex is the active oxide which catalyses the natural direct oxidation. It is suggested that the quinol acts by combining with this acid oxide, liberating cobalt abietate, the antioxygenic action of quinol with abietic acid itself being attributed to the combination of quinol with this active constituent of the oxidised acid. The greater part of the cobalt abietate is present in the active form when the velocity is at its maximum, whilst in the direct autoxidation of abietic acid a very small proportion of the oxidation product is in the active form. R. BRIGHTMAN.

Activity of surfaces. J. R. PARTINGTON (Nature, 1930, 126, 917).—The idea underlying many theories concerning the catalytic effect of a surface and its structure was published by the author in a qualitative form in 1911 (cf. J.C.S., 1911, 99, 475).

L. S. THEOBALD. Dissolution of metals in acids. G. WALPERT (Z. physikal. Chem., 1930, 151, 219–233).—The influence of foreign substances on the rate of dissolution of metals in acids has been studied by measuring both the rate of evolution of hydrogen and the potential of the dissolving metal. Dissolution of iron in SNsulphuric acid is retarded by hydrochloric acid, by formic, acetic, propionic, and butyric acids (in order of increasing influence), gelatin, and methyl-violet. Salts have little effect in dilute solution. Chromium, zinc, and cadmium behave similarly, except that salts accelerate their dissolution. The effects observed are attributed to adsorption, which is considered to be the first stage in the process of dissolution.

F. L. USHER.

Catalytic activity of cadmium. R. J. HARTMAN and O. W. BROWN (J. Physical Chem., 1930, 34, 2651-2665).—The catalytic activity of cadmium in the reduction of nitrobenzene to aniline has been investigated. With catalysts prepared in different ways, the highest yield of aniline is always obtained at  $319^{\circ} + 1^{\circ}$ . The most active catalyst is that prepared by precipitating the hydroxide on asbestos, roasting at 250°, and then reducing with hydrogen at 300°. When used above its m. p., cadmium gives high yields of aniline and shows less tendency to coalesce in nitrobenzene and hydrogen than in hydrogen alone. A catalyst prepared by reduction of the oxalate roasted at 250° is somewhat more active than that obtained from the unroasted oxalate, whilst that prepared from the hydroxide roasted at 250° is more active than that from the hydroxide roasted at 350°. A rate of flow of 0.3794 g. of nitrobenzene per hr. per g. of supported catalyst gives a quantitative yield of aniline, but the unsupported catalyst does not give quantitative yields at this rate. Support of the catalyst, however, on pumice or asbestos does not increase the yield at suitable rates; it only accelerates reduction. Shredded asbestos is a better support for cadmium than is

pumice. The aniline produced at 319° is colourless; at lower temperatures it contains some carbylamine and at higher temperatures the product is slightly coloured. No formation of ammonia has been detected in any of the experiments. L. S. THEOBALD.

Reactions at the surface of hot metallic filaments. B. L. SRIKANTAN (Rec. trav. chim., 1930, 49, 1146—1149; cf. A., 1930, 550).—A general discussion of previous work. The order of efficiency of different catalysts for the reaction between carbon dioxide and hydrogen deduced from the apparent heats of activation agrees with that given by velocity measurements. F. L. USHER.

Rates and temperature coefficients of the catalytic decomposition of ammonia over molybdenum, tungsten, and promoted iron. C. H. KUNSMAN, E. S. LAMAR, and W. E. DEMING (Phil. Mag., 1930, [vii], 10, 1015-1037; cf. A., 1929, 520).--The theory of the decomposition of ammonia on hot surfaces is examined kinetically, taking into consideration the condensation on the catalyst surface and the evaporation therefrom of the products of decomposition, and a formula is derived for the "true heat of activation" in terms of the temperature coefficient and the heats of desorption of the reactant and products. Ammonia was decomposed on molybdenum and tungsten in the form of electrically heated filaments, and on promoted iron catalysts applied on electrically heated platinum strips. The adsorption of nitrogen from the gas phase was negligible, but the active surface remained covered with hydrogen and ammonia during a run over a wide temperature range. The heat of activation and the heat of desorption of ammonia less that of hydrogen were computed. Evidence indicates that no nitride exists in presence of hydrogen above 740° in the case of molybdenum, and that decomposition on the iron catalyst may take place on nitrides formed from the nitrogen in the N. M. BLIGH. ammonia.

Catalytic formation of hydrogen cyanide. II. Formation from hydrocarbons and ammonia [with E. DEMME]. III. Formation from carbon monoxide and ammonia [with R. K. MÜLLER]. IV. [Mechanism of the] formation from carbon monoxide and ammonia [with G. KORTÜM]. G. BREDIG and E. ELÖD (Z. Elektrochem., 1930, 36, 991-1003, 1003-1007, 1007-1023; cf. A., 1927, 838).-II. The reaction between ammonia and ethylene, acetylene, and methane in presence of catalysts such as alumina and quartz has been investigated. At temperatures above 700° hydrogen cyanide is formed and with rise of temperature the yield increases to a maximum and then diminishes. The greatest yield (about 70%) is obtained with mixtures of ammonia and ethylene at equal partial pressures; the reaction is a catalytic surface reaction, the most effective catalysts being pure alumina and a mixture of alumina and quartz. Addition of hydrogen to the gaseous mixture reduces the yield of hydrogen cyanide very considerably, whereas nitrogen produces a much smaller effect, although the quantity of methane formed is reduced. The decomposition of the ethylene proceeds according to the equations  $C_2H_4 \longrightarrow$  $2C+2H_2$  and  $2C_3H_4 \rightarrow 2C+2CH_4$ ; the ratio of hydrogen to methane formed depends on the temperature, but although at 800° it is independent of the rate of passage of the mixture over the catalyst, the quantity of ethylene decomposed decreases with reduction of the time of contact, and since the hydrogen cyanide is formed only from the carbon produced according to the first equation, the yield diminishes simultaneously. The yield from ammonia and acetylene is, on the contrary, independent of the time of contact, whilst no yield is obtained when methane is employed until conditions suitable for the formation of acetylene are attained. It appears that in all cases the intermediate formation of acetylene is a necessary condition for the production of hydrogen cyanide.

III. The reaction between ammonia and carbon monoxide when passed over catalysts of alumina, thoria, and ceria at 500°, 600°, and 700° has been studied. The greatest yields of hydrogen cyanide are obtained with alumina and with ceria deposited on alumina; silica catalysts are unsatisfactory. The yield, calculated on the quantity of ammonia initially present in the mixture, increases with rise of temperature and with increasing excess of carbon monoxide, but diminishes as the velocity of the gas stream increases. With a twenty-fold excess of monoxide and a contact period of 6 sec. a 65% conversion of ammonia into hydrogen cyanide is obtained, 14% of ammonia being lost by dissociation: at 500° this loss is only about 2-6%. Since the rate of increase of the hydrogen content of the mixture, expressed as a fraction of the ammonia employed, corresponds with the rate of formation of hydrogen cyanide, it is suggested that the principal reactions concerned are  $NH_3 + CO \longrightarrow HCN + H_2O$  and  $H_2O + CO \longrightarrow H_2 + H_2O$  $CO_2$ , which may either take place as one reaction or be independently catalysed to about the same extents.

IV. The influence of nitrogen, hydrogen, carbon dioxide, and water on the reaction has been studied for various periods of contact and at various temperatures with the object of deciding among a number of possible mechanisms. Increase of the carbon monoxide excess favours the formation of hydrogen cyanide to a greater extent than does increase of the ammonia excess, whilst nitrogen is without appreciable influence except for low contact periods. Hydrogen, and especially carbon dioxide, displace the apparent equilibrium in the direction of less formation of hydrogen cyanide; hydrogen also diminishes the dissociation of the ammonia. The reduction of yield caused by water is due, not to displacement of the equilibrium, but to hydrolysis of the hydrogen cyanide. In the light of these observations the mechanism suggested in III cannot be correct; the most probable mechanism is expressed by 2CO+  $\rm NH_3 \longrightarrow HCN + CO_2 + H_2$  and  $\rm CO_2 + H_2 \longrightarrow CO + H_2O$ , and by the side reactions  $\rm 2CO \longrightarrow C + CO_2$  and  $\rm C + NH_3$  $\rightarrow$ HCN+H<sub>2</sub>. Minor reactions involving the formation and decomposition of formaldehyde may take place to some extent. Attempts to attain equilibrium from the hydrogen cyanide-water side confirm the mechanism suggested, although a true equilibrium is, on account of hydrolysis, not attainable.

H. F. GILLBE.

Catalysis of autoxidation : anti- and pro-oxygenic action of iron and its compounds. C. DUFRAISSE and R. HORCLOIS (Compt. rend., 1930, 191, 1126—1128).—The catalytic effect as regards autoxidation of metallic iron and 21 of its compounds on acraldehyde, benzaldehyde, furfuraldehyde, styrene, turpentine, and sodium sulphite solution is shown to be, like that of all other catalysts, sometimes pro- and sometimes anti-oxygenic. Examples of anti-oxygenic action are : of ferric chloride on benzaldehyde, ferric acetylacetonate on sodium sulphite, oxy-, carboxy-, and met-hæmoglobin on acraldehyde or sodium sulphite,  $\beta$ -chlorohæmin, hæmin, and  $\beta$ -bromohæmin on acraldehyde, benzaldehyde, or sodium sulphite, and of all the foregoing, as also of ferrous oxide,  $\beta$ -chlorohæmin, and its dimethyl ether on furfuraldehyde. Iron is thus no exception to the general rule in this respect.

C. A. SILBERRAD.

Reaction between vapours of methyl alcohol and water as example of heterogeneous catalysis. J. A. CHRISTIANSEN and J. R. HUFFMAN (Z. physikal. Chem., 1930, 151, 269—302; cf. A., 1926, 358).— The velocity of the above reaction has been observed at temperatures from 190° to 250°, the catalyst being in every case 0·1 g.-at. of copper dispersed in varying quantities of magnesium oxide. The copper loses its activity in the course of time, but it can be restored by treatment with air. The initial velocity is proportional to the square root of the concentration of methyl alcohol, and the reaction is strongly inhibited by hydrogen and to a smaller extent by carbon dioxide. Formulæ for the velocity and for its variation with temperature are given. The velocity decreases with increasing dispersity of the copper.

F. L. USHER.

Use of oscillating discharges in the formation of gaseous hydrides. B. FORESTI (Gazzetta, 1930, 60, 745-754).-By passing oscillating discharges between electrodes of tin, of bismuth, and of lead in a current of hydrogen at ordinary pressure it is possible to obtain the respective hydrides of these metals even in the absence of organic substances. The best results were obtained with tin, the yield being the greater the smaller was the distance between the electrodes. If the discharge is aperiodic practically no hydride is formed. The amount of hydride formed is not related to the period of the oscillating discharge. The work of Paneth and his co-workers, who obtained negative results in absence of organic substances, is discussed. The catalytic action of hydrocarbons in the formation of metallic hydrides is probably due to the decomposition of the hydrocarbons by the discharge into free radicals of great chemical activity and atomic hydrogen. O. J. WALKER.

Electrolytic combination with compressed nitrogen at the ordinary temperature. F. FICH-TER, P. GIRARD, and H. ERLENMEYER (Helv. Chim. Acta, 1930, 13, 1228—1236; cf. A., 1922, ii, 372).— On electrolysis of a solution of lithium chloride in absolute ethyl or butyl alcohol in contact with compressed nitrogen using a platinum cathode lithium nitride is formed and gives rise to ammonia by the reaction  $Li_3N+3EtOH=3LiOEt+NH_3$ . The current yield with nitrogen under a pressure of 1000 atm. may amount to 12%. R. CUTHILL.

Electrolytic reduction of acid solutions of vanadium. F. FOERSTER and F. BÖTTCHER (Z. physikal. Chem., 1930, 151, 321-400).-The static potentials of platinum, iridium, and gold electrodes in solutions containing equimolecular proportions of V'O2 and V''O", V''O" and V", and V" and V" have been determined and compared with the cathode potentials measured during the respective electrolytic reductions. The static potentials are independent of the metal of the electrode. The experimental procedure was the same as that previously described in the investigation of molybdenum compounds (A., 1930, 432), and the general results obtained are similar. The reduction of V<sup>v</sup> to V<sup>iv</sup> at a platinised gauze cathode proceeds without appreciable polarisation, but at a smooth platinum surface the cathode potential is considerably increased, without, however, giving rise to evolution of hydrogen. Reduction of  $V^{1v}$  to  $V^{111}$  is accompanied by evolution of hydrogen, but the current yield increases during the reduction. The reaction  $V^{\mu\nu} \longrightarrow V^{\mu}$  cannot occur at a platinised surface, but may be carried to completion at a smooth platinum surface, the current yield steadily decreasing during the reduction. The irregularities observed in the first two stages of reduction are due to the formation of membranes of insoluble products of hydrolysis on the surface of the cathode, leading to an increased potential and to evolution of hydrogen. No such membrane is formed during the final stage, in which the decreased current yield is due solely to the simultaneous discharge of hydrogen ions. Variations in the amount of free sulphuric acid present affect the results in the sense required by the above explanation. F. L. USHER.

Vanadous salts. J. MEYER and (FRL.) M. AULICH (Z. anorg. Chem., 1930, 194, 278-292).-The cause of the discrepancies between the work of Piccini and Marino (A., 1902, ii, 663) and that of Rutter (A., 1906, ii, 366) on the electrolytic preparation of vanadous sulphate has been traced to the influence of the sulphuric acid concentration. The solubility at 25° and 100° of vanadium pentoxide in sulphuric acid of concentrations from 0 to 98.5% exhibits two maxima, between which colloidal solutions are formed. In contradiction of the reports of the earlier observers, the nature of the cathode is without influence on the electrolytic reduction, which in presence of air yields compounds of tervalent vanadium; in presence of sufficient sulphuric acid the solution becomes green and then contains the complex acids  $[V(H_2O)_4SO_4]SO_4H$ and  $[V(H_2O)_2(SO_4)_2]_4H$ . If air be excluded the solution becomes violet owing to the production of vanadous salt, and by concentration over phosphorus pentoxide violet crystals of vanadous sulphate heptahydrate may be isolated. Details are given of the preparation of the relatively stable ammonium, potassium, and rubidium vanadous sulphates. The preparation of the vanadous salts of other acids is difficult owing to their instability; cathodic dissolution of the metal yields always compounds of higher valency. The stability of vanadous sulphate solutions increases with increase of concentration and of the free acid concentration; addition of alcohol, sodium hydrogen sulphite, etc. is without influence. H. F. GILLBE. Electrolytic preparation of zinc and lanthanum persulphates. V. ARNAL (Helv. Chim. Acta, 1930, 13, 1254—1257).—Solutions containing zinc and lanthanum persulphates have been obtained by electrolysis of aqueous solutions of the corresponding hydrogen sulphates, but it has not been possible to isolate the solid salts. R. CUTHILL.

Electrolytic deposition of gold at high current densities. H. PAWEOK and R. WEINER (Z. Elektrochem., 1930, 36, 972-980).-Experiments have been performed on the electrodeposition of gold from alkaline ferrocyanide solutions with the object of establishing a process which may be operated at relatively high current densities. The ferrocyanide concentration is of little consequence; increase of the quantity of sodium carbonate in the solution causes at low gold concentrations an increase of the electrode potential, whereas at higher gold concentrations the reverse effect obtains. Increase of the gold concentration markedly reduces the polarisation, and the potential attains a value which is almost independent of the current density. Dilution of a solution of constant composition causes a considerable increase of chemical polarisation. The ordinary dilute ferrocyanide bath exhibits such a rapid increase of electrode potential, even at low current densities, that passivity results and the employment of a gold anode becomes useless, whereas with a bath containing potassium ferrocyanide (200 g.), hydrochlorauric acid (50 g.), and sodium carbonate (50 g./per litre), the potential remains at a constant low value at current densities up to 10 amp. per dm.<sup>2</sup> and anodic dissolution proceeds unhindered; such a bath may be successfully employed for rapid cathodic deposition.

H. F. GILLBE.

Electrodeposition of chromium. V. P. ILIN-SKI.—See B., 1931, 25.

Electrolytic production of antimony. F. Vogel. —See B., 1931, 25.

Polarographic studies with the dropping mercury cathode. XVI. Electro-reduction of acetaldehyde. I. SMOLER (Coll. Czech. Chem. Comm., 1930, 2, 699-711).-The cathodic reduction of acetaldehyde in 0.1 - 0.0001 M-solutions containing lithium chloride at concentrations from 0.02N to 0.01N by the dropping mercury cathode has been investigated by means of polarographically recorded currentvoltage curves. The reduction potential in M-solution is -1.60 volt, and is not influenced by variation of the  $p_{\rm H}$  of the solution within wide limits; with decreasing  $p_{\rm II}$ , however, the reduction is retarded, and in presence of acid at a concentration comparable with that of the aldehyde is entirely inhibited. The electrode potential  $\pi$  is related to the current I by the equation  $\pi = -(RT/F) \log I$ , whilst the change of  $\pi$  due to a change dC of the aldehyde concentration is given by  $d\pi = (RT/F) \log dC$ . The insensitivity of the reduction process to changes of  $p_{\rm H}$  indicates that the reaction is irreversible; the most probable product is dimethylglycol. The application of polarographic methods to the determination of traces of acetaldehyde is described; 0.0005 mg. in 1 c.c. may be determined to within 10%. For the determination in ethyl alcohol, 10 c.c. are diluted with 90 c.c. of

water, and to the first 10 c.c. obtained on distillation lithium chloride is added. Vinegar should be neutralised with 2N-lithium hydroxide, and the first fifth of the distillate treated with lithium chloride until the salt concentration is 0.01N. Fermentation vinegars suppress strongly the maxima on the current-voltage curves, but synthetic and pyroligneous acetic acid have no such influence. H. F. GILLBE.

Anodic oxidation of acetic acid in sulphuric acid solution. R. SCHREINER (Z. Elektrochem., 1930, 36, 953-963).-0.5M-Solutions of formaldebyde. methyl alcohol, and formic, acetic (0.5M and 5M), oxalic, glyoxylic, and glycollic acids have been subjected to anodic oxidation in 2N-sulphuric acid solution at a platinum anode and with constant current density with the object of establishing the mechanism of the oxidation of acetic acid; the observations made include determinations of the variation with time of the nature and quantity of gas evolved and of the anode potential, of the nature of the products formed in solution, and of the change of weight, if any, of the anode. The main process is represented by  $CH_3 \cdot CO_2H \longrightarrow OH \cdot CH_2 \cdot CO_2H \longrightarrow CH(OH)_2 \cdot CO_2H \longrightarrow$  $(CO_2H)_2 \rightarrow 2CO_2$ , but at higher potentials there are side reactions commencing with the products of the first and second stages and resulting in the formation of formaldehyde, formic acid, methyl alcohol, and carbon monoxide. Increase of the anode potential favours the true exidation stages, as compared with those involving removal of hydrogen: the latter takes place most readily from the alcoholic group and least readily from the carboxyl group. Simultaneous removal of two hydrogen atoms which are attached to two different carbon atoms occurs only when they form the end members of a six-membered chain, and to only a small extent if an alternative mode of oxidation is possible. H. F. GILLBE.

Mechanism of the synthesis of the nitrogen oxides. L. A. M. HENRY (J. Physical Chem., 1930, 34, 2782-2791).-The reaction between oxygen and nitrogen has been investigated at low pressure and temperature in the Geissler, the electrodeless, and the dark electronic discharges. With the Geissler discharge, no reaction occurs at the ordinary temperature, but at the temperature of liquid air the reaction has been followed for mixtures of oxygen and nitrogen in the ratios 1:1 and 1:2. The best yields of nitrogen dioxide are obtained with the stoichciometric mixture. With the electrodeless discharge no reaction occurs at the temperature of liquid air unless a luminous discharge of high energy content is present. A mechanism between one molecule of oxygen and one atom of nitrogen is proposed.

## L. S. THEOBALD.

Organic reactions in gaseous electrical discharge. I. Normal paraffin hydrocarbons. E. G. LINDER (Physical Rev., 1930, [ii], 36, 1375– 1385).—With the object of investigating chemical action in electrical discharges, an apparatus for subjecting vapours to an electrical discharge at various pressures and currents is described; different fractions of the gaseous reaction products can be collected, and their rates of accumulation have been measured for various discharge currents and vapour pressures.

Results reported for *n*-decane indicate that electric conduction in gases may follow an electrochemical equivalence law similar to Faraday's law of electrolytic conduction in liquids, and that the amount of reaction is proportional to the current and independent of voltage and vapour pressure. Curves are given for the relation between molecular size and rate of production of various gaseous reaction product fractions for *n*-pentane, hexane, heptane, octane, decane, dodecane, and tetradecane. A theoretical discussion of the results is given. N. M. BLIGH.

Chemical decomposition by radiation. G. HARKER (J. Cancer Res. Comm. Sydney, 1930, 2, 160—181).—A general survey of contemporary theory and some experimental data. N. M. BLIGH.

Thermal and photochemical decomposition of ozone. H. J. SCHUMACHER and G. SPRENGER (Z. physikal. Chem., 1930, B, 11, 38–44; cf. A., 1930, 425).—A reply to Ricsenfeld and Wassmuth (A., 1930, 1135). F. L. USHER.

Photochemical union of hydrogen and chlorine. I. Effect of light intensity. II. Effect of wavelength. Measurements with filtered light. A.J. ALLMAND and E. BEESLEY (J.C.S., 1930, 2693-2708, 2709-2721).-I. The velocity of the photochemical combination of hydrogen and chlorine has been measured under widely varying conditions of illumination. With monochromatic light of wavelengths 4050 and 4360 Å. the velocity is proportional to the light intensity over intensity ratios of 180:1 and 440: 1, respectively, and with polarised light the same holds for a ratio of 4:1. obtained by the use of crossed Nicols. The velocity is proportional also to the average intensity when intermittent monochromatic or complex light is employed, and is independent of the rate of intermission. Under certain conditions there appears to be a destruction of inhibitors present in the gas, and it is suggested that this phenomenon may be the cause of the results obtained by Baly and Barker (J.C.S., 1921, 119, 653).

II. The quantum efficiencies of the photochemical reaction between moist hydrogen and chlorine at 5460, 4360, 4050, 3650, and 3030-3130 Å. are 0.45, 1.41, 2.06, 1.08, and 1.00, respectively, and the threshold is on the longer wave-length side of 5460 Å., since the green mercury line of this wave-length is active. The velocity of the reaction is considerably greater at 25° than at 19.7°, probably as a result of the increased sensitivity of the gas mixture consequent on the destruction of inhibitors: nevertheless, despite the maximum in the quantum efficiency-wave-length curve, the true temperature coefficient of the quantum efficiency probably increases continuously with increase of wave-length. The effect of radiations of two different wave-lengths appears to be additive; the sum of the effects produced when the two act successively is equal to the total effect when they act H. F. GILLBE. simultaneously.

Photosensitised decomposition of nitrogen trichloride and the induction period of the hydrogen-chlorine reaction. J. G. A. GRIFFITHS and R. G. W. NORRISH (Nature, 1931, 127, 14).— Mixtures of chlorine and small quantities of nitrogen 180

chloride give total pressure increments corresponding with the net reaction  $2NCl_3 = N_2 + 3Cl_2$ . Measurements of quantum efficiency with light of wavelength 366 and 436 µµ indicate that the photosensitised decomposition of the nitrogen trichloride proceeds by short reaction chains, the efficiency falling to a limiting value of 2 as the pressure of chlorine is increased. The addition of helium, argon, nitrogen, and oxygen has specific retarding effects, and as the pressures are increased it depresses the quantum efficiency towards the limiting value. The reaction chains appear to be initiated and controlled in the gas phase. Hydrogen has a retarding influence on the decomposition of nitrogen trichloride numerically equal to that of helium. In the inhibition of nitrogen trichloride on the hydrogen-chlorine reaction, confirmation has been obtained of the view that small quantities of hydrogen chloride, comparable in amount with the nitrogen trichloride destroyed, should be formed during the induction period.

## L. S. THEOBALD.

Photo-reaction of hydrogen and iodine monochloride. D. P. Mellor and T. IREDALE (Nature, 1931, 127, 93).-Contrary to the conclusions of Rollefson and Lindquist (A., 1930, 1135), hydrogen and iodine monochloride react rapidly in light when the pressure of the hydrogen is large compared with that of the iodine monochloride. The reaction is slow in artificial light, rapid in diffuse daylight, and very rapid in direct sunlight; iodine and hydrogen chloride are the main products. The reaction indicates that conditions favour the greater probability of the reaction H<sub>2</sub>+Cl=HCl+H and that excited chlorine atoms may not be necessary for it to take L. S. THEOBALD. place.

Photochemical reaction between ethylene iodide and iodine in carbon tetrachloride solution. H. J. SCHUMACHER and E. O. WIIG (Z. physikal. Chem., 1930, B, 11, 45-55; cf. A., 1930, 1255).—A solution of ethylene iodide and iodine in carbon tetrachloride is only slightly changed when illuminated with a quartz mercury lamp at the ordinary temperature, but at 100° the photochemical decomposition is considerable. The reaction has been studied in relation to the intensity of the light absorbed and the concentration of the reactants. The reaction and the concentration of the reactants. The reactants is of the "chain" type, the stages being: (1)  $I_2+E$  $\rightarrow I+I$ ; (2)  $I+C_2H_4I_2 \rightarrow I_2+C_2H_4I$ ; (3)  $C_2H_4I$  $= C_2H_4+I$ ; (4)  $I+I \rightarrow I_2$ . The temperature co-efficient of the velocity is 1.57 for 10°, and the heat of activation 11.8 kg.-cal., in agreement with the value (11.5 kg.-cal.) previously found for the thermal reaction. The velocity is given by the equation  $-d[C_2H_4I_2]/dt = k\sqrt{I_{abs}}[C_2H_4I_2]$ , in which  $I_{\rm abs}$  is the intensity of the absorbed light.

## F. L. USHER.

Photosensitising action by iodine : isomeric transformation of allocinnamylideneacetic acid into the normal form in methyl alcohol, ethyl alcohol, chloroform, and in mixtures of alcohol, chloroform, and water. J. C. GHOSH, D. N. D. GUPTA, N. C. ROY, and H. K. CHATTERJEE (J. Physical Chem., 1930, 34, 2771-2781; cf. A., 1926, 400).—The conversion of the allo-acid into the normal

acid at equilibrium is 90% in the various solvents used and is independent of the concentration of iodine or allo-acid, the intensity or wave-length of the light used, and the temperature. The measured velocity coefficients are in agreement with the deduced formula  $K = A[1 - e^{-\epsilon c}]e^{-\alpha c}$ , where A and  $\alpha$  are constants and c and c are the molecular extinction coefficient and the molar concentration, respectively, L. S. THEOBALD. of the iodine.

Point-concentration or centripetal theory of light effect. A. STEIGMANN (Kolloid-Z., 1930, 53, 318-322).-A discussion of published work. E. S. HEDGES.

Lattice energies of the silver halides and their photochemical decomposition. II. S. E. SHEP-PARD and W. VANSELOW (J. Physical Chem., 1930, 34, 2719-2748; cf. A., 1929, 408).-Theoretical. The importance of lattice energy for light absorption and photodecomposition of crystals is maintained. Sommerfeld's "electron gas" theory of metals is discussed and criticised in its application to photoionisation in ionic crystals, whilst Pauling's theory and conception of "electron affinity of the crystal which is based on this is analysed and shown to be inadequate in certain respects. It is suggested that replacement of this electron affinity by the virtual field or lattice potential of the metal gives better agreement between calculated and observed wavelength limits of absorption. Deformation of anions by cations with large external electron sheaths tends to shorten the wave-length limit of absorption rather than to extend it. Adsorption effects supporting the opposite view are ascribed to lattice loosening. The relation of photodecomposition to lattice loosening appears to be more restricted than was previously indicated and photodecomposition may be able to take place irrespective of lattice loosening for waves within the absorption band. The loosening, however, increases the probability of its commencing at a given point and extends the active wave-length region by lowering the potential of the crystal lattice.

L. S. THEOBALD. New photochemical effect on "celloidin" paper as a radiation problem. H. MEWES (Z. wiss. Phot., 1930, 28, 311-324).—All substances (except wood and similar dielectrics) are stated to emit a new kind of radiation (L-rays) which will affect certain brands of printing-out paper at a short distance. These rays are emitted in a narrow pencil, so that on development (with rodinal etc.) images of exact shape are produced, slightly enlarged, and surrounded by concentric haloes at definite distances and of varying colours. Possible theories are discussed. J. LEWKOWITSCH.

Action of sodium thiosulphate on a slightly acid solution of potassium iodate. E. CARRIÈRE and JULLIARD (Compt. rend., 1930, 191, 1133-1135). -The result of the addition of solution of sodium thiosulphate to potassium iodate in (hydrochloric) acid solution may result in the reactions: (i)  $HIO_3$ +  $6Na_2S_2O_3+2H_2O=5NaOH+NaI+3Na_3S_4O_6$ ; or (ii)  $4\mathrm{HIO}_3 + 3\mathrm{Na}_2\mathrm{S}_2\mathrm{O}_3 + 3\mathrm{H}_2\mathrm{O} = 4\mathrm{HI} + 6\mathrm{NaHSO}_4.$ The results of varying (a) temperature, (b) concentration of hydrochloric acid, (c) concentration of iodate, and

(d) speed of addition of thiosulphate show that with (a), (b), and (c) constant the amount of thiosulphate required diminishes, *i.e.*, reaction (ii) is favoured, as (d) increases; the same is the case when (b) is increased with (a), (c), and (d) constant, or when (a) is increased with (b), (c), and (d) constant. With (a), (d), and the ratio (b)/(c) constant dilution favours (i).

C. A. SILBERRAD. Periodic process in a chemical reaction. W. T. GIBSON (Nature, 1931, 127, 13).—The periodic formation of rings of potassium oxide by the slow oxidation of a layer of potassium is described.

L. S. THEOBALD. Action of boric acid on alkali chlorides and nitrates. L. HACKSPILL, A. P. ROLLET, and L. ANDRÈS (Compt. rend., 1931, 192, 48—50).— Intimate mixtures of alkali chlorides or nitrates with a large excess of boric acid were heated in steam at  $100-150^{\circ}$ . After 30 min. the hydrochloric acid was completely evolved, leaving a pentaborate ( $R_2O,5B_2O_3$ ) except in the case of sodium salts when, unless there is an excess of sodium chloride, a chloroborate,  $(5B_2O_3,Na_2O)NaCl$ , is produced, whilst sodium nitrate and excess of boric acid yield a triborate,  $Na_2O,3B_2O_3$ . J. GRANT.

Ammonium and potassium dimagnesium acid carbonates. E. URBAIN (Compt. rend., 1930, 191, 1339—1340).—The salts MgCO<sub>3</sub>,2KHCO<sub>3</sub>,4H<sub>2</sub>O, MgCO<sub>3</sub>,KHCO<sub>3</sub>,4H<sub>2</sub>O (cf. Engel, A., 1881, 1087), and potassium dimagnesium hydrogen carbonate, 2MgCO<sub>4</sub>KHCO<sub>4</sub>(H) of the salts of the salts in the salts of the salts

 $2MgCO_{3}$ , KHCO<sub>3</sub>, 4H<sub>2</sub>O, were prepared by the addition of various quantities of potassium hydrogen carbonate to an aqueous suspension of magnesium carbonate, the mixture being stirred by a stream of carbon dioxide and the crystals separated by cooling to 0°. The reaction  $5MgCO_3+2RCI+CO_2+4H_2O \rightarrow MgCl_2+$  $2(MgCO_3)_2$ , RHCO<sub>3</sub>, 4H<sub>2</sub>O gives quantitative yields. Ammonium behaves analogously to potassium in both reactions, mixtures of isomorphous potassium and ammonium chlorides (" potazote ") giving a mixture of the carbonates. J. GRANT.

Heterogeneous complex salts. I. G. SPACU and G. SUCIU (Bull. Soc. Stiinte Cluj, 1930, 5, 191— 219; Chem. Zentr., 1930, ii, 534—535).—The following compounds have been prepared: [Men<sub>3</sub>]HgI<sub>4</sub> (M=Zn, Cd, Ni); [Cu en<sub>2</sub>]HgI<sub>4</sub>; [Ni en<sub>3</sub>]CdI<sub>4</sub>; [Co en<sub>3</sub>]CdI<sub>4</sub>; [Co en 1][Bill i: [Cu en [HgCl(CN)]]:

A. A. ELDRIDGE.

Complex thiosulphates of copper with ammonium, potassium, and sodium. II. G. SPACU and I. G. MURGULESCU (Bul. Soc. Stiinte Cluj, 1930, 5, 254-272; Chem. Zentr., 1930, ii, 535).—The compounds K<sub>5</sub>Cu(S<sub>2</sub>O<sub>3</sub>)<sub>3</sub>,3H<sub>2</sub>O and K<sub>7</sub>Cu(S<sub>2</sub>O<sub>3</sub>)<sub>4</sub>,2KNO<sub>3</sub> are described. In solutions more concentrated than M, interaction of cupric and thiosulphate ions affords sulphur and sulphur dioxide as well as tetrathionate. A. A. ELDRIDGE.

Action of carbonic acid under pressure on salts of the alkaline-earth metals. I. Action on calcium phosphate. E. Müller and J. KNÖFEL. II. Action on alkaline-earth silicates. E. MüL-LER and W. LUBBERGER (Z. anorg. Chem., 1930, 194, 258—260, 261—267).—I. By the action of aqueous solutions of carbon dioxide on calcium phosphate at 60 atm. pressure solutions are obtained in which the ratio CaO:  $P_2O_5$  is less than unity for temperatures above 80°. The reaction appears to be  $2CaHPO_4+$  $H_2CO_3=Ca(H_2PO_4)_2+CaCO_3$ , followed by the formation of calcium hydrogen carbonate, which decomposes at the higher temperatures. With bone ash, and particularly with phosphorite, markedly smaller quantities enter into solution, probably as a result of the greater compactness of these materials.

II. The quantities x of calcium, strontium, and barium dissolved from the corresponding silicates by solutions of carbon dioxide at pressures up to 50 atm. have been determined as functions of the temperature. In all cases x diminishes with rise of temperature, the decrease being especially marked above 80° owing to the decomposition of the hydrogen carbonate formed; x is not influenced by increase of pressure above 30 atm. Since addition of colloidal aluminium hydroxide solution does not alter the values of x, silica, and not free silicic acid, must be formed during the process of dissolution. Experiments with ordinary and ignited silicates demonstrate the great influence of the available surface on the reactivity; approximately the same values of x are obtained for ignited artificial calcium silicate as for wollastonite. H. F. GILLBE.

Action of bivalent metals on persulphates of the alkali metals. Synthesis of double salts of the type M<sup>I</sup><sub>2</sub>M<sup>II</sup>(SO<sub>4</sub>)<sub>2</sub>. O. ASCHAN (Z. anorg. chem., 1930, 194, 139-146).—The exothermic dissociation of a number of metals in solutions of sodium, potassium, and ammonium persulphates has been studied. By crystallisation of the filtered solutions a series of hexahydrated complex salts of the type  $M_{2}^{II}M^{II}(SO_{2})_{2}$ , where  $M^{I} = K$ , Na, or NH<sub>4</sub>, and  $M^{II} = Mg$ , Mn, Fe, Ni, Co, or Cu, have been prepared; the *zinc* and *cadmium* compounds are obtained only with the sodium and potassium persulphates. All these compounds crystallise in well-defined oblique rhombohedra. Their mode of formation is represented by :  $(M^{I}O \cdot SO_{2} \cdot O)_{2} + M^{II} \longrightarrow M^{I}O \cdot SO_{2} \cdot O \cdot M^{II} \cdot O \cdot SO_{2} \cdot O M^{I},$ in accordance with the peroxide constitution of the persulphates. Mercury reacts vigorously with the persulphate solutions, but yields compounds of abnormal composition, and the reaction between ammonium persulphate and zinc and cadmium also yields abnormal compounds. H. F. GILLBE.

Mercury fulminate. F. H. VAN LEENT (Chem. Weekblad, 1930, 27, 670—671).—The structure of mercury fulminate is discussed. The reaction between the fulminate and sodium thiosulphate has been investigated alkalimetrically and iodometrically: the quantity of alkali liberated is twice the quantity which would be produced by hydrolysis of the sodium salt formed according to the equation  $Hg(CNO)_2+$  $2Na_2S_2O_3 \longrightarrow Na_2[Hg(S_2O_3)_2]+2NaCNO$ , and it appears that the reaction involves oxidation of the thiosulphate, 2 mols. of oxygen being given up by 1 mol. of the fulminate:  $4Na_2S_2O_3+2O+2H_2O\longrightarrow$  $2Na_2S_4O_6+4NaOH$ . Titration with a variety of indicators shows that part of the alkali thus produced combines with complexes containing mercury which are simultaneously produced and behave as very weak acids. Iodometric titration of the neutralised solution indicates that only one half the quantity of iodine solution is required as compared with the quantity of acid necessary for neutralisation, and it is therefore suggested that the residue of the fulminate, after reduction, reacts additively with iodine according to the equation  $Hg(NC)_2+2I+H_2O \longrightarrow Hg(NC\cdotHI)(NC\cdotI\cdotOH)$ . The metallic fulminates are

to be regarded as carbylamines of the metal peroxides. H. F. GILLBE.

Formation of double ammines in aqueous solution. II. Metallic thiocyanates. R. RIPAN and L. DIMA (Bul. Soc. Stiinte Cluj, 1930, 5, 220-249; Chem. Zentr., 1930, ii, 708-709).-The following compounds have been prepared (X = hexamethylene-

 $\begin{array}{l} compounds \ \text{have been prepared } (X = \text{hexamethylene-tetramine}): \ [\text{Hg}(\text{SCN})_4][\text{MX}(\text{H}_2\text{O})_3] \ (\text{M}=\text{Co}, \ \text{Ni}, \ \text{Fe}, \\ \text{Mn}); \ [\text{Hg}(\text{SCN})_4][\text{MX}(\text{C}_5\text{H}_5\text{N})_4] \ (\text{M}=\text{Co}, \ \text{Ni}, \ \text{Mn}, \ \text{Cd}); \\ [\text{Hg}(\text{SCN})_4][\text{Co}X(\text{C}_5\text{H}_5\text{N})_3]; \\ [\text{Hg}(\text{SCN})_4[(\text{C}_5\text{H}_5\text{N})_2][\text{MX}(\text{C}_5\text{H}_5\text{N})(\text{H}_2\text{O})_3] \ (\text{M}=\text{Ni}, \ \text{Fe}, \\ \ \text{Mn}); \ [\text{Hg}(\text{SCN})_4][\text{Cd}X]; \\ \ [\text{Co}(\text{SCN})_4(\text{H}_2\text{O})_3][\text{Ni}X_2(\text{H}_2\text{O})_4]; \\ [\text{Co}(\text{SCN})_4(\text{H}_2\text{O})_3][\text{Ni}X_2(\text{H}_2\text{O})_4]; \\ \ [\text{Co}(\text{SCN})_4(\text{C}_5\text{H}_5\text{N})_2][\text{Ni}X_2(\text{C}_5\text{H}_5\text{N})_4], \text{H}_2\text{O}; \\ \ [\text{Ni}(\text{SCN})_6][\text{Mn}X_2(\text{H}_2\text{O})_4][\text{Ni}X(\text{C}_5\text{H}_5\text{N})_5], 12\text{H}_2\text{O}. \\ \ \text{A. A. ELBRIDGE.} \end{array}$ 

Preparation of anhydrous stannous chloride. H. STEPHEN (J.C.S., 1930, 2786-2787).-A rapid and strongly exothermic reaction takes place when 2 mols. of acetic anhydride are added to 1 mol. of hydrated stannous chloride; the anhydrous stannous chloride which separates may be washed free from acetic acid by means of ether, and is then apparently nonhygroscopic. It is readily soluble in acetone and in methyl, ethyl, and amyl alcohols, but is insoluble in benzene and chloroform. Traces of water in the solvents cause the immediate appearance of opalescence, presumably due to the formation of stannous H. F. GILLBE. oxychloride.

Cerium. L. LORTIE (Ann. Chim., 1930, [x], 14, 407-460).-By interaction of ammonium cerinitrate and sodium carbonate in aqueous solution, Na<sub>6</sub>[Ce(CO<sub>3</sub>)<sub>5</sub>,2H<sub>2</sub>O],10H<sub>2</sub>O sodium cericarbonate, (yellow), is formed and the corresponding thallous salt (orange-yellow) may be obtained from thallous sulphate in a similar manner. The sodium salt is isomorphous with sodium thoricarbonate and in aqueous solution forms basic ceric carbonate,

 $Ce(OH)_2CO_3$  (yellow). By the action of the halogen acids on cerous tartrate, cerous tartrate hydrochloride, Ce2(C4H4O6)3,3HCl,14H2O, hydrobromide,

 $Ce_2(C_4H_4O_6)_3,3HBr,14H_2O$ , and hydriodide may be obtained. Cerous tartrate also reacts with tartaric acid to form cerotartaric acid, H[Ce(C4H4O6)2,2H2O]. The sodium salt of this acid,

Na[Ce(C4H4O6)2,2H2O]6H2O, may be prepared by interaction of cerous nitrate and sodium hydrogen tartrate. Investigation of the oxidation of cerous and ceric salts to the perceric state in presence of alkalimetal salts of hydroxy- and phenolic acids has shown that these compounds exert a stabilising effect on perceric salts. Perceric salicylate,

 $Ce_2O_3(O \cdot C_6H_4 \cdot CO_2)_3, 6H_2O$  (red), is formed by the

interaction of a mixture of sodium carbonate, sodium salicylate, and ammonium cerinitrate. On passing oxygen through a mixed solution of potassium hydroxide and cerous tartrate, potassium ceritartrate, 2CeO(C<sub>4</sub>H<sub>2</sub>O<sub>6</sub>)K<sub>2</sub>,K<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>,11H<sub>2</sub>O (red), results. R. CUTHILL.

Mechanism of precipitation processes. I. Reaction between lead chloride and ammonium chromate. Z. KARAOGLANOV and B. SAGORTSOHEV (Z. anorg. Chem., 1930, 194, 151-158).-The quantity of chloride retained by lead chloride when precipitated in presence of chloride has been determined. The chloride content x of the precipitate, when hot ammonium chromate solution is added rapidly to a boiling solution of lead chloride containing hydrochloric acid, bears a linear relationship to the hydrochloric acid concentration, and although this holds also if the order of the addition is reversed, xassumes higher values; precipitation in the cold also leads to higher values of x, which tend to a maximum at high chloride concentrations. With solutions of sodium, potassium, and ammonium chlorides the values of  $\hat{x}$  are relatively small for precipitation in the cold, but with hot solutions high values are attained and a specific influence of the cation becomes evident. In all cases x diminishes as the time of precipitation increases, and increases with increase of the volume of solution used. None of the precipitates contains dichromate, and the chlorine content is non-volatile. The results are compared with those obtained for the interaction of lead chloride and sulphuric acid (A., 1930, 563); the secondary reaction is probably  $2PbCl^++CrO_4^{\prime\prime}=Pb_2Cl_2CrO_4^{\prime}$ . H. F. GILLBE.

Nitrogen tri-iodide. H. W. CREMER and D. R. DUNCAN (J.C.S., 1930, 2750-2754).-Nitrogen triiodide, NI<sub>3</sub>, has been isolated by passing dry ammonia over solid cæsium, potassium, and pyridinium iododibromides and washing the black product rapidly with water to remove residual bromides. The process appears to be essentially a reaction between the ammonia and iodine bromide produced by dissociation of the iododibromide, since the more stable compounds of this type, i.e., those of low dissociation pressure, yield with ammonia additive compounds. It is apparently possible to sublime nitrogen tri-iodide in a vacuum at the ordinary temperature, the sublimate being condensed by means of liquid air.

H. F. GILLBE.

Reaction between nitrite and aminosulphonic acid. F. L. HAHN and P. BAUMGARTEN (Ber., 1930, 63, [B], 3028-3029).-Nitrite can be removed from aqueous solution by reaction with aminosulphonic acid or precipitation with 2:4-diamino-6-hydroxypyrimidine. If a 4% solution of nitrite "purissimum" is used, the sum of the originally present and newly formed nitrate in the residual solution amounts to 0.002-0.004 mg. per c.c. H. WREN.

Isomorphism and chemical homology. W. LANGE (Nature, 1930, 126, 916).-Priority is claimed for the preparation of monofluophosphates and the discovery that the PO<sub>3</sub>F" ion resembles SO<sub>4</sub>" (cf. Ray, A., 1930, 1351; Lange, A., 1929, 662). L. S. THEOBALD.

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Reduction by hydrogen of the oxygenated compounds of phosphorus. P. VILLARD (Compt. rend., 1930, 191, 1035-1038).-Metaphosphoric acid and anhydride are reduced in a stream of hydrogen (50 litres per hr.) at 900-950° to elementary phosphorus which, after condensation in a vessel at 0°. is obtained as ordinary (? white) phosphorus, or is deposited near the heated portion of the tube in an orange-yellow (pyromorphic) form, and in the cooler parts as brilliant gold to violet scales. Both the latter types are transformed into ordinary phosphorus if heated in a vacuum. Similar results are obtained with sodium and barium pyrophosphates, calcium pyrophosphate being converted into tricalcium phosphate, which is not further reduced to an appreciable extent. Trisodium phosphate gives traces of phosphorus at 1200° by indirect reduction resulting from dissociation and subsequent formation of the pyrophosphate (above). At lower temperatures phosphorescence and an odour of garlic are obtained

J. GRANT.

Action of halogens on ethyldi-iodostibine. Antimony bromodi-iodide. R. E. D. CLARK (J.C.S., 1930, 2737—2739).—By the action of iodine on ethyldi-iodostibine highly coloured unstable products, which on decomposition leave only antimony tri-iodide, are formed. If to 12 g. of ethyldi-iodostibine dissolved in 15 c.c. of chloroform 1.6 c.c. of bromine dissolved in 5 c.c. of chloroform are added, and the liquid is refluxed for a few minutes and cooled, a mixture of iodine and antimony bromodi-iodide, m. p. 88°, separates. The action of chlorine on the stibine yields only the tri-iodide. H. F. GILLBE.

Oxidation of trithiocarbonate in alkaline solution. J. G. WEELDENBURG (Rec. trav. chim., 1930, 49, 1180—1188; cf. A., 1928, 602).—When solutions of sodium trithiocarbonate are oxidised in alkaline solution with bromine, permanganate, or hydrogen peroxide, the sulphate produced is about 9% less than that corresponding with the sulphur content. The discrepancy has been traced, in the case of hydrogen peroxide, to the occurrence of a reaction in which dithionic and formic acids are produced in the molecular ratio of 1:4. Addition of nickel nitrate before the oxidation reduced the error to about 3%.

F. L. USHER. Selenocyanammines. II. G. SPACU and C. G. MACAROVICI (Bul. Soc. Stiinte Cluj, 1930, 5, 169– 187; Chem. Zentr., 1930, ii, 708).—The following compounds have been prepared:  $[CoAu_2](SeCN)_2$ ;  $[CdAu_2](SeCN)_2$ ;  $[Ni en_3](SeCN)_2$ , KCNSe;  $[Cd en_3](SeCN)_2$ , KCNSe;  $[Zn en_3](SeCN)_2$ , KCNSe;  $[Co en_3](SeCN)_2$ , KCNSe;  $[Co en_3](SeCN)_3$ ;  $[Ni en_3](SeCN)_2$ ;  $[Cr en_2Cl_2]SeCN$ .

A. A. ELDRIDGE.

Complex thiocyanates of quadrivalent molybdenum. G. A. BARBIERI (Atti R. Accad. Lincei, 1930, [vi], 12, 55-61).—Complex thiocyanates of quadrivalent molybdenum may be prepared by oxidising the corresponding compounds of tervalent molybdenum by means of potassium ferricyanide. The pyridine tervalent molybdenum salt,

3C<sub>5</sub>H<sub>5</sub>N,H<sub>3</sub>Mo(SCN)<sub>6</sub>,3H<sub>2</sub>O (cf. Sand and Burger, A., 1906, i, 487; Sand and Maas, A., 1908, i, 11, 397, 513;

Rosenheim and Garfunkel, ibid., 614), prepared by treating an aqueous solution of Chilesotti's salt (Å., 1906, ii, 263, 365) with pyridine and acetic acid, yields the pyridine quadrivalent molybdenum salt,  $2C_5H_5N,H_2Mo(SCN)_6$ , on oxidation. The hexa-methylenetetramine tervalent molybdenum salt (+2H<sub>2</sub>O) (cf. Scagliarini and Tartarini, A., 1924, i, 312) gives the corresponding quadrivalent molybdenum salt, (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>)<sub>2</sub>H<sub>2</sub>Mo(SCN)<sub>6</sub>,2H<sub>2</sub>O, on oxidation. The degree of oxidisability of the molybdenum in such compounds as the above may be determined by treating a known weight of the compound, mixed with a known weight of potassium ferricyanide, in ammoniacal solution, with excess of silver nitrate solution and then with a definite volume of standard ferrous sulphate solution, which rapidly reduces the silver ferricyanide to ferrocyanide. Determination of the residual ferrous sulphate by titration with permanganate gives the amount of the potassium ferricyanide converted into silver ferricyanide and hence the amount of ferricyanide reduced to ferrocyanide by the molybdenum. The quadrivalency of the molybdenum in the above compounds is deter-T. H. POPE. mined in this way.

Amphoteric oxide hydrates, their aqueous solutions and crystalline compounds. XI. Molybdates, polymolybdates, and polymolybdic acids as examples of the formation and decomposition of complex inorganic compounds in solution. G. JANDER, K. F. JAHR, and W. HEUKES-HOVEN (Z. anorg. Chem., 1930, 194, 383-428).-A survey is given of previous work on the molybdates and on the products obtained on acidification of alkali molybdate solutions. Measurements have been made of the diffusion coefficients at about 13° of 0.2N-sodium molybdate solutions of  $p_{\rm H}$  from 14 to 0 diffusing into solutions of the same  $p_{\rm fl}$  containing sodium nitrate and nitric acid. The diffusion coefficients remain practically constant at 0.58 as the  $p_{\rm H}$  is diminished from 14 to 6.5 and thereafter fall abruptly in a series of stages at  $p_{\rm H}$  4.5, 1.25, and 1.0, which correspond with the formation of di-, para-, octo-, and deca-molybdates; with further increase of acidity the diffusion coefficients rise steadily as a result of the breakdown of the highly complex aggregates formed at the isoelectric point, which contain at least 24 mols. of molybdic oxide. The change of the absorption coefficients at wave-lengths between 2880 and 3760 Å. of sodium molybdate solutions on gradual addition of acid confirm the results of the diffusion measurements. Conductometric titration shows the paramolybdates to be of the form  $M_5(HMO_6O_{21})$ , the dimolybdates,  $M_3H(MO_3O_{11})$ , and the metamolybdates,  $M_3(H_3MO_6O_{21})$ ; formation of the other complex molybdates is not apparent on the conductivity curves. The trimolybdates are regarded as tetrabasic salts of hexamolybdic acid, M4(H2M06O21), and the octomolybdates as tribasic salts of a dodecamolybdic acid,  $M_3H_7(Mo_{12}O_{41})$ , whilst the higher molybdates are derivatives of an acid,  $H_{12}(Mo_{24}O_{78})$ ; thus the decamolybdates are  $M_3H_7(Mo_{24}O_{78})$  and the hexadecamolybdates  $M_3(H_9Mo_{24}O_{78})$ . Thermometric titration of neutral and of acidified molybdate solutions indicates that the and of acidified molybdate solutions indicates that the

process of aggregation is exothermic. The conclusions reached regarding the nature of the aggregates formed are compared with the views of other workers.

H. F. GILLBE.

Reactions with liquid chlorine. J. MEYER and W. AULICH (Z. angew. Chem., 1931, 44, 21-23).-Liquid chlorine was put into sealed tubes containing the other reagent and the tubes were then heated. No reaction occurred with powdered vanadium at low temperatures, but at  $0^{\circ}$  the mixture exploded, forming vanadium trichloride. No appreciable reaction occurred with platinum, even at 100°, but gold was readily attacked, forming auric chloride. Silver acquired a protective coating of the chloride, but was attacked in the simultaneous presence of water and liquid chlorine. Lead was attacked only by a mixture of liquid chlorine and carbon tetrachloride at 320°, the dichloride being formed. No reaction occurred with dry chromium, but slight attack in the presence of water. Manganese produced manganous chloride at 100° when water was also present. No reaction occurred with silicon or boron. Selenium and tellurium were attacked readily even at  $-80^\circ$ , the corresponding tetrachlorides being formed. E. S. HEDGES.

Oxidation of chlorites to chlorates by permanganates. G. R. LEVI and D. GHIRON (Atti R. Accad. Lincei, 1930, [vi], 11, 1005–1008).—The oxidation of alkali chlorites by neutral potassium permanganate solutions is retarded by the accumulation of hydroxyl ion during the reaction  $3\text{ClO}_2'+2\text{MnO}_4'+\text{H}_2\text{O}=$  $3\text{ClO}_3'+2\text{MnO}_2+2\text{OH}'$ . The presence of calcium or zinc ion removes the hydroxyl ion formed in the reaction and renders the oxidation to chlorate rapid and quantitative in the cold. F. G. TRYHORN.

New tetramminocobaltic complexes. P. B. SARKAR and T. DAS-GUPTA (J. Indian Chem. Soc., 1930, 7, 835-837).—By the action of sodium thiosulphate at temperatures below 0° on trans-tetramminodichlorocobaltic chloride or on cis-tetramminoaquochlorocobaltic chloride, trans-tetramminoaquothiosulphatocobaltic thiosulphate is formed as green very soluble crystals; by double decomposition the corresponding chloride, bromide, sulphate, nitrate, thiocyanate, chromate, and dithionate have been prepared. Aqueous solutions of all these compounds have identical ultra-violet absorption spectra, with two characteristic heads. By keeping a solution of the thiosulphate at 30-35° gradual conversion into the green insoluble trans-tetramminohydroxythiosulphatocobalt takes place, and after prolonged hydrolysis, a red compound of the structure

 $[Co^{II}{(OH)_2Co^{III}(NH_3)_4}_2(H_2O)_2](S_2O_3)_2$  was isolated. It is suggested that in aqueous solutions of tetramminodichlorocobaltic salts there exists an equilibrium of the type  $[Co(NH_3)_4Cl_2]Cl \implies [Co(NH_3)_4H_2OCl]Cl_2$  $\implies [Co(NH_3)_4OHCl]Cl;$  at low temperatures the first action of the thiosulphate ion is one simply of substitution, but on raising the temperature hydrolysis causes the formation of the hydroxy-compound, whilst on prolonged hydrolysis the liberated thiosulphuric acid reduces part of the tervalent cobalt. H. F. GILLBE.

Rôle of water in the aquotetramminoruthenium compounds. R. CHARONNAT (Compt. rend., 1930, 191, 1453—1455).—Ethylenediamine and potassium ruthenium nitrosoiodide,  $K_2Ru(NO)I_5$ , interact to form hydroxynitrosodiethylenediaminoruthenium iodide,  $[Ru(NO)(OH) en_2]I_2$ , as pale yellow leaflets. Concentrated hydrochloric acid converts these into orange needles of  $Ru(NO) en_2CII_2, H_2O$ . Although this loses water fairly readily, the loss is accompanied by change in colour to pale yellow, indicating that the water is constitutional; moreover, silver nitrate precipitates only iodide from a solution. The formula must therefore be  $[Ru(NO)(H_2O) en_2CI]I_2$ . Pyridine and potassium ruthenochloronitrosodioxalate,

 $K_2[Ru(NO)Cl(C_2O_4)_2]$  (cf. A., 1924, i, 707), interact to form, besides a soluble monopyridino-derivative, almost insoluble deep red crystals of

Ru(NO)( $C_5H_5N$ )<sub>2</sub>Cl( $C_2O_4$ ). Concentrated hydrochloric acid converts them into red needles of Ru(NO)( $C_5H_5N$ )<sub>2</sub>Cl<sub>3</sub>,3H<sub>2</sub>O. This readily loses 2H<sub>2</sub>O, but the third only with decomposition. In contact with water it becomes salmon-coloured in consequence of the reaction Ru(NO)( $C_5H_5N$ )<sub>2</sub>Cl<sub>3</sub>( $H_2O$ ) = Ru(NO)( $C_5H_5N$ )<sub>2</sub>Cl<sub>2</sub>(OH)+HCl. The dehydrated product dissolved in alcohol gives no precipitate with silver nitrate until water is added. Its constitution must therefore be [Ru(NO)( $H_2O$ )( $C_5H_5N$ )<sub>2</sub>Cl<sub>3</sub>]. These results indicate, not a co-ordination number 7 for ruthenium, but that the HCl is attached by a secondary valency to the OH, (ClH·OH) occupying one coordination position, thus : [Ru(NO) en<sub>2</sub>(ClHOH)]Cl<sub>2</sub>, and [Ru(NO)( $C_5H_5N$ )<sub>2</sub>(ClHOH)Cl<sub>2</sub>]. Similarly, aquonitrosotetramminoruthenium chloride is [Ru(NO)(NH<sub>3</sub>)<sub>4</sub>(ClHOH)]Cl<sub>2</sub>, and not [Ru(NO)(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)]Cl<sub>3</sub>. C. A. SILBERRAD.

Adjustment of achromatic indicators. E. L. SMITH (Quart. J. Pharm., 1930, 499-507).—A number of mixtures of indicators (or of an indicator and a dye) are described, such that the colour of one constituent is complementary to that of the other at the mid-point of its colour change, so that the colour at the transition point is grey. These mixtures (for which the term " achromatic indicator " is suggested) are suitable for the titration of coloured, turbid, or very dilute solutions, and for use in artificial light. Mixtures of phenolphthalein with methyl-red and methylene-blue have been prepared with transition points ranging from  $p_{\rm H}$  8 to 10. A solution of bromocresol-green (0.02 g.), neutral-red (0.0045 g.), p-nitrophenol (0.05 g.), and phenolphthalein (0.60 g.) in alcohol (100 c.c.) shows sharp achromatism at  $p_{\rm H}$  4.5 and 8.5 and may be used for the titration of the first and second hydrogen ions of phosphoric acid.

R. CHILD.

Determination of  $p_{\rm B}$  at temperatures above 100°. S. STONE (Rec. trav. chim., 1930, 49, 1133— 1145).—A platinised platinum hydrogen electrode gives reproducible potentials at temperatures above 100° and can be used in conjunction with a suitable standard to determine  $p_{\rm H}$ . Calomel electrodes are unsatisfactory at high temperatures, but good results have been obtained with a silver-silver chloride reference electrode. The construction of the electrodes and electrode vessels is described. The  $p_{\rm H}$  values of a series of buffer mixtures, covering a range of  $p_{\rm H}$  from 1 to 10, have been determined at 150°. The alteration of  $p_{\rm H}$  due to temperature may be either positive or negative and, except with borate buffers, remains approximately constant over a considerable range of  $p_{\rm H}$ . F. L. USHER.

Protective influence of liquid paraffin on the alteration of volumetric solutions. C. J. BLOK (Pharm. Tijds. Nederl.-Ind., 1930, 7, 406-408).— Sodium hydroxide solutions ( $0\cdot1-0\cdot5N$ ) when covered with a 3-mm. layer of liquid paraffin and kept in open vessels showed practically no change of concentration after 24 days even when titrated with phenolphthalein as indicator. H. F. GILLBE.

Rapid determination of moisture. T. H. FAIRBROTHER and R. J. WOOD (Ind. Chem., 1930, 6, 442—444).—Moisture can rapidly be determined with an accuracy of  $\pm 0.5\%$  by measuring the volume of water obtained when the sample is distilled with carbon tetrachloride. The Burton-Pitt method (cf. A., 1928, 712), depending on the change in strength of current when the sample is introduced into a rapidly alternating electric field, and a modification of Berliner and Ruter's method, in which the effect of the sample on the capacity of an electrical condenser is measured, give trustworthy results for the natural moisture content of wheat; added moisture behaves differently. D. K. MOORE.

Detection of traces of hydrochloric acid in the presence of hydrobromic acid. G. G. LONGIN-ESCU and T. I. PIRTEA (Bull. Acad. Sci. Roumaine, 1930, 13, 195-196) .- The mixed silver halides, obtained by addition of silver nitrate to the solution acidified with nitric acid, are dissolved in 10% ammonia solution and 1 c.c. of 1% potassium bromide is added to the ammoniacal solution, which is then just acidified with nitric acid and filtered. Addition of silver nitrate to the filtrate produces a precipitate which is pure white as long as only chloride is present. The volume of 1% potassium bromide, in c.c., which can be added without giving a yellow precipitate gives the number of mg. of chloride present in the original solution. Potassium bromide can be replaced by hydrobromic acid. P. G. MARSHALL.

Determination of iodides in presence of other halogens. H. DITZ (Z. anorg. Chem., 1930, 194, 147-150).—The statement of Gorbatschev and Kasatkina (A., 1930, 1143), that iodate should not be employed as an oxidising agent for the determination of iodide in presence of other halides, is criticised, and by reference to earlier work of the author (A., 1902, ii, 12; 1904, ii, 366) it is shown that by suitable choice of the hydrogen-ion concentration the method yields satisfactory results, although if bromide or chloride and bromide be present, only the extraction process at the ordinary temperature is trustworthy. Only in absence of bromide is it permissible to titrate the excess of iodate after heating with 0-1N-acid and iodate to remove the liberated iodine.

### H. F. GILLBE.

Spectrographic determination of various gases. B. DE LA ROCHE (Bull. Soc. chim., 1930, [iv], 47, 1326-1331).—An extension of the method previously described (A., 1930, 1145) to other gas mixtures. The spectral lines suitable for determining the gas and the general appearance of the intensity curves have been studied for fluorine (as silicon or boron fluoride), chlorine, bromine, iodine, sulphur, oxygen, nitrogen, boron, and silicon. Precautions must be taken to eliminate effects due to impurities, more particularly water vapour, which superpose a continuous spectrum on that of the gas studied. This effect may render the results untrustworthy. It may be obviated by employing spectral lines in regions not affected by these impurities, or by working with the gas in some standard state-perfectly dry, or having the same degree of humidity, e.g., saturated vapour. The method is applicable to fluorine, chlorine (admixed with dry air), and nitrogen (admixed with hydrogen or carbon dioxide), to an accuracy of 1 in 1000. Bromine and iodine (studied as hydrogen bromide and iodide) give inaccurate values, whilst the gaseous compounds of sulphur, boron, silicon, and phosphorus are decomposed by the spark, the elements being deposited on the electrodes, so that the results are meaningless. Oxygen also behaves anomalously, in that the intensity of the emission lines is independent of the concentration in the gas mixture; the effect is ascribed to oxidation at the electrode.

J. R. I. HEPBURN.

Determination of small quantities of oxygen in gases. H. R. AMBLER.—See B., 1931, 19.

Determination of oxygen in steel. G. THAN-HEISER and C. A. MÜLLER.—See B., 1931, 24.

Rapid determination of sulphur dioxide in air. K. ZEPF and F. VETTER.—See B., 1931, 60.

Titrimetric determination of sulphates. M. DOMINIKIEWICZ (Bull. trav. dep. chim. inst. hyg. état [Poland], 1930, 31, No. 1, 3—6).—The solution (100 c.c.) is acidified with hydrochloric acid and heated to the b. p.; 0-1N-barium chloride (20— 25 c.c.) is added and, after boiling, the solution is neutralised with ammonia. The excess of barium chloride is titrated with 0-1N-ammonium potassium chromate, using benzidine as external indicator.

CHEMICAL ABSTRACTS.

Rapid determination of selenium. E. BENESCH and E. ERDHEIM (Chem.-Ztg., 1930, 54, 954-955).-The method is applicable to the determination of selenium present as element, selenious or selenic acids. If the selenium is in solution a quantity of this equivalent to 0.1-0.15 g. Se is diluted to 400 c.c., acidified with 5 c.c. of hydrochloric acid, and treated with 30 g. of hydrazine hydrochloride or sulphate. It is boiled in a covered beaker until the red modification of selenium precipitated is converted into the black variety, which is washed, dried, and weighed. If the selenium is present in a powdered substance a weight of the substance containing 0.1-0.15 g. Se is mixed with 3 g. of powdered pure iron oxide, 3 g. of potassium chlorate, and 4 g. of sodium hydrogen carbonate and the mixture is heated in a nickel crucible until it just sinters. It is then washed into a measuring flask and the liquid diluted to 250 c.c. The liquid is filtered through a folded filter and 200 c.c. of it are mixed with 200 c.c. of water; the solution is neutralised and the selenium determined as described. above. Directions are given for the reclamation of the hydrazine. Tests of the method on selenic acid

solutions and mixtures of known selenium content gave concordant results. An analysis of selenium sludge is appended. H. E. BLAYDEN.

Separation and determination of selenium and tellurium. K. WAGENMANN and H. TRIEBEL (Metall u. Erz, 1930, 27, 231—236; Chem. Zentr., 1930, ii, 273—274).—In Keller's method (A., 1900, ii, 573) the selenium is incompletely precipitated; precipitation with ferric acetate leads to an error of 33%. Selenium is preferably precipitated with a hydrazine salt from slightly acid solution; the determination of selenium in metallic and non-metallic substances is described. Separation of selenium and tellurium by means of potassium cyanide is inaccurate; Keller's method is accurate but inconvenient. Lenher and Smith's method (A., 1924, ii, 698), with some modification of the apparatus, is preferred.

A. A. ELDRIDGE.

Spot reaction for nitrite. F. L. HAHN (Mikrochem., 1931, 9, 31-33).— $\alpha$ -Naphthylamine oxalate is a delicate reagent for nitrite and can conveniently be used on paper, a small drop of nitrite solution then giving a red spot on the test-paper. Special directions are given for the preparation of the reagent paper. The limit of sensitivity is 1 in 10<sup>7</sup>. E. S. HEDGES.

Argentometric determination of azides. A. MAJRICH (Chem. Obzor, 1930, 5, 3-4; Chem. Zentr., 1930, ii, 949).—The solution of alkali azide is titrated with 0.1N-silver nitrate solution in presence of potassium chromate. The error is not greater than 0.2%. A. A. ELDRIDGE.

Colorimetric determination of phosphorus. H. B. BENNETT (J. Lab. Clin. Med., 1927, 13, 251— 257).—Modified concentrations of reagents in Briggs' method are recommended. CHEMICAL ABSTRACTS.

Determination of phosphoric acid as ammonium phosphomolybdate and as phosphomolybdic anhydride. A. von ENDREDY (Z. anorg. Chem., 1930, 194, 239-257).-The conditions of precipitation of ammonium phosphomolybdate in presence of tartaric acid have been investigated. According to the procedure recommended, the solution, containing 0.0003-0.035 g. of  $P_2O_5$ , is treated with 8 g. of ammonium nitrate and 20 c.c. of 4N-nitric acid, diluted to 100 c.c., and heated to boiling; 20 c.c. of the ammonium molybdate reagent are added with stirring, and after 24 hrs. the precipitate is collected, washed with 25 c.c. of cold and 50 c.c. of hot solution containing 50 g. of ammonium nitrate and 40 c.c. of nitric acid per litre, and dried in a current of warm air after washing with 20 c.c. of acetone in several portions. The molybdate solution is prepared by mixing solutions containing 100 g. of tartaric acid in 300 c.c. and 150 g. of ammonium molybdate in 600 c.c., filtering, adding 10-12 drops of hydrochloric acid, and diluting to 1 litre. The precipitate, in which the ratio P: NH4 is 1:3, may if desired be weighed as  $P_2O_5,24MoO_3$  by heating to constant weight in a porcelain crucible. From the weight of the dried precipitate the empirical factor 0.0355 gives the P2O5 content, and for the ignited precipitate the factor is 0.0392; by application of a correction which is approximately -3.0 mg. for dried precipitates

weighing 0.05—0.08 g. and for ignited precipitates weighing 0.10—0.80 g., the error may be reduced to  $\pm 0.6$  and 0.02 mg., respectively. The adsorption of molybdic acid by a precipitate of constant composition is in accordance with the isotherm  $a=0.863c^{-0.328}$ . H. F. GILLBE.

Analysis of phosphates. V. VINCENT.—See B., 1931, 60.

Determination of silicon in steel and iron. H. WOLF and R. HEILINGÖTTER.—See B., 1931, 24.

Determination of carbon dioxide in sea-water and of carbonate in soils. M. NICLOUX (Compt. rend. Soc. Biol., 1929, 101, 182—186; Chem. Zentr., 1930, ii, 285).—By the use of a simplified form of the apparatus previously described the carbon dioxide content of sea-water at Roscoff has been found to be 4.93 vol.-% (cf. A., 1927, 996). A. A. ELDRIDGE.

Volumetric determination of sodium. **A**. BLENKINSOP (J. Agric. Sci., 1930, 20, 511-516).-Sodium, in solutions containing 0.1-12.0 mg., is determined by precipitation as uranium zinc sodium acetate. The complex salt is dissolved in acid and reduced with excess of titanous chloride, the excess being titrated with iron alum solution using a thiocyanate indicator. Iron, aluminium, and phosphates are removed, prior to the determination, by gentle ignition and extraction of the residue with water. Calcium and magnesium salts in relatively large amounts do not interfere with the reaction, but excessive amounts are sufficiently reduced by a single precipitation with ammonia and ammonium carbonate. A. G. POLLARD.

Micro-determination of silver in oligodynamic water. C. EGG (Schweiz. med. Woch., 1929, 59, 84—86; Chem. Zentr., 1930, ii, 1256).—The silver is removed electrolytically from an alkaline bath after suitable concentration of the water and is finally determined volumetrically with 0.001*N*.iodide solution. A. A. ELDRIDGF.

Potentiometric precipitation titration of silver iodide. E. LANGE and R. BERGER (Z. Elektrochem., 1930, 36, 980-988).-A technique is described whereby the potentiometric precipitation titration of silver iodide may be conducted with an average deviation from the mean of  $\pm 0.003\%$ . The influence on the observed equivalence point of adsorption and occlusion of ions has been investigated; on the assumption that the effect is symmetrical on either side of the equivalence point, the probable error is  $\pm 0.03$  volt. The mean error of a determination is of the order of  $\pm 0.01\%$ . Rubbing the electrode with a soft insulating material such as rubber causes on the silver side a negative displacement of potential and on the iodine side a positive displacement, whilst in the neighbourhood of the equivalence point a maximum displacement of -220 millivolts has been observed. The cause of this effect is discussed and the necessity of eliminating possible causes of energy displacement during measurements of E.M.F. is emphasised.

H. F. GILBE.

Separation and determination of calcium and strontium. L. SZEBELLÉDY (Magyar Chem. Fol., 1929, 35, 59-62; Chem. Zentr., 1930, ii, 274).—The mixed nitrates are dried at  $180^{\circ}$ , and then extracted first with absolute alcohol and then with *iso*butyl alcohol until not more than 5 mg. are removed. The calcium nitrate solution so obtained is evaporated and the residue dried, whilst the strontium nitrate is dried at  $140^{\circ}$ . A correction of 0.2 mg. for each extraction is applied. A. A. ELDRIDGE.

Separation and determination of calcium and barium. L. SZEBELLÉDY (Magyar Chem. Fol., 1929, 35, 63—64; Chem. Zentr., 1930, ii, 274).—The procedure employed for the separation of calcium and strontium (preceding abstract) is applicable.

#### A. A. ELDRIDGE.

Determination of strontium and barium in presence of one another. Separation as bromides. L. SZEBELLEDY (Magyar Chem. Fol., 1929, 35, 100-105; Chem. Zentr., 1930, ii, 274).-The nitrates (0.5g.) are converted into the bromides by treatment with hydrobromic acid (free from sulphate), dried at 100°, and finely ground with hot isobutyl alcohol (10 c.c.). The filtrate containing the strontium bromide is evaporated, the residue being heated with ammonium sulphate, and the strontium weighed as sulphate. The remainder of the salt mixture is dissolved in water, evaporated with hydrobromic acid (1 g. HBr), and the extraction repeated until not more than 5 mg: of strontium sulphate are recorded. The residual dry barium bromide is weighed. A correction of 0.5 mg. is transferred from the strontium sulphate to the barium bromide for each extraction.

A. A. ELDRIDGE.

Volumetric determination of barium. L. ZOM-BORY (Magyar Chem. Fol., 1929, 35, 90—94; Chem. Zentr., 1930, ii, 274).—The salt is titrated with 0.2Nammonium or alkali sulphate (neutral or slightly acidified with hydrochloric acid) or sulphuric acid in presence of sodium rhodizonate as indicator.

A. A. ELDRIDGE. Volumetric determination of calcium and magnesium in drinking water. M. E. STAS.—See B., 1931, 92.

Spectral analysis of foreign elements in a metal. L. AMY (Compt. rend., 1930, 191, 1049—1050).—The spark spectra of metals often change during exposure of the plate on account of alterations in the surfaces of the metallic electrodes due to different rates of volatilisation of the elements present. The author therefore makes a number of exposures for 1 sec. only after striking the arc, using a fresh metal surface each time. Lines due to small amounts of magnesium, calcium, and carbon in lead, zinc, or copper, and to magnesium and calcium in iron are thereby reinforced about 100 times, less marked effects being obtained for small traces of tin, copper, antimony, and iron.

J. GRANT. Determination of cadmium in mill and smelter products. W. E. KECK, G. L. OLDRIGHT, and F. K. SHELTON.—See B., 1931, 25.

Separation of lead from mercury or copper and its determination. H. FUNK and J. SCHOR-MÜLLER (Z. anal. Chem., 1930, 82, 361–365).—The lead is precipitated from a hot 2.5% solution of sodium chloride containing 1—2 g. of sodium acetate and a few drops of acetic acid by the addition of a boiling 5% solution of potassium dichromate in slight excess. The precipitated lead chromate is washed with 1-2% acetic acid, dried at 120°, and weighed. The filtrate is acidified with hydrochloric acid, boiled with alcohol to reduce chromic acid, and saturated with hydrogen sulphide to precipitate copper or mercury sulphide. A. R. POWELL.

Iodometric determination of copper and its application to the determination of reducing sugars. R. INTONTI (Annali Chim. Appl., 1930, 20, 583-590).-Addition of carbamide serves as a suitable means of removing nitrous fumes from copper solutions prior to determination of the copper by the iodometric method. The copper (0.05-0.3 g.) is dissolved in 15-20 c.c. of 20% nitric acid with only gentle heating. After addition of ammonia in slight excess, the ammonia and nitrous fumes above the liquid are expelled by a current of air. The solution is neutralised with dilute sulphuric acid, 10 c.c. of 20% sulphuric acid and 3 g. of carbamide being added and the liquid stirred vigorously until effervescence ceases. After addition of 3 g. of potassium iodide, the solution is titrated with 0.1N-thiosulphate, with continual stirring; starch paste is added towards the end of the titration. The method is applicable to the determination of reducing sugars by means of Fehling's solution, and details of the procedure are given. T. H. POPE.

Electrolytic deposition of copper from tartaric acid chloride solutions. H. HÖLEMANN (Z. anal. Chem., 1930, 82, 273—276).—With increasing concentration of tartaric acid the deposition potentials of copper and antimony from chloride solutions become slightly more positive at 70° and more negative at 0°. With constant concentration of tartaric acid increase in the concentration of hydrochloric acid causes the deposition potentials of the two metals to diverge from one another, but the deposition of copper is accompanied by a strong chemical polarisation and is not complete at a potential below that at which antimony begins to be deposited. A. R. POWELL.

Analysis of copper-zinc and copper-zincnickel alloys. E. DI NOLA.—See B., 1931, 68.

Determination of mercury in mercuric cyanide. E. CATTELAIN (J. Pharm. Chim., 1930, [viii], 12, 529-531).-Although mercuric chloride, sulphate, or nitrate may be determined by reduction to mercurous chloride by hypophosphorous acid in the presence of hydrochloric acid and hydrogen peroxide, under similar conditions the cyanide is reduced to the metal. Quantitative yields of mercurous chloride may be obtained by heating 10 c.c. of approximately 0.1Nmercuric cyanide, 10 c.c. of 10% sodium chloride, 2 c.c. of 20% ammonia, and 10 c.c. of saturated potassium permanganate solution on the water-bath for 0.5 hr. in order to convert the cyanide into cyanate. The excess of permanganate is reduced by 2 c.c. of 95-96% alcohol and the manganese dioxide formed is reduced and dissolved by the addition of 5 c.c. of hydrochloric acid (d 1·19). After cooling, the addition of 20 c.c. of 10—12-vol. hydrogen peroxide followed by 2 c.c. of 50% hypophosphorous acid gives an immediate precipitate of mercurous chloride.

T. MCLACHLAN.

Quinoline as a microchemical reagent for some heavy metals. I. M. KORENMAN (Pharm. Zentr., 1930, 71, 769—772).—The characteristics of the crystalline precipitate formed, and the sensitivity of the reaction between quinoline and salts of mercury, copper, bismuth, cadmium, zinc, lead, and tin in presence of alkali halogen salts are described, as also is a reaction between quinoline nitrate solution and salts of iron, zinc, cobalt, and cadmium in presence of ammonium thiocyanate. E. H. SHARPLES.

Organic reagents in mineral qualitative analysis (cations). B. TOUGARINOFF (Ann. Soc. Sci. Bruxelles, 1930, 50, *B*, 145-246).—Methods of detection of aluminium, antimony, arsenic, barium, bismuth, cadmium, calcium, chromium, cobalt, copper, tin, iron, magnesium, manganese, mercury, nickel, lead, strontium, and zine by means of organic reagents which have been proposed during the last 20 years are summarised and notes are given in each case on the nature of the reaction, conditions favouring the test, and sensitivity. An experimental investigation of the possibilities of using certain organic reagents for the qualitative analysis of cations has been carried out, with the following results. The red lake formed when ammonia and alizarin are added to aluminium salts is recommended as a test for aluminium; it permits the detection of 0.03 mg. of aluminium in 10 c.c. Iron, chromium, and manganese should be absent and the precipitate does not form in the presence of tartaric or citric acid. The violet coloration formed by rhodamine B with antimony forms a useful test. The antimony must be in the quinquevalent state; the presence of tin does not interfere. Tervalent antimony gives a characteristic white crystalline precipitate with pyrogallol up to dilutions of 1 in 50,000, but the reaction is not serviceable in the presence of tin, and the test is considered to be less valuable than that with rhodamine B. The crystalline orange precipitate obtained with feebly acid tervalent antimony and benzidine in the presence of potassium iodide has a low sensitivity (1 in 600), but the form and colour of the precipitate are very characteristic. Hexamethylenetetramine is not recommended as a test for antimony; the test is neither sensitive nor specific. The benzidine test for bismuth is suitable only for microchemical identification. The hexamethylenetetramine test for bismuth is useful only in microchemical analysis; it succeeds best in 15% hydrochloric acid solution and the sensitivity is only I in 1000. The dimethylglyoxime test for bismuth is useful for confirmation in the ordinary course of analysis, since it does not succeed with other members of the same analytical group; the sensitivity of the reaction is 1 in 100,000. Rhodamine B is also recommended for the identification of bismuth; the solution should be only feebly acid so that the bismuth salt is partly hydrolysed; the sensitivity is 1 in 6000. In the presence of ammonium thiocyanate, antipyrine gives characteristic precipitates with some metals as follows: zinc, white; copper, brown; ferrie iron, reddish-purple; cobalt, blue; nickel, chromium, aluminium, tin, and antimony are incompletely precipitated from concentrated solutions. The reaction with cobalt has been studied in detail. The

reagents consist of 5-10% antipyrine and 50% ammonium thiocyanate solutions, the neutral cobalt solution being made feebly acid by the addition of 5 drops of 15% hydrochloric acid to 10 c.c. The sensitivity is 1 in 500,000, but nickel at concentrations greater than 0.1% and traces of iron interfere with the reaction. A sensitive reaction for cobalt, which is not affected by the presence of nickel or iron, is provided by potassium xanthate. It has no particular advantages over other methods except for the qualitative separation of cobalt and nickel; it does not effect a quantitative separation. A new qualitative reagent for magnesium consists of a solution of alizarin in glacial acetic acid. A few drops of the reagent are added to a feebly acid magnesium solution and on the subsequent addition of excess of sodium hydroxide a sky-blue lake is precipitated. Several other metals interfere and the procedure is valueless in the presence of ammonium salts. Benzidine gives a blue coloration with lead compounds, which are first oxidised to lead peroxide by means of hydrogen peroxide. If care is taken to eliminate excess of the oxidising agent the test is useful for ordinary analytical work and detects 0.1 mg. of lead in 10 c.c. The colour reactions given by diphenylamine, diethylaniline, and orange IV, respectively, with zinc salts in the presence of potassium ferricyanide form excellent tests for zinc, particularly as they permit the detection of small quantities of zinc in the presence of aluminium. The red coloration produced with diphenylamine is the most sensitive; 0.004 mg. of zinc may be detected.

E. S. HEDGES.

Determination of iron with potassium dichromate. L. SZEBELLÉDY (Magyar Chem. Fol., 1930, 36, 40—44; Chem. Zentr., 1930, ii, 274—275).— The solution diluted to 50 c.c. is treated with 10 c.c. of aqueous sulphuric acid (1:3) and 1 c.c. of 1%*p*-phenetidine solution as indicator. After expulsion of air by means of potassium hydrogen carbonate (1 g.), ammonium fluoride (3 g.) is added and the mixture is titrated with 0·1*N*-potassium dichromate from yellowish-green to reddish-violet. A. A. ELDRIDGE.

Determination of iron with ethyl ether. T. SZAFFKA (Magyar Chem. Fol., 1929, 35, 44-51; Chem. Zentr., 1930, ii, 275).—Ethyl ether extracts ferric chloride from (hydrochloric) acid solution; 99.8% is extracted in 30 min. in presence of 20.6%of hydrogen chloride. The etherate is of indefinite composition and is unstable, being decomposed by water. A. A. ELDRIDGE.

Determination of iron in aluminium. G. AGAMENNONE.—See B., 1931, 68.

Rapid determination of tin and antimony in alloys with a high copper content. A. M. BELOUsov.—See B., 1931, 25.

Colorimetric microanalysis. I. Determination of bismuth, aluminium, and zinc. M. TEITELBAUM (Z. anal. Chem., 1930, 82, 366—374).— Bismuth, aluminium, and zinc precipitates obtained by the addition of 8-hydroxyquinoline to feebly acid acetate solutions (containing tartrate also in the case of bismuth) may be determined colorimetrically by centrifuging the precipitate, dissolving it in 1 c.c. of 4N-hydrochloric acid, and treating the solution with 6 c.c. of a cold saturated solution of sodium carbonate and 0.5—1 c.c. of a solution of 4 g. of phosphomolybdic acid and 20 g. of sodium tungstate in 150 c.c. of water which has been boiled for 2 hrs. under reflux with 10 c.c. of 85% phosphoric acid, cooled, and diluted to 200 c.c. The resulting blue colour is compared with that produced by standard solutions prepared under similar conditions. Bismuth may also be precipitated with pyrogallol from neutral solution and the precipitate treated similarly for colorimetric determination of the metal. A. R. POWELL.

Determination of bismuth in lead ores by internal electrolysis. E. M. Collin.-See B., 1931, 25.

Micro-balance. J. DONAU (Mikrochem., 1931, 9, 1-14).-A description of a new micro-balance, with directions for its manipulation. E. S. HEDGES.

Apparatus for fluorescence microscopy and fluorescence photomicrography. P. METZNER (Mikrochem., 1931, 9, 72-89). An apparatus for the microscopical examination of fluorescence is described, a parabolic mirror serving as the source of illumination. When an ultra-violet lamp is used with the apparatus photomicrographs can be obtained.

E. S. HEDGES. Micro-m. p. apparatus. L. KOFLER and H. HILBCK (Mikrochem., 1931, 9, 38-44).—The microm. p. apparatus described has been tested on a number of substances and the results are compared with those in the literature. For m. p. below 200° the greatest error was  $\pm 1^{\circ}$  and for m. p. between 200° and 300° the greatest error was  $\pm 2^{\circ}$ . The mean errors are less.

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Determination of the m. p. of platinum. G. RIBAUD and P. MOHR (Compt. rend., 1931, 192, 37-38).—Optical extrapolation from the m. p. of gold (1063°) was employed (cf. Ribaud and Nikitine, A., 1929, 366, 967), the mid-point of a hole in the wall of an electrically-heated platinum tube being directed on a potentiometrically-compensated thermoelectric cell calibrated in terms of a pyrometer for 1° intervals 10° below the m. p. The pyrometer was then directed on a black body at a temperature corresponding with the current obtained at the m. p., the brilliance of which was then adjusted by means of a revolving sector to correspond with a temperature approximately equal to that of the m. p. of gold. The difference in temperatures could then be calculated from the effective wave-length of the light concerned and the transmission factor of the sector. The value  $1762\pm2^{\circ}$  was found for platinum (purity 99.99%).

J. GRANT.

Electric furnace for elementary micro-analysis according to Pregl. B. FLASCHENTRÄGER (Mikrochem., 1931, 9, 15-19).-The advantages of a short type of electric heater for the elementary analysis of organic compounds are pointed out and an apparatus of the type has been constructed. E. S. HEDGES.

Electric tube furnaces, especially for microanalysis. P. A. THIESSEN (Chem. Fabr., 1930, 493-495).-The furnace comprises a thick-walled hollow cylinder of aluminium silicate refractory, the upper longitudinal half of which is removable to allow the introduction of the combustion tube. Heating is effected by means of longitudinal spirals of nickelchromium wire laid in a series of longitudinal grooves around the central hole of the refractory cylinder. The use of the furnace in the micro-analysis of organic compounds by combustion is described.

A. R. POWELL.

Shelf to increase ashing capacity of laboratory electric furnace. R. HERTWIG (Cereal Chem., 1930, 7, 556).—A removable asbestos shelf is described. E. B. HUGHES.

Immersion liquids for determination of refractive index of solids. A. MAYRHOFER (Mikro-chem., 1931, 9, 52-71).—For the determination of the refractive index of solids by the immersion method, the optical properties of some liquid mixtures have been investigated with the object of supplying the widest possible range. Water-glycerol mixtures are available for refractive indices between 1.333 and 1.465, cincole-paraffin mixtures between 1.456 and 1.482, paraffin-1-bromonaphthalene mixtures be-tween 1.482 and 1.658, and 1-bromonaphthalenemethylene iodide mixtures between 1.658 and 1.740. The temperature coefficients of the refractive indices of the mixtures have been determined.

E. S. HEDGES.

Interference method for measuring the refractive index of solutions. C. BORTOLOTTI (Nuovo Cim., 1930, 7, 148-152; Chem. Zentr., 1930, ii, 948).—An apparatus for the measurement of small differences in n of dilute solutions with change of concentration is described. A. A. ELDRIDGE.

Conductivity measurements and conductometric determinations. F. L. HAHN (Z. Elektrochem., 1930, 36, 989-991).-A galvanometer employed as a null instrument in conjunction with a copper-cuprous oxide-lead detector affords a convenient and accurate means of measuring the conductivity of electrolytes and is especially suitable for conductometric titrations. H. F. GILLBE.

Apparatus for electrometric analysis employing an electron tube. E. BERL, W. HERBERT, and W. WAILLIG (Chem. Fabr., 1930, 445-446, 458-460). -The electron tube is an ideal voltmeter, as direct readings can be obtained without any compensating device. The bridge, rhcostats, etc. formerly necessary are eliminated and only a simple and cheap milliammeter is required. The practical absence of current also gives much more liberty in the construction of the electrodes. The tube used is a vacuum bulb containing three electrodes; the heated element is a tungsten wire covered with alkali oxide. The effect of the screen-grid potential on the anode current is described. Slight changes in this potential produce an easily measured current change. The authors derive the compensating current for the ammeter from the heating battery, thus eliminating one battery and rendering the zero of the instrument almost constant. The anode current must not be less than 100 volts for  $p_{\rm ff}$  measurement, but for electrometric titration 50-100 volts is suitable. Measurement of  $p_{\rm ff}$  values can be made in a few seconds, using a buffer solution of

known  $p_{\rm H}$ , with an accuracy of 0.05—0.1  $p_{\rm H}$ . The apparatus requires standardising once a month. For electrometric titration a beaker is mounted on a tripod and supplied with a calomel electrode, agitator, and burette with bent delivery tube. A potential curve is obtained from the first titration, and the exact point of discontinuity obtained by a second one.

C. IRWIN.

Portable  $p_{\rm H}$  apparatus. A. ITANO (Ber. Ohara Inst. Landw. Forsch., 1930, 4, 471-474).—A combined galvanometer and millivoltmeter has been introduced into a modification of an earlier apparatus (A., 1929, 1034). A. COHEN.

Determination of the fall in potential in a micro-electrophoresis cell. J. GIBBARD (Science, 1930, 72, 398—399).—Apparatus and method for determining the fall in P.D. at any stage of an experiment without loss of time are described.

L. S. THEOBALD.

Automatic mercury still. A. KRETHLOW (Z. tech. Physik, 1930, 11, 159–160; Chem. Zentr., 1930, ii, 947).—An electrically operated automatic mercury still of pyrex glass is described. A. A. ELDRIDGE.

Micro-sublimation. A. CHALMETA.—See this vol., 246.

Apparatus for measurement of the surface tension of liquids. M. CHOPIN (Compt. rend., 1930, 191, 1293-1295).—The apparatus is designed for quantities of sap or latex of the order of 0.15 - 0.3 c.c. It consists of a cylinder suspended from the beam of a balance so that the base is immersed in a thin crown of the liquid placed in the right angle formed at the point of intersection of a slightly smaller cylinder (diameter 40 mm.) and a metallic block, above which the cylinder projects by about 3 mm., and which is perforated to allow access of air to both sides of the film. Increasing weights are applied to the other arm of the balance (e.g., by means of a long, thin glass rod dipping below a water level which is falling continuously), when the top cylinder rises carrying a narrow ring of liquid with it, which eventually breaks. An electrical heater serves to clean the apparatus between experiments, and cold water may be circulated through the metal block for cooling purposes. The weight of the film may be determined from that of the drop adhering to the top cylinder after the experi-J. GRANT. ment.

Colour measurement. C. SCHAEFER and H. PESE (Physikal. Z., 1931, 32, 1—16).—The Ostwald method is considered. An indirect test of the method is described involving the neutralisation of opposite colours. A direct test is also arranged, but in many of the examples there is disagreement. The numerical calculation of "white content" and brightness is given. A. J. MEE.

Continuous extraction apparatus. P. A. W. SELF and C. E. CORFIELD (Quart. J. Pharm., 1930, 3, 408—409).—A perforated glass container rests on a coil of wire at the constriction of the cylindrical outer vessel which connects the flask with the condenser. The apparatus is suitable for general work and for the extraction of vegetable drugs.

R. CHILD.

Integrating photometer for X-ray crystal analysis. B. W. ROBINSON (Proc. Roy. Soc., 1930, A, 130, 120-133).-A detailed account is given of an improved form of Astbury's a-ray photometer (A., 1927, 912; 1929, 745), and the precautions to be observed in order to obtain accurate results are discussed. In practice, the background estimation sets the limit to the accuracy of the instrument. The results obtainable are reviewed. A set of measures made on the equatorial planes of the c zone of anthracene are found to be in fair agreement with the corresponding intensities obtained by means of the ionisation spectrometer. It is considered that the  $\alpha$ -ray photometer is the best instrument to employ for the complete survey of the intensities of reflexion from a crystal, particularly when the crystal is small or easily L. L. BIRCUMSHAW. volatile.

Optical pyrometry. A. C. EGERTON and M. MILFORD (Proc. Roy. Soc., 1930, A, 130, 111-119).-The advantages of the magnifying pyrometer are discussed. A special composite glass filter has been devised in which use is made of the sharp edge of an absorption band of a "didymium" glass at about 5750 Å.; a band of light 130-140 Å. in visible width is transmitted between 5740 and 5600 Å., about 70% of the energy being within the region  $5670\pm25$  Å. Simple methods of calibrating a pyrometer are described, using a wedge as a black-body source or a platinum tube provided with a small hole. The temperatures are determined by melting small pieces of metal on the outside of the tube or wedge, or preferably by hanging a wire down the centre of the tube. It is an advantage to provide two monochromatic glasses for the pyrometer, as observations can then be made in two wave-lengths at a definite temperature. L. L. BIRCUMSHAW.

Measurement of surface temperatures. W. F. ROESER and E. F. MUELLER (Bur. Stand. J. Res., 1930, 5, 793—802).—Two types of contact thermometer are described and illustrated. For the measurement of surface temperatures up to 700° a heavily heatinsulated chromel-alumel couple with the hot junction embedded in a gold disc is used; the instrument is calibrated to allow for a standard difference of 10%between the temperature of the surface and that which the gold disc attains in contact with the surface. For surface temperatures up to 250° a compensated thermocouple terminating in a disc of hard bearing metal gives results for moving surfaces, *e.g.*, milk-drying rolls, within 1° of the actual value. A. R. POWELL.

Instantaneous locking clamp for universal stand. A. BARBOT (Bull. Soc. chim., 1930, [iv], 47, 1331—1332).—A simple form of clamp, suitable for gripping apparatus of very variable dimensions up to 60 mm. diameter, is illustrated.

J. R. I. HEPBURN.

**Pyknometer.** F. G. HOFFMANN (Chem.-Ztg. 1930, 54, 936—937; cf. B., 1930, 974).—An openmouthed pyknometer consists of a small (50-c.c.) beaker in which the level of the liquid is controlled by a gauge-point. The density of solids, powders, etc. can be readily determined; for liquids a sinker of known volume is used in order to avoid error due to meniscus differences. E. LEWKOWITSCH. Oxygen bomb calorimeter. E. STANSFIELD and J. W. SUTHERLAND (Canad. J. Res., 1930, 3, 464—472).—An improved type of bomb calorimeter, constructed of acid-resistant steel (Hadfield's Era steel, C.R.2), is described. By improvement of the heat conduction of the crucible and its supports thermal equilibrium is attained within 5 min. of the firing of the charge. The use of a vacuum-insulated calorimeter is criticised, since irregular changes in the water equivalent and rate of cooling of the system have been observed. T. H. MORTON.

X-Ray tube to furnish the homogeneous Kradiations of uranium. W. MOPPETT (J. Cancer Res. Comm. Sydney, 1930, 2, 147—152).—A demountable water-cooled glass X-ray tube operates at 140 kilovolts continuous current supplied by a Gaiffe-Gallot constant-potential generator, and is designed to give a maximum output of homogeneous penetrating K radiation (0.10842—0.13095 Å.) of uranium. The tube has steel end-pieces, one forming the anode, and the target is a copper plate, into which is ground uranium oxide, and is covered by a lead-arsenic alloy shield; the cathode is a Coolidge filament and focussing bowl. The radiation generated is filtered free of L-rays and stray secondary radiation, the efficiency being increased by utilising the radiation passing through a thin target of uranium. Experimental energy curves and a spectrogram are reproduced.

N. M. BLIGH.

Vacuum evaporation and distillation [in the laboratory]. H. N. NAUMANN (Chem. Fabr., 1930, 505-507).—Continuous vacuum evaporation may be performed by an apparatus with a continuous feed into the distillation flask. The end of a Liebig condenser is connected to a water-jet vacuum pump and the distillate passes away with the water. Two types of collecting vessel are described for distillation purposes when the distillate is to be recovered. One suitable for up to 3 litres of liquid per hr. consists of a double tube with cock connected to a second pump, the lower tube being emptied from time to time. For higher distillation rates a single tube with 3-way cock connected to two receivers used alternately is more suitable. This apparatus requires in all 3 pumps. A boiling capillary of V2A steel previously described has been improved by increasing the diameter to 0.7 mm.; a wire of the same material is also used. It is resistant to all reagents except concentrated hydrochloric acid and has many advantages over glass capillaries.

C. IRWIN. Arrangement for fractional distillation in the laboratory. W. PRAHL (Chem. Fabr., 1930, 517—519).—The essential feature of the apparatus is a glass tap which regulates the rate at which the vapour enters the receiving condenser, thus providing a control of the equilibrium. E. S. HEDGES.

Resistance thermometers. C. G. MAIER (J. Physical Chem., 1930, 34, 2860—2868).—A copper resistance thermometer which eliminates hysteresis and drift due to differential thermal expansions is described and a method of calibration is given. A formula giving the resistance of a thermometer of commercial copper wire is recorded and a modified type of thermometer suitable for laboratory use at temperatures below 100° is described. The advantages of copper resistance thermometers are discussed. L. S. THEOBALD.

## Geochemistry.

Occurrence of elements of the vanadium group in volcanic minerals. G. von HEVESY, E. ALEXANDER, and K. WÜRSTLIN (Z. anorg. Chem., 1930, 194, 316—322).—The mean niobium, tantalum, and vanadium contents of 282 specimens of volcanic rocks were  $3 \cdot 2 \times 10^{-7}$ ,  $2 \cdot 4 \times 10^{-7}$ , and  $2 \times 10^{-4}$  g. per g., respectively. The protoactinium content, calculated from the radium content, was  $7 \times 10^{-13}$  g. The relative frequency of occurrence of the elements of the vanadium group in volcanic rocks and in meteorites is discussed. H. F. GILLBE.

Zeolites. I. General review. M. H. HEY (Min. Mag., 1930, 22, 422-437).—A review of the literature, with bibliography, on the constitution, dehydration, and base-exchange of the zeolites.

L. J. SPENCER.

Simple method of observing the magnetic properties of mineral grains. F. SMITHSON (Min. Mag., 1930, 22, 419—421).—Two darning needles with their points 0.5—4.0 mm. apart are mounted in a cardboard frame over a horseshoe magnet. This is brought near the grains immersed in a heavy liquid under the microscope; grains of ilmenite, garnet, tourmaline, staurolite, biotite, and monazite can be distinguished by their behaviour. L. J. SPENCER. Cupriferous melanterite from Skouriotissa mine, Cyprus. M. H. HEY (Min. Mag., 1930, 22, 413—418).—A fine group of large  $(18 \times 13 \text{ cm.})$ crystals, transparent and sky-blue in colour, was found in an ancient (Roman?) stope in the cupriferous pyrites ore. In colour and habit the crystals suggest chalcanthite, but a crystallographic and optical examination proves them to be monoclinic, although of unusual habit for melanterite, being tabular parallel to the plane of symmetry and with several new crystal forms. A partial analysis gave CuO  $2\cdot15\%$ , corresponding with CuSO<sub>4</sub>,7H<sub>2</sub>O 7·72\% in isomorphous mixture with FeSO<sub>4</sub>,7H<sub>2</sub>O. The amount of copper is not sufficient to refer the mineral to pisanite. L. J. SPENCER.

Tellurium ores. H. BORCHERT (Neues Jahrb. Min., 1930, A, 61, 101—138; Chem. Zentr., 1930, ii, 711).—Corrosion figures and colours, obtained by the use of nitric acid, aqua regia, or ferric chloride solution, are described for the following minerals: calaverite, sylvanite, krennerite, petzite, hessite, nagyagite, altaite, and coloradorite. A. A. ELDRIDGE.

Amethysts and quartz rich in solid inclusions. R. WEIL (Compt rend., 1930, 191, 1350-1352).—In (e.g.) crystals of Brazilian origin, inclusions perpendicular to the ternary axis may be of two types: (a) The birefringent compensation planes are parallel to the (1010) face of the prism, and, to some extent, repeated as in ordinary quartz. (b) The neutral planes are perpendicular to the prism faces, extending towards the centre at inclinations of 120° or 60°. The two types of plane are analogous to those of L- and S-quartz, respectively (this vol., 46), and, when they coexist, may exhibit interpenetration. Planes having optical rotation are always present. J. GRANT.

Chemical and crystallographic investigations on Vesuvian litidionite. G. CAROBBI (Rend. Accad. Sci. Fis. Mat. Napoli, 1930, [iii], **36**, 21-31).—The identity of Scacchi's neocianite (A., 1882, 370) with litidionite (cf. Zambonini, Rend. Accad. Sci. Fis. Mat. Napoli, 1909—1910, [ii], **14**) is established, and the formula determined to be (Cu,Na<sub>2</sub>,K<sub>2</sub>)Si<sub>3</sub>O<sub>7</sub>. The crystallographic and physical constants are given.

T. H. POPE.

Infusorial earth from Akhaltzikh (Caucasus). D. WEINBERGER (Masloboino Zhir.-Delo, 1929, No. 1, 16—17).—The infusorial earth, d 0.53, contains SiO<sub>2</sub> (soluble in sodium hydroxide solution) S2.30, (insoluble), 4.90, FeO 0.215, Fe<sub>2</sub>O<sub>3</sub> 0.559, Al<sub>2</sub>O<sub>3</sub> 0.560, CaO 0.400, MgO 0.072, P 0.008, loss on ignition 4.30, H<sub>2</sub>O (105°) 6.70%. It rapidly adsorbs dyes from aqueous solution and decolorises vegetable oils.

CHEMICAL ABSTRACTS.

Curtisite, a new organic mineral from Skaggs Springs, Sonoma County, California. F. E. WRIGHT and E. T. ALLEN (Amer. Min., 1930, 15, 169–173).—The mineral, H < 2,  $d \ 1.235$ —1.237, orthorhombic, yellow to yellowish-green, plcochroic,  $n_{\rm D} \alpha \ 1.557$ ,  $\beta \ 1.734$ ,  $\gamma \ 2.07$ , when recrystallised from benzene, contained C 93.91, H 5.57%; mol. wt. 292; m. p. about 370°. The probable formula is  $C_{24}H_{18}$ . CHEMICAL ABSTRACTS.

Moors of Tekir-Ghiol and Agigea. N. T. DELEANU and R. HOFMANN (Bull. Acad. Sci. Roumaine, 1930, 13, 111—128).—Soil from Tekir-Ghiol is richer in sulphides, organic sulphur compounds, sodium, chlorine, and iodine than that from Agigea, whilst the latter has a larger content of potassium, calcium, iron, and aluminium. The Tekir-Ghiol soil has a greater heat capacity. P. G. MARSHALL.

Physical and chemical characteristics of certain American peat profiles. I. C. FEUSTEL and H. G. BYERS (U.S. Dept. Agric., Tech. Bull., 1930, No. 214, 26 pp.).—Numerous physical and chemical data concerning various types of peat are recorded. Of physical properties the moisture-holding capacity and moisture equivalent are the most definitely indicative of type. In the segregation of peat profiles the most useful chemical characteristics include the ether and alcohol extractives, hemicelluloses and cellulose, lignin-humus complexes, soluble and insoluble nitrogen, and ash composition. No evidence was obtained in support of the theory of lignite formation from present peat deposits. These probably consist of indefinitely preserved layers of plant remains, once permanently submerged, the degree of decomposition of which is indicated by the lignin-humus complexes. A. G. POLLARD.

Development of the soil profile in N. Wales as illustrated by the character of the clay fraction. G. W. ROBINSON (J. Agric. Sci., 1930, 20, 618—639).— Variations in the composition of the clay fractions in the different horizons of soil profiles are utilised in the classification of soil series. Changes in the ratio silica : sesquioxides throughout a profile are indicative of the course of the eluviation process. In the soils examined there was an accumulation of sesquioxides (notably ferric oxide) in the lower layers at the expense of the surface layers. A. G. POLLARD.

Types of clay in south-west Finland. B. AARNIO (Stat. Markforskningsinst. Agrogeol. Medd., 1928, Nr. 28; Proc. Internat. Soc. Soil Sci., 1930, 5, 243).—Chemical and physical characteristics, manurial requirement, and cropping power of numerous types of clays are recorded. A. G. POLLARD.

Tuff-soils of Maifeld. P. PFEFFER (Sitzungsber. Preuss. Geol. Landesanst., 1930, [5]; Proc. Internat. Soc. Soil Sci., 1930, 5, 212).—An examination of pumiceous soil profiles is recorded. The relative ease of decomposition of pumice largely influences chemical variations in the profile, there being a general decrease in hydrochloric acid-soluble constituents from the surface downwards. The molecular ratio  $SiO_2: Al_2O_3:$  bases of the acid-soluble material remains practically constant throughout the profile. Magnesium is the most important base in the surface soils. The exchangeability of bases increases from the surface downwards, and univalent bases are more in evidence than is the case with normal soils.

A. G. POLLARD.

Principal soils of the Black Sea region and their agricultural characteristics. S. A. ZAKHAnov (Ann. Rep. Soils N. Caucasus, 1929; Proc. Internat. Soc. Soil Sci., 1930, 5, 245).

Natural acidity of the chief virgin soil types of Roumania. J.F. RADU (Bul. Agric. Bukarest, 1930; Proc. Internat. Soc. Soil Sci., 1930, 5, 208).

# Organic Chemistry.

Physico-chemical organic analysis. M. LECAT Gazzetta, 1930, 60, 704—719).—A scheme for the recognition of the chemical type of an organic compound is based on the type of azeotropism shown by the compound when mixed with certain test substances, which differ according to the b. p. of the unknown compound. For compounds of b. p. at about 150° glycol, methyl oxalate, and s-tetrachloroethane are suggested as test substances; for liquids of b. p. at about 185°, phenol, aniline, and acetamide, and for liquids of b. p. at about 225°, glycol, o-nitrotoluene, and pyrocatechol are suggested. The nature of the azeotropism shown by these substances with various classes of compounds is tabulated. F. G. TRYHORN. Determination of the empirical formula of a hydrocarbon. E. W. WASHBURN (Bur. Stand. J. Res., 1930, 5, 867—890).—Mathematical. Methods and tables are given for deducing the empirical formula of any hydrocarbon containing less than 100 carbon atoms from a determination of the mol. wt. alone (when less than 300) or in conjunction with a combustion analysis; sometimes the determination of the bromine addition number may be used instead of one of the first-mentioned determinations. The determination of a trustworthy "average formula" for a mixture of hydrocarbons and the influence of impurities and of polymerisation are also discussed.

A. R. POWELL.

Formation of methane during the electrolysis of potassium acetate and the mechanism of Kolbe's electrosynthesis. S. N. SHUKLA and O. J. WALKER (Trans. Faraday Soc., 1931, 27, 35-40).--Under certain conditions methane is present together with ethane amongst the gases evolved at a platinum anode during the electrolysis of aqueous potassium acetate solutions of various concentrations. Methane is formed in appreciable amounts only at low current densities (below about 10 milliamp./cm.<sup>2</sup>), and for a given current density the proportion of methane to ethane is greater the more concentrated is the solution. The mechanism of Kolbe's electrosynthesis and the recent work of Fichter (cf. A., 1929, 1247, 1403) are discussed. O. J. WALKER.

Synthesis and spectrochemistry of *n*-alkanes. A. KARVONEN (Suomen Kem., 1930, 3, 101-111).-Reduction of  $\gamma$ -iodopentane with zinc dust and a saturated solution of hydrogen iodide in acetic acid at 0° (bath) gives *n*-pentane, b. p.  $36\cdot3^{\circ}$  (corr.)/758.8 mm.,  $d_4^{20}$  0.62783,  $n_D^{20}$  1.35828 (cf. Philipov, A., 1916, i, 551). The density and refractive index are higher than the corresponding values for various specimens of n-pentane described in the literature [all of which have been obtained from natural sources (e.g., petroleum)], indicating that these products contain small amounts of impurities (e.g., isopentane). Comparisons of the molecular and specific refraction or dispersion alone are valueless, as all the samples show the same value. *n*-Heptane, prepared by similar reduction of  $\delta$ -iodoheptane, has b. p. 98.0—98.2° (corr.)/762 mm.,  $d_4^{s0}$  0.68480,  $n_D^{s0}$  1.38939 (cf. Tafel and Jürgens, A., 1909, i, 545). The refractivity data are similar to those for *n*-heptane prepared by other methods and obtained from natural sources. Reduction of hept-aldehyde (Clemmensen, A., 1913, i, 733) gives impure n-heptane. H. BURTON.

Polymerisation and ring formation. VII. *n*-Paraffins of high mol. wt. prepared by the action of sodium on decamethylene bromide. W. H. CAROTHERS, J. W. HILL, J. C. KIRBY, and R. A. JACOBSON (J. Amer. Chem. Soc., 1930, 52, 5279— 5288; cf. Franke and Kienberger, A., 1913, i, 2).— Treatment of decamethylene bromide (0.25 mol.) with powdered sodium (1.52 atoms) in ether affords an ether-insoluble product, m. p. 85—100°, containing about 2% of bromine (removed by treatment with sodium in boiling butyl ether). The halogen-free product, m. p. 87—105°, is separated by fractionation in a molecular still and crystallisation into *n*-eicosane, *n*-triacontane, n-tetracontane, m. p.  $80.5-81^{\circ}$ , npentacontane, m. p.  $91.9-92.3^{\circ}$ , n-hexacontane, m. p.  $98.5-99.3^{\circ}$ , n-heptacontane, m. p.  $105-105.5^{\circ}$ , and a non-distillable residue, m. p.  $110-114^{\circ}$ , which probably contains higher members of the series. The physical properties of the new paraffins are discussed. A mechanism is suggested which involves reaction between the intermediate sodium derivatives and ether. Improved methods of preparation of decamethylene glycol and bromide are given.

H. BURTON. Errors in analytical bromination. Thermal cleavage of hydrogen bromide from brominated substances. Procedure for determination of organic unsaturation. H. M. BUORWALTER and E. C. WAGNER (J. Amer. Chem. Soc., 1930, 52, 5241-5254).—An apparatus is described for the bromination of compounds in carbon tetrachloride in absence of moisture at 0-75°; excess of bromine and the hydrogen bromide formed during the experiment are removed in dry nitrogen, absorbed in aqueous potassium iodide, and determined by the usual methods. Under favourable conditions of temperature, the method gives better results (for about 40 substances examined) than does that of McIlhiney (A., 1903, ii, 340); "negative" results (cf. McIlhiney, loc. cit.) are completely eliminated. The values obtained for various unsaturated substances are affected greatly by the reaction temperature. This is due to the elimination of hydrogen bromide from the additive compounds first formed (e.g., from the bromides from retene, abietic acid, and phenanthrene); this can be obviated by regulating the temperature at which bromination is carried out. H. BURTON.

Phosphoric acid. III. Use of phosphoric acid in the preparation of ethylene. A. G. WEBER and J. H. WALTON (J. Physical Chem., 1930, 34, 2693-2700; cf. A., 1930, 537).—In the preparation of ethylene from ethyl alcohol and phosphoric acid, the highest yields are obtained with syrupy phosphoric acid which has been heated for at least 41 hrs. at 250°. The reaction is continuous at this temperature, giving a yield of 81% of ethylene so long as alcohol is added to the previously-heated acid. The yield decreases by 10-20% at 240° and at 260° is not markedly increased. The addition of metaphosphoric acid decreases the yield by about 15%, but that of the pyro-acid or of phosphoric oxide lowers it only temporarily. Copper oxide, anhydrous copper or aluminium sulphate, silver oxide or sulphate, iron oxide, and animal charcoal give a 10% increase, and ferric chloride, molybdenum or tungsten trioxide, nickel oxide, and silica gel a smaller increase, whilst normal sodium phosphate tends to decrease the normal yield. In each case the yield approaches a maximum and then decreases to a normal value and the yield of the first run of a series is always low owing to the formation of esters. Generally, the gas obtained contains less than 1% of impurity. The catalysts appear to render the intermediate complex of alcohol and acid less stable or to provide a slightly different " pivot " for the reaction.

L. S. THEOBALD.

Pyrolysis of propylene. C. D. HURD and R. N. MEINERT (J. Amer. Chem. Soc., 1930, 52, 4978-4990).-Propylene decomposes to the extent of 60 and 72.5% when passed through pyrex-glass tubes at  $650^{\circ}$  and  $700^{\circ}$  with contact times of 120 and 50 sec., respectively. No decomposition occurs below  $600^\circ$ ; at  $900-950^\circ/0.5$  sec., 90-95% of the propylene is decomposed. The gaseous product consists mainly of hydrogen, methane, othylene, and other gaseous parafins (chiefly ethane); the total volume of gaseous products and the amounts of hydrogen and methane increase with rise in temperature and contact time. In pyrex (or quartz) tubes, 20-25% of the propylene used is converted into aromatic hydrocarbons (benzene, toluene, and probably small amounts of naphthalene and anthracene). The reaction in pyrex is predominantly homogeneous and unimolecular, and pyrolysis is of the same type as that of isobutylene (A., 1930, 58). Decomposition of a mixture (approximately 1:1) of propylene and hydrogen gives increased amounts of methane and ethylene; fission of the propylene molecule occurs.

Decomposition of propylene in monel metal tubes begins at  $350^{\circ}$  and is almost complete at  $375^{\circ}/30$  sec. The reaction is autocatalytic and the products formed are carbon and hydrogen. H. BURTON.

Isoprene and caoutchouc. XXXI. Polymerisation of *iso*butylene. H. STAUDINGER and M. BRUNNER (Helv. Chim. Acta, 1930, **13**, 1375—1379). *iso*Butylene is polymerised by Florida earth (cf. Lebcdev and others, A., 1925, i, 225; 1930, 316) first at  $-80^{\circ}$  and then at 5°, and the mixture of products separated by distillation and subsequent extraction with alcohol into tri*iso*butylene, penta*iso*butylene, and a poly*iso*butylene,  $d_4^{17}$  0.9007,  $n_6^{17}$ 1.5022. The poly*iso*butylene is purified by precipitation from an ethereal solution with alcohol; it is stable towards nitric acid and potassium permanganate but absorbs some bromine. Its physical properties are similar to those of a hemicolloidal hydrocaoutchouc. H. BURTON.

Nitrosites and nitrosates. L. MONTI (Gazzetta, 1930, 60, 787—797).—That higher members of the olefine series form additive compounds when treated with nitrous fumes (from arsenious oxide and nitric acid) is shown by the preparation of the nitrosite,  $C_8H_{16}O_3N_2$ , in this way from diisobutylene and by determining the proportion of nitrogen peroxide absorbed by octylene, diisobutylene, and hexadecylene when left in contact with the gas; under the latter conditions, hexadecylene yields the compound  $C_{16}H_{32}O_4N_2$ . When heated in a current of an inert gas, amylene nitrosate and  $\alpha$ - and  $\beta$ -styrene nitrosites yield nitrogen and nitric oxide, the total nitrogen thus evolved in the two forms constituting 40.5—41.8% of the nitrogen present in the original compound.

T. H. POPE.

Synthesis of  $\Delta^{ab}$ -pentadiene. P. N. KOGERMAN (J. Amer. Chem. Soc., 1930, 52, 5060—5065).— Magnesium is treated with a small amount of allyl bromide in presence of ether and iodine, and after reaction has begun, vinyl bromide (improved method of preparation given) is added. This mixture is treated gradually with allyl bromide; the reaction is carried out in a closed system under a pressure of 260— 270 mm. The distillate from this is brominated, whereby  $\Delta^{ab}$ -pentadiene tetrabromide, m. p. 85—86°, is obtained in 22% yield (on vinyl bromide used).  $\Delta^{ab}$ -Pentadiene has b. p. 25·8—26·2°/756 mm.,  $d_4^{39}$ 0·6594,  $n_D^{ab}$  1·3883, when regenerated from the tetrabromide by treatment with magnesium in ether containing a little iodine. The hydrocarbon is also formed when ethylene dibromide and allyl bromide are treated with magnesium. Treatment of magnesium allyl bromide with vinyl bromide gives no hydrocarbon. H. BURTON.

Action of nitric acid on acetylene. III. A. QUILICO and M. FRERI (Gazzetta, 1930, 60, 721— 744; cf. A., 1930, 622).—The explosive compound  $C_4H_2O_7N_6$  obtained by the action of fuming nitric acid on acetylene is reduced by stannous chloride as follows:  $C_4H_2O_7N_6+7H_2\longrightarrow C_4H_7O_3N_5+NH_2$  OH  $+3H_2O$ , and the resulting hydrochloride,  $C_4H_8O_3N_5Cl$ , m. p. about 182° (decomp.), has been isolated. The hydrochloride gives a characteristic orange-yellow coloration with alkalis, which is due to the compound  $C_4H_5O_2N_5$ . The above-mentioned explosive compound decomposes when heated in glacial acetic acid as follows:  $C_4H_2O_7N_6\longrightarrow C_4H_2O_3N_4+N_2O_4$ . The compound  $C_4H_2O_3N_4$  has m. p. 108°.

O. J. WALKER.

Hexa-w-tert.-butylpropinylethane and acetylenic carbinols. I. L. OZANNE and C. S. MARVEL (J. Amer. Chem. Soc., 1930, 52, 5267-5272).-Magnesium tert.-butyl chloride and β-bromoallyl bromide give β-bromo-δδ-dimethyl-Δa-pentene, b. p. 135-138°,  $d_4^{20}$  1.030,  $n_D^{20}$  1.4630, converted by sodamide in highboiling mineral oil into  $\delta\delta$ -dimethyl- $\Delta^{\alpha}$ -pentinene, b. p. 73-75°,  $d_1^{20}$  0.7154,  $n_D^{20}$  1.4028 [mercury derivative, m. p.  $125-126\cdot5^{\circ}$  (corr.)]. Successive treatment of this with magnesium ethyl bromide and ethyl carbonate (cf. A., 1928, 988) affords tri- $\omega$ -tert.-butylpropinylcarbinol, b. p. 140-142°/0.7 mm., m. p. 50-51°, which with acetyl bromide and "molecular" silver in light petroleum yields hexa-w-tert.-butyl-propinylethane, m. p. 127.5—128.5°. This is unstable to oxygen, gives a red alkyl with liquid sodiumpotassium alloy in ether, is not cleaved by 1% sodium amalgam, and is oxidised by ozone in carbon tetrachloride to \$\$-dimethylbutyric acid (p-bromophenacyl ester, m. p. 81-81.5°).

Treatment of the reaction product from magnesium ethyl bromide and  $\delta\delta$ -dimethyl- $\Delta^a$ -pentinene (ozonolysis product  $\beta\beta$ -dimethylbutyric acid) with benzophenone gives diphenyl- $\omega$ -tert.-butylpropinylcarbinol, m. p. 55—56°, the bromide of which is converted by "molecular" silver into s-tetraphenyldi- $\omega$ -tert.-butylpropinylethane, m. p. 116—118°. Phenyldi- $\omega$ -tert.butylpropinylcarbinol, b. p. 135—137°/0·4 mm.,  $d_4^{39}$ 0·9325,  $n_D^{39}$  1·5080; diphenyl- $\omega$ -cyclohexylpropinylcarbinol, b. p. 165—166°/0·003 mm.,  $d_4^{39}$  1·058,  $n_D^{39}$ 1·5750, and phenyldi- $\omega$ -cyclohexylpropinylcarbinol, b. p. 180—185°/0·017 mm.,  $d_4^{39}$  1·014,  $n_D^{39}$  1·5390, are also described. H. BURTON.

**Preparation of allyl derivatives.** R. BRECKPOT (Bull. Soc. chim. Belg., 1930, **39**, 462–469).—Allyl chloride is prepared in excellent yield by the action of a mixture of concentrated hydrochloric and sulphuric acids on allyl alcohol in presence of a little cuprous chloride. Instead of allyl alcohol, allyl formate or the mixture of aqueous allyl alcohol and allyl formate obtained from glycerol and formic acid may be used.  $\Delta^{\beta}$ -Butenonitrile may be prepared in good yield by the action of cuprous cyanide on allyl chloride, on a mixture of concentrated hydrochloric acid and allyl alcohol, or on a mixture of concentrated hydrochloric acid and allyl formate. J. D. A. JOHNSON.

Stereoisomeric pairs of chloro-n-butenes. L. NAVEZ (Bull. Soc. chim. Belg., 1930, 39, 435-443).-The butenes prepared (A) by the action of concentrated sulphuric acid +5% of aluminium sulphate on n-butyl alcohol on treatment with chlorine give a mixture of dichlorobutanes of which 41% boils below 121°, whereas the mixture of butenes prepared (B) by the catalytic dehydration of n-butyl alcohol at 410-420° using alumina as catalyst gives a mixture of dichlorobutanes of which 90% boils below 121°. The mixture of dichlorobutanes is separated by fractional distillation into I, m. p.  $-80.4\pm0.1^{\circ}$ , b. p.  $115.9^{\circ}$ ,  $d_4^{15}$  1.1147,  $n_{15}^{15}$  1.4445; II, b. p. 119.5°,  $d_1^{15}$  1.1183,  $n_{15}^{15}$  1.4458; III, b. p. 124°,  $d_1^{15}$  1.1224,  $n_{15}^{15}$  1.4474. By the action of alcoholic potassium hydroxide (1.25 mols.) on each of these dichlorobutanes (1 mol.), chlorobutenes are obtained which are separated by fractional distillation of their azeotropic mixtures with alcohol. From III, azeotropes of alcohol with three chlorobutenes are obtained; III (a) b. p. 53.6-54°,  $d_{4}^{15}$  0.8945; III (b) b. p. 57.8–58.2°,  $d_{4}^{15}$  0.8946; III (c) b. p.  $61.2-61.6^{\circ}$ ,  $d_{1}^{15}$  0.8912. The chlorobutenes corresponding have the following constants; (a) b. p.  $58.4 - 58.6^{\circ}$ ,  $d_{4}^{15} 0.9107$ ,  $n_{p}^{141} 1.4166$ ; (b) b. p.  $63 \cdot 4 - 63 \cdot 6^{\circ}$ ,  $d_4^{15}$  0.9153,  $n_D^{15}$  1.4194; (c) b. p. 68-68.2°,  $d_4^{15}$  0.9205,  $n_D^{14}$ ° 1.4225. The azeotropes contain respectively 88.5%, 85.2%, and 79.8% of the corresponding chlorobutene. From I and II, the same azeotropes of two chlorobutenes are obtained; I or II (d) b. p.  $56.8-57.2^{\circ}$ ,  $d_4^{15}$  0.8960; I or II (e) b. p. 60-60.4°,  $d_4^{15}$  0.8964. The chlorobutenes corresponding had the following constants: (d) b. p.  $62 \cdot 4 - 62 \cdot 8^{\circ}$ ,  $d_4^{15} \ 0.9185$ ,  $n_D^{13 \cdot 4} \ 1 \cdot 4217$ ; (e) b. p.  $66 \cdot 6 - 67^{\circ}$ ,  $d_4^{15} \ 0.9246$ ,  $n_D^{13 \cdot 4} \ 1 \cdot 4250$ . The azeotropes contain respectively 84.6% and 81.6% of the corresponding chlorobutene. Since III yields three chlorobutenes, whereas I and II yield two only (all five different), it is considered to be  $\alpha\beta$ -dichlorobutane, I and II being the meso- and r-forms of By-dichlorobutane, respectively. Method A is to be preferred to method B, therefore, for the preparation of  $\Delta^{\alpha}$ -butene from *n*-butyl alcohol. The rates of elimination of hydrogen chloride from (d) and (e) by means of alcoholic potassium hydroxide are held to show that (d) is trans- $\beta$ -chloro- $\Delta^{\beta}$ -butene and (e) is the cis-form. For similar reasons (b) and (c) are considered to be the cis- and trans-forms of  $\alpha$ -chloro- $\Delta^{\alpha}$ -butene respectively, whilst (a), because of its volatility, is considered to be  $\beta$ -chloro- $\Delta^{\alpha}$ -butene.

Geometrical inversion of these unsaturated substances under the influence of sunlight does not take place. J. D. A. JOHNSON.

Stereochemistry of organic compounds. II. Spatial arrangement of the atoms in the pentaerythritol molecule. L. ORTHNER and G. FREYSS (Annalen, 1930, 484, 131—154).—The specific conductivity of boric acid is not increased by the *iso*propylidene or dimethyl ethers of pentaerythritol or by pentaerythritol dibenzoate. The difficult formation of the disopropylidene ether from the *iso*propylidene ether and the inability of the above compounds to form complexes with boric acid are explained thus : after inactivation of two hydroxyl groups by substitution, the remaining hydroxyl groups become removed from one another in space, owing to their taking up a position of minimal potential energy. Pentaerythritol causes an increase in the conductivity of boric acid; this is ascribed to the formation of the complex

 $\begin{bmatrix} (CH_2 \cdot OH)_2 C < CH_2 \cdot O \\ CH_2 \cdot O \end{bmatrix} B < \begin{bmatrix} O \cdot CH_2 \\ O \cdot CH_2 \end{bmatrix} C \\ (CH_2 \cdot OH)_2 \end{bmatrix} H,$ in which the free hydroxyl groups are arranged so that further reaction with boric acid is not possible. The above points are illustrated by models.

The sodium derivative of pentacrythritol isopropylidene ether (A., 1928, 270) and methyl iodide in xylene give pentaerythritol isopropylidene methyl ether, b. p. 129-130°/12 mm. (p-nitrobenzoate, m. p. 90°), hydrolysed by aqueous methyl-alcoholic sodium hydroxide to pentaerythritol methyl ether, m. p. 72°. Treatment of the isopropylidene ether with methyl sulphate and potassium hydroxide solution at 70-100° gives a mixture of pentaerythritol dimethyl, b. p. 139°/12 mm., m. p. 32° (dibenzoate, m. p. 70°), and trimethyl ethers, b. p. 103-104°/12 mm. (p-nitrobenzoate, m. p. 53-54°). Pentaerythritol dibenzoate, m. p. 75°, and diacetate, b. p. 159°/0.3 mm., are obtained from the corresponding isopropylidene ethers, m. p. 110° and 48-49°, respectively, by hydrolysis with dilute hydrochloric acid at the ordinary temperature. Pentaerythritol tetrabenzoate has m. p. 94°.

The dipole moments of pentaerythritol tetraacetate and disopropylidene ether are  $2\cdot 18\pm 0\cdot 03 \times 10^{-18}$  (cf. Ebert, A., 1928, 1308; Williams, *ibid.*, 1180) and  $2\cdot 26\pm 0\cdot 07 \times 10^{-18}$  c.g.s. unit, respectively.

H. BURTON.

Automatic distillation of ether, alcohol, chloroform, etc. under reduced pressure. C. LAPP (J. Pharm. Chim., 1930, [viii], 12, 498-502).-The liquid to be distilled is automatically drawn from a reservoir along a glass tube and through a three-way tap into the top of a fractionating column the side arm of which is connected to a condenser and the bottom to another, smaller condenser inclined at an angle of about  $20^\circ$  from the horizontal. This latter condenser, which is of the bulb type and contains pieces of nickel foil in each bulb, is heated to about 80° by means of water, which siphons through the jacket and through a glass spiral enclosing an ordinary 30 c.-p. electric lamp, the whole being insulated by cotton wool. The solvent is volatilised during its passage through this condenser and the vapours pass up the fractionating column, thereby scrubbing the incoming liquid from the receiver, and are condensed and pass into the receiver, which is connected to the vacuum pump. The heavier, unvaporised fractions pass through the heating condenser into a second receiver. The most satisfactory temperature for the distillation of the three above-mentioned solvents is

10-20°, using water at a correspondingly low temperature in the condenser. E. H. SHARPLES.

Catalytic decomposition of gaseous ethers. P. A. K. CLUSIUS (J.C.S., 1930, 2607-2615; cf. A., 1929, 1148).-Methyl ethyl ether is decomposed at 460—550° according to the equations : Me·O·Et $\rightarrow$  $CH_4 + Me \cdot CHO$ ,  $Me \cdot CHO \longrightarrow CH_4 + CO$ , the heat of activation of the former, which has only 1/45th of the velocity of the latter, being 38,000 g.-cal. per mol. The reaction is homogeneous in the presence of iodine vapour (derived from thermal decomposition of isopropyl iodide) as catalyst, the velocity being proportional to the partial pressure of iodine, but independent of the initial pressure of ether. The decomposition of methyl isopropyl ether at 450-520° is in accordance with the simultaneous reactions:  $Me \cdot O \cdot Pr \longrightarrow CH_4 + COMe_2$ , and  $Me \cdot O \cdot Pr \longrightarrow CH_2O +$  $C_3H_8 \longrightarrow CO + H_2 + C_3H_8$ , the heat of activation being 29,500 g.-cal. per mol. for the net reaction, which is homogeneous and independent of the original pressure of ether. Methyl tert.-butyl ether is stable at 420°, but is immediately decomposed in presence of iodine to a complex mixture containing unsaturated hydrocarbons but free from aldehydes and ketones. Iodine is without catalytic effect on the thermal decomposition of dimethyl ether. H. A. PIGGOTT.

Preparation of the pure isomerides of amyl nitrite. S. D. WILSON and E. F. YANG (Chinese J. Physiol., 1930, 4, 391-392).-The following isomerides were prepared from the appropriate amyl alcohol, sodium nitrite, and sulphuric acid: n-amyl nitrite, b. p. 51.5-52.1°/132 mm., d19.5 0.8817, nies 1.3902; isoamyl nitrite, b. p. 98.2-99.2°/760 mm., d<sup>195</sup> 0.8828, n<sup>108</sup> 1.3909; sec.-amyl nitrite, b. p. 96.0-96.5°/760 mm., d<sup>195</sup> 0.8626, n<sup>163</sup> 1.3864; tert.amyl nitrite, b. p. 62.0-63.0°/345 mm., d105 0.8758, W. O. KERMACK. n188 1.3904.

Interaction of ammonium sulphite with certain polybromoparaffins. W. J. POPE and F. B. KIPPING (J.C.S., 1930, 2591-2594).-Interaction of  $\alpha\beta\gamma\delta$ -tetrabromo- $\beta\gamma$ -dimethylbutane with boiling aqueous ammonium sulphite, followed by successive treatment with barium hydroxide and silver oxide, gives the barium salt  $(+1H_{0}O)$  of a  $\beta\gamma$ -dimethylbutenedisulphonic acid (ammonium and sodium salts; pyridine salt, m. p. 215-216°; chloride, m. p. 125-126°). βγ-Dibromobutane similarly treated gives two isomeric  $\beta$ -hydroxybutane- $\gamma$ -sulphonic acids, the brucine salts of which may be separated by repeated crystallisation from 90% alcohol [(A), brucine salt, m. p. 270°,  $[\alpha]_{3\mu_1}^{3\nu_1} - 23.9°$  in water; barium salt,  $[\alpha]_{3\mu_1}^{3\nu_2} - 5.4°$  in water; 1-menthylamine salt, m. p. 196°. (B), brucine salt, m. p. 180-185°, [α]<sup>30</sup><sub>1401</sub> -29.6° in water; barium salt, optically inactive].

H. A. PIGGOTT.

Addition of alkali alkoxides to esters. IV. Addition of sodium ethoxide to formic esters. F. ADICKES [with O. LÜCKER, A. WACHTEROWITZ, and H. DU MONT] (Ber., 1930, 63, [B], 3012-3027).-The author's supposition (A., 1927, 228) that the product obtained by the action of ethvl formate on sodium ethoxide according to Scheibler's first method (A., 1926, 711) has the homogeneous composition

CH(OEt). ONa cannot be maintained, although the

substance is present to some extent. Contrary to Scheibler, a large proportion of the ester is decomposed into alcohol and carbon monoxide and another portion does not react with the ethoxide. The product consists mainly of sodium ethoxide with more or less alcohol of crystallisation (about 30%), some sodium formate (about 8%), and generally only about 10-20% of the additive compound CH(OEt), ONa. Scheibler's second method of preparation in which the product is heated to 40° (A., 1927, 338) involves the more rapid decomposition of ethyl formate, which occurs slowly at the ordinary temperature (Scheibler's "vigorous reaction"). The final product is not sodiumoxyethoxymethylene, but mainly sodium ethoxide more or less free from alcohol of crystallisation according to the duration of heating. In the products obtained by both methods the presence of formic acid is shown quantitatively by titration and by reduction of mercuric chloride. It exists partly as sodium formate (due to incomplete removal of water from the alcohol used) and partly as ethyl formate, which is liberated as such when the ethereal suspension of the product is treated with carbon dioxide. Presumably it is contained as the compound CH(OEt), ONa, since sodiumoxyethoxymethylene could not regenerate the ester under these conditions. Homogeneous sodiumoxyethoxymethylene or sodiumoxydiethoxymethane cannot be present in the product obtained by either method; in the first product the last-named substance may occur to the extent of 25%, but not at all in the second. There is no possibility of the existence of sodiumoxyethoxymethylene with the properties recorded by Scheibler, since in no case is evolution of carbon monoxide observed on decomposition with water, and the ester is completely accounted for partly as carbon monoxide evolved during the reaction, partly as sodium formate and regenerated ester. The production of diethoxymethylene from the additive compound according to Scheibler is readily possible on theoretical grounds. The additive compound of ethyl formate (1 mol.) and sodium ethoxide (1 mol.) is easily prepared from the components in ethereal suspension at 0°. It is very hygroscopic and readily decomposed at the ordinary temperature with formation of carbon monoxide. It is not possible to prepare derivatives of ethyl orthoformate from it by means of ethyl chloroformate or benzyl bromide, so that its constitution (as sodiumoxydiethoxymethane) cannot be established directly. When its ethereal suspension is treated with ethyl oxalate, ethyl formate is liberated.

It is certain that sodiumoxyethoxymethylene with the properties indicated by Scheibler cannot be prepared by either of his methods, whereas the production of a differing sodiumoxyethoxymethylene in small amount at the ordinary temperature is not completely negative, although rendered very improb-H. WREN. able.

Preparation of ethyl A'-elaidate by partial reduction of ethyl  $\Delta^{\theta_{\kappa}}$ -linoleate, and the corresponding acid as member of the elaidic acid series. J. BOESEKEN and R. HOEVERS (Rec. trav. chim., 1930, 49, 1161-1164).-Ethyl  $\Delta^{\theta \kappa}$ . linoleate when catalytically partly hydrogenated gives ethyl  $\Delta$ '-elaidate, the position of the double linking acid being proved by ozonolysis. The m. p. of the (42°) is considered to show that the acid has the elaidic acid configuration. J. D. A. JOHNSON.

Polymerisation of the methyl esters of higher unsaturated fatty acids. V. Esters with one 4-carbon ring. K. KINO (J. Soc. Chem. Ind. Japan, 1930, 33, 444—445 B; cf. A., 1930, 577, 741, 1272).— The polymerisation of the methyl esters of the highly unsaturated acids (clupanodonic acid, *loc. cit.*) has been repeated, the products being purified by vacuum distillation; a product having  $d_4^{40.5}$  0.9192,  $n_{20.5}^{50.5}$  1-4820 and corresponding almost to  $C_{22}H_{33}O_2Me$  was separated, and on hydrogenation yielded a solid fatty acid (lead salt-alcohol separation), m. p. 79—79-3°, probably identical with the acid (m. p. 78—78-2°) obtained previously. The earlier conclusions appear to be confirmed. E. LEWKOWITSCH.

Photochemical oxidation of lactic acid. G. R. BURNS (J. Amer. Chem. Soc., 1930, 52, 5272—5278; cf. A., 1929, 1424).—Aqueous solutions of lactic acid containing dissolved oxygen are decomposed by radiations of less than 2890 Å. The main products of the decomposition are carbon dioxide, acetic acid (75%; the percentages are based on the amount of carbon dioxide evolved), a peroxide (32%), and acetaldehyde (28%); small amounts of formaldehyde and carbon monoxide, but no alcohol or pyruvic acid, are formed. The quantum yield is several times that of the decomposition in absence of oxygen (cf. loc. cit.).

### H. BURTON.

Hydrogenation of ethyl acetoacetate and its derivatives over nickel. H. ADKINS, R. CONNOR, and H. CRAMER (J. Amer. Chem. Soc., 1930, 52, 5192—5198).—Ethyl acetoacetate is reduced by the method previously described (this vol., 47) in absence of solvent at 100—150° to a mixture of 2 parts of ethyl  $\beta$ -hydroxybutyrate (I) and 1 part of ethyl  $\beta$ -( $\beta$ 'hydroxybutyryloxy)butyrate (II),

OH·CHMe·CH<sub>2</sub>·CO<sub>2</sub>·CHMe·CH<sub>2</sub>·CO<sub>2</sub>Et, b. p. 154- $156^{\circ}/15$  mm.,  $d_{23}^{25}$  1.0678,  $n_{12}^{25}$  1.4360, together with small amounts of alcohol and dehydroacetic acid. When the reduction is carried out in presence of alcohol, I is the sole product; in presence of ether, methylcyclohexane, or ethyl \$-hydroxybutyrate, mixtures of approximately 2 parts of I and 1 part of II are formed, whilst in n-butyl alcohol a mixture of 66% of I and 34% of n-butyl  $\beta$ -hydroxybutyrate results. The formation of II supports the mechanism postulated by Arndt and Nachtwey (A., 1924, i, 1223) for the production of dehydroacetic acid from ethyl acetoacetate. Ethyl a-methylacetoacetate is reduced to a mixture of ethyl β-hydroxy-a-methylbutyrate and ethyl  $\beta$ -( $\beta'$ -hydroxy- $\alpha'$ -methylbutyroxy)- $\alpha$ -methylbutyrate, b. p.  $155-158^{\circ}/17$  mm.,  $d_{25}^{25}$  1.0332,  $n_{0}^{25}$  1.4393, whilst ethyl aa-dimethyl- and a-methyl-a-ethylacetoacetates furnish quantitative yields of the corresponding hydroxybutyrates both in absence and presence of solvent. Reduction of dehydroacetic acid in presence of methylcyclohexane at 185-190°/ about 300 atm. gives 40-45% of dipropyl ketone, together with small amounts of alcohol and acetone, Alcoholysis of dehydroacetic acid to ethyl acetoacetate occurs at 190°.

The *a-naphthylcarbinide* derivative of dipropylcarbinol has m. p. 79–80°. H. BURTON.

Decomposition of ethyl *n*-butylacetoacetate to hexoic acid and methyl *n*-amyl ketone. N. L. DRAKE and R. W. RIEMENSCHNEIDER (J. Amer. Chem. Soc., 1930, **52**, 5005—5008).—Optimum yields (about 60%) of hexoic acid are obtained when ethyl *n*-butylacetoacetate is decomposed with  $59 \cdot 5\%$  potassium hydroxide solution (8 mols. of hydroxide) at  $75-110^\circ$ . The best yield of ketone is obtained with approximately 17% alkali at  $105^\circ$  (bath). H. BURTON.

Lævulic acid and its esters. P. P. T. SAH and S. MA (J. Amer. Chem. Soc., 1930, 52, 4880—4883).— When commercial dextrose (500 g.) is heated with diluted (1:1) hydrochloric acid for 24 hrs. (after a preliminary, short treatment and removal of humin substances), lævulic acid is obtained in yields of about 75 g. The following esters of lævulic acid were prepared: methyl, b. p. 191—193°,  $d_1^{39}$  1·05113,  $n_1^{99}$ 1·4231 (semicarbazone, m. p. 142—1143°; phenylhydrazone, m. p. 94—96°); ethyl, b. p. 199—201°,  $d_1^{49}$  1·01336,  $n_1^{59}$  1·4225; n-propyl, b. p. 214—216°,  $d_1^{49}$ 0·98988,  $n_2^{51}$  1·4255 (semicarbazone, m. p. 129—130°; phenylhydrazone, m. p. 88—90°); isopropyl, b. p. 203—205°,  $d_1^{49}$  0·98422,  $n_2^{59}$  1·4220 (semicarbazone, m. p. 141—142°; phenylhydrazone, m. p. 108—109°); n-butyl, b. p. 229—231°,  $d_1^{49}$  0·97452,  $n_1^{51}$  1·4290 (semicarbazone, m. p. 102—103°; phenylhydrazone, m. p. 79—81°); isobutyl, b. p. 222—224°,  $d_2^{49}$  0·97047,  $n_2^{59}$ 1·4264 (semicarbazone, m. p. 112—113°; phenylhydrazone, m. p. 84—86°); isoamyl, b. p. 238—240°,  $d_2^{51}$  0·95921,  $n_2^{50}$  1·4310 (semicarbazone, m. p. 91—92°; phenylhydrazone, m. p. 70—72°). H. BURTON.

Reactivity of atoms and groups in organic compounds. XI. Influence of structure of the substituent on the temperature of decomposition of derivatives of malonic acid. J. F. NORRIS and R. C. YOUNG (J. Amer. Chem. Soc., 1930, 52, 5066-5069).--The decomposition temperatures of the following acids, determined by a method similar to that Ing actus, determined by a method similar to the previously described (A., 1930, 470), are given in parentheses: malonic, m. p.  $129-131^{\circ}$  ( $128^{\circ}$ ); methylmalonic, m. p.  $120-122^{\circ}$  ( $120^{\circ}$ ); ethyl-malonic, m. p.  $110-111\cdot5^{\circ}$  ( $110^{\circ}$ ); *n*-propylmalonic, m. p.  $94-96^{\circ}$  ( $99^{\circ}$ ); *n*-butylmalonic, m. p.  $99\cdot5-$ 101.5° (108°); isopropylmalonic, m. p. 85-87° (90°). The influence of the alkyl group (R) on the decomposition temperature is the same as that found for the triphenylmethyl alkyl ethers, CPh3. OR (loc. cit.). The decomposition temperatures in both series fall in the same order as the velocity coefficients for the reactions between p-nitrobenzoyl chloride and the alcohols R.OH (A., 1925, i, 626; 1927, 1166). H. BURTON.

Ether-like compounds. III. Polyether-acids of the type  $OR \cdot [CH_2 \cdot CH_2 \cdot O]_n \cdot CH_2 \cdot CO_2 H$ . M. H. PALOMAA and T. A. SHTONEN (Ber., 1930, 63, [B], 3117-3120).—The action of chloroacetic acid on the sodium derivative of ethylene glycol monomethyl ether affords  $\beta$ -methoxyethoxyacetic acid,

OMe·CH<sub>2</sub>·CH<sub>2</sub>·O·CH<sub>2</sub>·O<sub>2</sub>H, b. p.  $121-122^{\circ}/4$  mm.,  $d_{4}^{20}$  1·1634,  $n_{10}^{20}$  1·43375, in 80% yield; the *cthyl* ester has b. p. 90°/10 mm.,  $d_{4}^{20}$  1·0369,  $n_{10}^{20}$  1·41908. β-*Ethoxyethoxyacetic acid*, b. p. 125-126°/4 mm.,  $d_{4}^{20}$  1·1103,  $n_{D}^{\infty}$  1·43572, and β-n-propoxyethoxyacetic acid, b. p. 131°/4 mm.,  $d_{40}^{20}$  1·07415,  $n_{D}^{\infty}$  1·43652, are described. *n*-Butyl glycol, b. p. 50°/4 mm.,  $d_{40}^{20}$  0·9015,  $n_{D}^{\infty}$  1·41980, is transformed into β-n-butoxyethoxyacetic acid, b. p. 141°/5 mm.,  $d_{40}^{20}$  1·04635,  $n_{D}^{20}$  1·43823. β-Methoxyethylglycol, b. p. 65°/4 mm.,  $d_{40}^{20}$  1·02695,  $n_{D}^{20}$  1·42686, yields ββ'-methoxyethoxyethoxyacetic acid, b. p. 155—156°/4 mm.,  $d_{40}^{20}$  1·1492,  $n_{10}^{10}$  1·44575. H. WREN.

Additive heteropolymerisation. T. WAGNER-JAUREGG (Ber., 1930, 63, [B], 3213—3224).—The term "homopolymerisation" is applied to the union of several similar molecules, whereas the union of different molecules to a large molecule is designated "additive heteropolymerisation." It is proposed to discriminate between true and false polymerisation according as the process is or is not accompanied by atomic displacement and to apply the term "condensation polymerisation" to processes involving the elimination of water, ammonia, etc.

Additive heteropolymerisation of two ethylenic compounds, one of which is maleic anhydride, has been investigated. Maleic anhydride and stilbene in boiling xylene afford in 45-70% yield an amorphous white, infusible substance, insoluble in most organic media, but sometimes yielding colloidal solutions after swelling, for example, in camphor. Direct determination of mol. wt. is impossible, but the more soluble polymeric homologues dissolved from the product by boiling xylene have mean mol. wt. about 4200 in molten camphor. Dry distillation in absence or presence of barium oxide yields stilbene. The ratio of the components in the polymeride is 1:1 when a mixture of hydrocarbon and anhydride in the ratio 2:1 is used, falling to 0.95:1 (stilbene to anhydride) when the composition of the original mixture is 1 mol. of hydrocarbon to 2 mols. of anhydride. The product has therefore the composition

-  $[CHPh \cdot CHPh \cdot CH < CH^{CH-CO}_{CO-O}]_{x}$ , in conformity with which it does not absorb bromine in boiling s-tetrachloroethane. The polymerisation resembles that of acrylic acid, since a little less highly polymerised material is formed in addition to the main polymerisate, whilst the remainder of the initial material remains unchanged. Non-occurrence of polymerisation in boiling benzene or toluene is explicable, since the molecules do not possess the necessary activating energy, but a specific influence of the solvent is involved, since poor yields are obtained in boiling s-tetrachloroethane or in a molten mixture of the components at the temperature of boiling xylene. Conversely, benzylidenefluorene and maleic anhydride at about 130°, but not in boiling xylene, yield a white, amorphous heteropolymeride which separates from the molten mixture and appears unaccompanied by less complex products. The molecular ratio of hydrocarbon to anhydride is exactly 1:1 when that in the initial mixture is 2:1, and passes to 0.9:1 when the initial ratio is 1:2; the tendency towards excess of anhydride is again obvious. Anisylidenefluorene at 130° gives a similar heteropolymeride. αδ-Diphenyl- $\Delta^{a}$ -butene gives a mixture of products of differing degree of polymerisation and not excessive mol. wt. in which the ratio of the components is displaced in

favour of the anhydride. Bromostilbene, tetraphenylethylene, and  $\alpha\delta$ -diphenyl- $\Delta^{\beta}$ -butene do not react with maleic anhydride, thus indicating a profound influence of substitution; steric influences also operate, since cis-stilbene gives a heteropolymerisate only in very poor yield. as-Diphenylethylene and maleic anhydride afford the compound,  $C_{22}H_{16}O_6$ , m. p. 279–281° (corr., decomp.), M=376. Stilbene does not condense with succinic anhydride, whereas dibenzyl and maleic anhydride yield a heteropolymeride (1:1) in very poor yield. Amylene and styrene give viscous, gum-like products with maleic anhydride. Certain substances containing the >C:N· group appear to give heteropolymerides with maleic anhydride. Thus fluorenoneimine in benzene or benzylidene- or cinnamylidene-azine in toluene or xylene afford yellow or brown amorphous products. In addition to the amorphous products, benzylideneazine and maleic anhydride yield a crystalline additive substance,  $C_{22}H_{16}O_6N_2$ , m. p. 243—244° (corr.), whilst methyl malcate yields the product  $C_{26}H_{28}O_8N_2$ , m. p. 232— 234° (corr.). H. WREN. 234° (corr.).

Action of maleic anhydride on  $\Delta^{\theta \kappa}$ -linoleic acid (m. p. 53°) and its ethyl ester. Products of dehydration of ricinoleic acid. J. BÖESEKEN and R. HOEVERS (Rec. trav. chim., 1930, 49, 1165— 1168).—Linoleic acid and its ethyl ester combine normally with maleic anhydride to give exclusively substances of m. p. 88° and 60°, respectively. The substance, m. p. 88°, is also formed when the product of the reaction between maleic acid and linoleic acid is heated with acetic anhydride. By means of this reaction, the product of the dehydration of ricinoleic acid is shown to contain about 75% of linoleic acid, 15% of  $\Delta^{\theta \lambda}$ -linoleic acid, and a small quantity of an aldehydic substance.

J. D. A. JOHNSON.

Polymorphism of the saturated dibasic fatty acids as a function of temperature. F. D. LA TOUR (Compt. rend., 1930, 191, 1348—1350).—Two forms,  $\alpha$  and  $\beta$ , of succinic acid exist, the unstable  $\beta$ -form being transformed into the  $\alpha$ -form at 137°. The spatial arrangement of the carboxyl groups probably corresponds with *cis*- and *trans*-forms.

P. G. MARSHALL. Highly-polymerised compounds. XLVII. Morphology of substances of high mol. wt. II. Polyoxymethylenes precipitated from solution. H. W. KOHLSCHUTTER (Annalen, 1930, 484, 155-178).—Polyoxymethylenes ( $\alpha$ -,  $\beta$ -,  $\beta$ + $\gamma$ -; for nomenclature, see Staudinger and others, A., 1930, 579) have been precipitated under various conditions and the genesis and development of the crystals determined; photomicrographs are given. Addition of 1 vol. of sulphuric acid to 1 vol. of an aqueous solution of paraformaldehyde (d<sup>19</sup> 1.086) gives two types of crystals: (a) hexagonal laminæ showing a normal growth, (b) round disc-shaped crystals completely penetrated by the mother-liquor (which are not observed until they are fully formed). With 0.7 vol. of acid, the precipitated material consists of prisms (isometric habit) which when treated with 0.1N-sodium hydroxide solution, are attacked in the centre of the prism β-Polyoxymethylene, precipitated very zones.

rapidly by 0.4 vol. of acid, consists of granular masses to which are attached sphærolith-like structures; freshly-prepared material is attacked rapidly by 0.1N-alkali, but old preparations are attacked only slowly. The polyoxymethylene precipitated by 0.1 vol. of acid can be completely freed from sulphuric acid. Increase in the amount of acid used causes a rise in the velocity of aggregation and the formation of larger crystals. These crystals contain sulphuric acid in the "inner" surfaces; crystallisation begins by the formation of a film of material over a gel-drop, which subsequently grows into a plastic primary part. Two of these parts join to give a prismatic crystal, the centre of which is the weakest part. The crystals shrink on keeping and sulphuric acid can be washed out. There are morphologically continuous transitions between the  $\alpha$ -,  $\beta$ -, and  $\beta + \gamma$ -polyoxymethylenes.

Precipitation of polyoxymethylene from formaldehyde solutions containing methyl alcohol gives preparations which are alkali-stable; this behaviour is ascribed to the formation of polyoxymethylene dimethyl ether. H. BURTON.

Replacement of halogen by hydrogen in  $\alpha$ -halogenoketones under the influence of the Grignard reagent. C. H. FISHER, T. S. OAKWOOD, and R. C. FUSON (J. Amer. Chem. Soc., 1930, 52, 5036-5040).- a-Bromoisobutyryl bromide reacts with mesitylene in presence of carbon disulphide and aluminium chloride, forming a-bromoisobutyrylmesitylene, m. p. 27° (dinitro-derivative, m. p. 117.5- $118.5^{\circ}$ ); the dibromo-derivative, m. p.  $106-107^{\circ}$  (corr.), of this is also formed by bromination of isobutyrylmesitylene with ice-cold bromine water. Reduction of 4:6-dibromo-2-a-bromoisobutyrylmesitylene with zinc dust and acetic acid gives 4:6dibromo-2-isobutyrylmesitylene, m. p. 69-70°, also obtained when the tribromo-compound is treated with magnesium methyl chloride or ethyl bromide and the products are decomposed with dilute hydrochloric acid. The following changes occur during the treatment with the Grignard reagents (cf. Löwenbein and Schuster, A., 1930, 1184):  $\cdot$  CO·CBrMe<sub>2</sub>  $\longrightarrow$  $\cdot \mathrm{C(OMgBr)}\mathrm{:}\mathrm{CMe}_2 \longrightarrow \cdot \mathrm{CO}\mathrm{\cdot}\mathrm{CHMe}_2.$ H. BURTON.

Dioximes. LXVIII. I. DE PAOLINI (Gazzetta, 1930, 60, 700-704; cf. A., 1930, 226).—By the action of bromine on the dihydroxytrioxime,  $OH \cdot [C:N \cdot OH]_3 \cdot OH$ , on hydroxyglyoximecarboxylic acid, on oximinomalonic acid, and on oximinoacetic acid the oxime of carbonyl bromide,  $CBr_2:N \cdot OH$ , m. p. 70-71° (vac.), is obtained due to reaction of bromine with oximinoacetic acid. This oxime represents the most easily obtained derivative of the simpler derivatives of fulminic acid, from which it has also been prepared by the reaction C:N  $\cdot OH + Br_2 \longrightarrow CBr_2:N \cdot OH$ , thus confirming its structure. By the action of mercuric nitrate it forms dibromoglyoxime peroxide,  $Br(C_2N_2O_2)Br$ , or dibromofuroxan,  $Br[(C_2N_2O)O]Br$ . O. J. WALKER.

Degradations in the sugar group. V. DEULO-FEU (J.C.S., 1930, 2602-2607; cf. A., 1929, 427).-Tetra-acetylarabonitrile, m. p. 118°, from *d*-arabinoseoxime, sodium acetate, and acetic anhydride, gave with ammoniacal silver oxide *d*-erythrosediacetamide,

erythrose, and with less ammonia triacetylerythrose, m. p. 133°. Degradation of the nitrile by sodium methoxide, or sulphuric acid followed by treatment with barium hydroxide and silver carbonate, gave only traces of erythrose. Similar results were obtained with tetra-acetylxylononitrile from d-xylose, and the syrup resulting from degradation with sodium methoxide gave tartaric acid on oxidation with nitric acid. l-Rhamnonamide (from the lactone and ammonia) gave methylerythrose with hypochlorite and alkali. Degradation of tetra-acetylrhamnononitrile with sodium methoxide or sulphuric acid gave methylerythrose in poor yield, but application of these methods to penta-acetylgalactonitrile gave 30% and 22%, respectively, of the theoretical yields of  $\beta$ -lyxose. Penta-acetylmannononitrile, prepared from dmannoscoxime, gave *d*-arabinosediacetamide with silver oxide and ammonia, and arabinose by degradation with sodium methoxide or sulphuric acid in yields of 33%, 61%, and 56%, respectively. Arabinose was also obtained by oxidation of calcium mann-onate with hydrogen peroxide and "colloidal" ferric acetate. H. A. PIGGOTT.

m. p. 210°, hydrolysed by 60% sulphuric acid to

Titration of aldose sugars with standard iodine and alkali. G. M. KLINE and S. F. ACREE (Bur. Stand. J. Res., 1930, 5, 1063—1084; cf. A., 1930, 1560).—In the titration of aldose sugars with iodine and alkali it is necessary to avoid both oxidation beyond the monobasic acid stage ("over-oxidation") and the exhaustion of the iodine in the formation of iodate before the completion of the oxidation. With the procedure recommended (*loc. cit.*) the iodate content becomes significant only after the completion of the reaction, and over-oxidation is absent unless large excess of reagents is employed.

Sucrose and lævulose are slightly attacked by large excess of reagents; iodine and sodium hydroxide are used up in the ratio of 4:5, indicating the oxidation of a primary alcoholic to a carboxyl group. With the oxidation of an aldose sugar the ratio is 2:3, and it is suggested that this reaction may be used to titrate iodine against standard alkali, with an error of 0.2%. The reaction is complete at  $p_{\rm H}$  9–10.

T. H. MORTON.

Cupro-potassium carbonate solution in the determination of reducing sugars. H. A. SCHUETTE and J. N. TERRILL (J. Amer. Chem. Soc., 1930, 52, 4960—4964).—The dextrose-copper equivalents of the cupro-potassium carbonate solutions of Ost and Nyns have been determined at  $48.9^{\circ}$  (reduction time 150 min.) by the method of Zerban and Sattler (A., 1930, 1165); the results are presented as mathematical expressions. The solution used by Beyersdorfer (B., 1920, 126) (containing 0.8 mg. Cuper c.c.) is also reduced by dextrose; the solution cannot be regarded as being selective for lævulose. Mathematical expressions are also derived for calculating the lævulose-copper equivalents of a reagent (Beyersdorfer's) containing 4.03 mg. Cuper c.c., using three sets of reduction conditions. H. BURTON.

Transformation reactions in the carbohydrate group. IV. Kinetics of the transformation of 3-acetylisopropylideneglucose. K. JOSEPHSON. (Ber., 1930, 63, [B], 3089-3102; cf. A., 1929, 912).--Re-examination of the change of specific rotation with time of solutions of 3-acetylisopropylideneglucose  $(p_{\rm H} 7.19)$  at  $20 \pm 0.02^{\circ}$  shows that the reaction constant calculated for a unimolecular change exhibits a decided progressive variation, probably due to the formation of an intermediate product of unknown optical activity. For purposes of comparison, Schmid's method (A., 1926, 480) of calculating the mean reaction coefficient is adopted. Variation of the hydroxyl-ion concentration shows a proportionality between the rate of acyl migration and concentration of hydroxyl ion over a considerable range of acidity. The temperature coefficients of the change are smaller than those generally observed in cases of catalysis by hydroxyl ions, whereas for similar hydrogen-ion concentrations the temperature coefficients are much greater owing to the marked change of the ionic products of water with temperature. H. WREN.

Structure of carbohydrates and their optical rotatory power. W. N. HAWORTH and E. L. HIRST. Introduction. II. 4-Glucosido-a-mannose I. and derivatives. [With H. R. L. STREIGHT, H. A. THOMAS, and J. I. WEBB.] III. 4-Galactosido- $\alpha$ -mannose and derivatives. [With (MISS) M. M. T. PLANT and R. J. W. REYNOLDS.] IV. Derivatives of  $\alpha$ - and  $\beta$ -methylmannopyranoside. [With H. G. BOTT and (in part) R. S. TIPSON.] V. Optical rotatory powers of methylated lactones derived from simple sugars. [With J. A. B. SMITH] (J.C.S., 1930, 2615-2635, 2636-2644, 2644-2653, 2653-2659, 2659-2663).—I. Polemical. The claim of Hudson (A., 1930, 747) to classify sugars on a basis of optical rotation leads to many inconsistencies and necessitates the postulation of structures at variance with the bulk of experimental evidence. The rotations of a number of derivatives of 4-glucosido- and 4-galactosido-a-mannose do not agree with those calculated by Hudson on the basis of a hypothetical mannose of  $[\alpha]_{\rm b} +77^{\circ}$ , but conform to ordinary mannose  $(+30^{\circ})$  as unit. Further experimental evidence indicates that rotation may vary considerably and irregularly according to the solvent where a choice of solvent is possible, e.g., with the fully-methylated lactones derived from monoses. Conclusive proof of the pyranoside structure of the mannoside residue in 4-glucosido- and 4-galactosido- $\alpha$ -methylmannoside and the absence of the hypothetical form is afforded by their hydrolysis by emulsin to  $\alpha$ -methylmannopyranoside,  $[\alpha]_{\rm p}$  +79°, a method already tacitly approved by Hudson as a test of structure.

II. The action of perbenzoic acid on carefullydried cellobial in methyl-alcoholic ethyl acetate gives 4-glucosido- $\alpha$ -methylmannoside, m. p. 227—228°,  $[\alpha]_D^{15}$ +46° in water (hepta-acetyl derivative, m. p. 184°,  $[\alpha]_D^{15}$  +30° in chloroform, +36° in acetone, +21.5° in benzene), hydrolysed by emulsin to dextrose and  $\alpha$ methylmannopyranoside,  $[\alpha]_D$  +79°, the identity of which is confirmed by mixed-m. p. determinations and conversion into acetyl derivative. The pyranoside structure of the glucoside is confirmed by the slow rate of hydrolysis by 0.01N-hydrochloric acid. 4-Glucosido- $\alpha$ -methylmannoside is also obtained by interaction of hepta-acetyl-4-glucosido- $\alpha$ -mannosidyl bromide with methyl alcohol in presence of silver carbonate or pyridine. The rate of mutarotation of 4-glucosido- $\alpha$ -mannose,  $[\alpha]_{10}^{18} + 20^{\circ} \longrightarrow +12.5^{\circ}$  in water, is comparable with, but rather slower than, that of mannose. 4-Glucosido- $\beta$ -mannose has  $[\alpha]_{10}^{18} - 1^{\circ}$ determined indirectly (cf. Hudson and Yanovsky, A., 1917, i, 445).

If during the reduction of hepta-acetylcellobiosidyl bromide (cf. Zemplén, A., 1928, 741) the temperature rises to 30—35°, *hexa-acetyl-2-deoxycellobiose*, m. p. 196°,  $[\alpha]_{\mathbb{P}}^{\mathbb{P}} + 15^{\circ}$  in chloroform, is formed.

III. Oxidation of lactal (cf. Bergmann, A., 1924, i, 265; slight modifications of the preparation described) with perbenzoic acid in methyl alcohol and ether in the cold gives 4-galactosido-a-methylmannoside, m. p. 207°,  $[\alpha]_{D}^{19} + 66^{\circ}$  in water (hepta-acetyl compound,  $[\alpha]_{D}^{19}$  $+36^{\circ}$  in chloroform,  $+19^{\circ}$  in benzene), hydrolysed by emulsin to galactose and  $\alpha$ -methylmannopyranoside,  $\left[\alpha\right]_{11}^{11}$  +79.2° in water (identified as above). Neither a-methylmanno-pyranoside nor -furanoside is altered by emulsin under identical conditions. Confirmation of the pyranose structure of the glucoside is afforded by its slow hydrolysis at the biose linking only by 0.01N-hydrochloric acid. The action of perbenzoic acid on aqueous lactal (cf. Bergmann, loc. cit.) gives 4-galactosido- $\alpha$ -mannose (+1H<sub>2</sub>O), m. p. 150–160° (indefinite),  $[\alpha]_{10}^{20}$  +38°—>+27° in water, the rate of mutarotation being comparable with that of mannose. 4-Galactosido- $\beta$ -mannose (loc. cit.) has  $[\alpha]_{\rm D}$  +16° in 76% alcohol, calculated by Hudson and Yanowsky's method. Details are given for the separation of a-methylmanno-pyranoside or -furanoside from galactose by precipitation of the last in aqueous solution with lead acetate and ammonia. The yields of recovered mannosides are 30% and 40%, respectively. IV. When heated with 2% methyl-alcoholic hydro-

gen chloride, mannose gives a mixture of  $\alpha$ - and  $\beta$ -methylmannosides (cf. Hudson, *loc. cit.*); the latter may be separated and characterised as its tetraacetyl derivative which regenerates  $\beta$ -methylmanno-pyranoside when treated with 0.5N-aqueous alkali or dimethylamine and methyl alcohol.  $\beta$ -Methylmannoside is very slowly hydrolysed by 0.01N or even 0.1N hydrochloric acid at  $100^\circ$ ; methylation of it or its acetyl derivative with methyl sulphate and alkali, followed by methyl iodide and silver oxide, gives tetramethyl- $\beta$ -methylmannopyranoside, b. p. 110—112°/0·1 mm., m. p. 36—37°,  $n_0^{14}$  1·4531 (supercooled liquid),  $[\alpha]_{77}^{\infty}$ —80° in water, —79° in methyl alcohol, —87° in chloroform, —72° in benzene,  $-82^{\circ}$  in ethyl alcohol, equilibrium value  $+60^{\circ}$  in 1%methyl-alcoholic hydrogen chloride, hydrolysed by 6% hydrochloric acid to tetramethylmannopyranose, identified as anilide and by conversion into 2:3:4:6tetramethyl-ô-mannonolactone (cf. A., 1927, 750). Methylation of mannose by methyl sulphate and alkali, followed by methyl iodide and silver oxide, gives a mixture of tetramethyl- $\alpha$ - and - $\beta$ -methylmannopyranosides, containing about 32% of the latter, and free from furanose derivatives as indicated by resistance to hydrolysis with 0.01 N-hydrochloric acid at 90°. It was identified by conversion into 2:3:4:6tetramethyl-8-mannonolactone free from y-lactone. Simultaneous deacetylation and methylation of tetra-acetyl- $\alpha$ -methylmannopyranoside by gradual addition of methyl sulphate and alkali to a solution in acetone gives tetramethyl- $\alpha$ -methylmannopyranoside,  $[\alpha]_{1s}^{ls} + 43^{\circ}$ , converted by hydrolysis into tetramethylmannopyranose.

V. The optical rotations of fully-methylated lactones are not appreciably affected by the nature of the solvent where cis-methoxy-groups are absent (dextrose series), are more affected where cis-methoxygroups occur in positions 3 and 4 (galactose series), and vary considerably where such occur in positions 2 and 3 (mannose series). In every case unchanged lactone is recovered by evaporation. The following values of  $[\alpha]_{D}^{20}$  in water, chloroform, ether, and benzene, respectively, are recorded for carefully-purified substances : d-2:3:4:6-tetramethylmannonolactone,  $+150^{\circ}$ ,  $+59.5^{\circ}$ ,  $+35^{\circ}$ ,  $+20^{\circ}$ ; d-2:3:5:6-tetra-methylmannonolactone,  $+65^{\circ}$ ,  $-9.7^{\circ}$ ,  $-36.3^{\circ}$ ,  $-49\cdot2^{\circ}$ ; d-2:3:4-trimethyl-lyxonolactone,  $+35\cdot5^{\circ}$  $-60\cdot4^{\circ}$ ,  $-87^{\circ}$ ,  $-102^{\circ}$ ; d-2:3:5-trimethyl-lyxono-lactone,  $+82\cdot5^{\circ}$ ,  $-28^{\circ}$ ,  $-70^{\circ}$ ,  $-70^{\circ}$ ; l-2:3:4trimethylrhamnonolactone,  $-130^{\circ}$ ,  $-67.5^{\circ}$ ,  $-39.3^{\circ}$ ,  $-15.0^{\circ}$ ; l-2:3:5-trimethylrhamnonolactone,  $-57^{\circ}$ ,  $+13^{\circ}$ ,  $+65^{\circ}$ ,  $+87^{\circ}$ ; d-2:3:4:6-tetramethyl-gluconolactone,  $+98^{\circ}$ ,  $+103^{\circ}$ ,  $+123^{\circ}$ ,  $+121^{\circ}$ ; d-22:3:5:6-tetramethylgluconolactone,  $+62^{\circ}$ ,  $+42^{\circ}$ +67°, +68°; d-2:3:4-trimethylxylonolactone,  $\pm 0^{\circ}$ , +9°, +12°, +17°; d-2:3:4:6-tetramothylgalact-onolactone, +153°, +101°, +96°, +128°; d-22:3:5:6-tetramethylgalactonolactone,  $-34^{\circ}$ ,  $-13^{\circ}$ ,  $-11^{\circ}$ ,  $-11^{\circ}$ ; l-2:3:4-trimethylarabonolactone, +181°, +125°, +105°, +166°; l-2:3:5-trimethyl-arabonolactone,  $-44^{\circ}$ ,  $-9^{\circ}$ ,  $-3^{\circ}$ , +16°. -11°,

## H. A. PIGGOTT.

Ring structure of mannose. Optical rotation of 4-glucosido-a-mannose. H. S. IsBELL (Bur. Stand. J. Res., 1930, 5, 1179-1187).-4-Glucosido-amannose has been prepared by the deacetylation of the octa-acetate by means of a small quantity of barium methoxide in dry methyl-alcoholic solution at 0° for 20 hrs. At the close of the reaction the barium methoxide is quantitatively removed by the addition of an equivalent quantity of sulphuric acid. This method of deacetylation is of general application. The mutarotation of 4-galactosido-a-mannose monohydrate in water,  $[\alpha]_{10}^{\infty} + 14.64^{\circ}$  to  $+5.88^{\circ}$ , is a uni-molecular reaction. The epimeric difference in molecular rotation between 4-glucosido-a-mannose and cellobiose is 16,900, approximating to the difference, 14,900, between  $\alpha$ -d-glucose and  $\alpha$ -d-mannose. This suggests that the ring structures of  $\alpha$ -d-mannose and 4-glucosido-α-mannose are identical, a result opposed to that of Hudson (A., 1930, 747) derived from a consideration of the epimeric differences of the accto-halogen derivatives of these sugars. In addition, it is pointed out that the epimeric difference between 4-galactosido-3-mannose and 3-lactose corresponds with that between  $\beta$ -d-glucose and  $\beta$ -dmannose. It therefore appears that the use of these pairs of sugars as a crucial test (cf. Hudson, loc. cit.) of the ring structures of  $\alpha$ - and  $\beta$ -mannose is unsatisfactory. T. H. MORTON.

Structures of acetylmethylmannosides. H. S. ISBELL (J. Amer. Chem. Soc., 1930, 52, 5298).—The

following hepta-acetyl-4-glucosidomethylmannosides have been prepared by the Koenigs-Knorr reaction : " $\alpha$ "-, m. p. 185°, [ $\alpha$ ]<sub>D</sub><sup>\*</sup> +26·7° (all rotations in chloroform); " $\beta$ "-, m. p. 161°, [ $\alpha$ ]<sub>D</sub><sup>\*</sup> -22·3°, and " $\gamma$ "-, m. p. 167°, [ $\alpha$ ]<sub>D</sub><sup>\*</sup> -12·7°. These appear to be analogous to the three known acetylmethylmannosides (cf. Hudson, A., 1930, 747). The " $\gamma$ "-compound can be converted into a hepta-acetyl-4-glucosidomannose, [ $\alpha$ ]<sub>D</sub><sup>\*</sup> +21·7°, which does not exhibit mutarotation, thus indicating that the methoxyl group in the original compound is not in position 1. This supports the ortho-ester formula of Freudenberg (A., 1930, 894) and of Bott, Haworth, and Hirst (*ibid.*, 1024) for compounds of the above types. H. BURTON.

Crystalline  $\alpha$ - and  $\beta$ -methyl-*d*-gulosides. H.S. ISBELL (Proc. Nat. Acad. Sci., 1930, 16, 699-703).-The additive compound of d-gulose and calcium chloride is treated with 1% methyl-alcoholic hydrogen chloride, the mixture neutralised with calcium carbonate, and the resulting solution evaporated, whereby the additive compound  $(+2H_2O)$ , [a] about  $+60^\circ$ , of 1 mol. of  $\alpha$ -methyl-d-guloside and 1 mol. of calcium chloride separates. Repeated crystallisation of this affords the additive compound  $(+3H_2O)$ ,  $[\alpha] + 83^\circ$ , of 2 mols. of the guloside and 1 mol. of calcium chloride, which when decomposed with silver oxalate furnishes  $\alpha$ -methyl-*d*-guloside (+H<sub>2</sub>O), decomp. 77° with loss of H<sub>2</sub>O,  $[\alpha]_{\nu}^{20}$  +109°. The mother-liquor from the above preparation deposits the additive compound  $(+2H_2O)$ , m. p. 155°,  $[\alpha] - 46°$ , of 1 mol. of  $\beta$ -methyl-d-guloside and 1 mol. of calcium chloride; this is converted by crystallisation from alcohol into the (2:1) compound,  $[\alpha] - 65^{\circ}$ , of the guloside and chloride.  $\beta$ -Methyl-d-guloside has m. p. 176°,  $[\alpha]$ H. BURTON. -83°.

Synthesis of glucosides. VI. Preparation of  $\beta$ -glucosides of phenols. A. ROBERTSON and R. B. WATERS (J.C.S., 1930, 2729—2733).—The phenol is allowed to interact with O-tetra-acetyl- $\alpha$ -glucosidyl bromide and "active" silver oxide in quinoline, and the tetra-acetate produced hydrolysed by methylalcoholic ammonia (cf. Takahashi, J. Pharm. Soc. Japan, 1925, 525, 4; Zemplén and Müller, A., 1929, 1281). This method, which fails with alcohols, produces the  $\beta$ -modification alone. Use of pyridine in place of quinoline gives an impure product. The following were prepared:  $\beta$ -phenyl- and  $\beta$ -naphthylglucoside,  $[\alpha]_{D}^{n} = -26.7^{\circ}$  in 95% acetone; helicin (from salicylaldehyde); O-octa-acetyl-m-phenylenediglucoside, m. p. 203°,  $[\alpha]_{D}^{n} = -83.1^{\circ}$  in acetone; and O-tetra-acetyl-  $\beta$ -glucovanillin. O-Monobenzoylquinol, m. p. 161°, is readily converted into its tetra-acetylglucoside, m. p. 154—155°,  $[\alpha]_{D}^{n} = -63.97^{\circ}$  in acetone, hydrolysed by the standard method to arbutin. H. A. PIGGOTT.

Synthesis of glucosidoferulic acid. R. M. HANN (J. Amer. Chem. Soc., 1930, 52, 5049—5051).— Acetobromoglucose reacts with the potassium derivative of methyl ferulate (4-hydroxy-3-methoxycinnamate) in ether and alcohol, forming methyl tetraacetyl- $\beta$ -d-glucosidoferulate, m. p. 142—143° (corr.),  $[\alpha]_{\rm p}^{\infty}$ —32·3° in chloroform, hydrolysed by 6% barium hydroxide solution at the ordinary temperature to  $\beta$ -d-glucisodoferulic acid, m. p. 198—199° (corr.),  $[\alpha]_{\rm p}^{\infty}$ —36·6° in alcohol. H. BURTON. Varieties of starch and constitution of starch. S. VON NÁRAY-SZABÓ (Z. physikal. Chem., 1930, 151, 420-424; cf. A., 1928, 1224).—Differences in the X-ray diagrams of starches of different origin are due to variation in the water content. There is no chemical distinction between different starches. Differences between amylose and amylopectin are due partly to admixture of other substances and partly to their physical character. The constitution of starch is briefly discussed. F. L. USHER.

Supposed depolymerisation of glycogen. J. REILLY and H. PRINGSHEIM (Ber., 1930, 63, [B], 3210-3211).—A refutation of the criticism of Berner (this vol., 74). H. WREN.

Constant occurrence of non-reducing disaccharides in hydrolysed inulin. R. F. JACKSON and E. McDONALD (Bur. Stand. J. Res., 1930, 5. 1151-1160).-Members of the family Composite, burdock, golden-rod, dandelion, artichoke, and wild chicory, yield inulin, which after two fractionations gives a mixture of hydrolytic products of very nearly constant composition. The mixture consists of 31.0% of lævulose, 3.7% of dextrose, and 5.3% of non-reducing diffuctose anhydrides,  $[\alpha]_{10}^{10} + 49^{\circ}$  (cf. Jackson and Goergen, A., 1929, 1280). Dahlia and artichoke inulins have been subjected to 11 "recrystallisations," whereby 85% and 96%, respectively, of the original material was rejected. The composition of the products derived from these materials by acid hydrolysis is similar to the above, with the exception that dahlia inulin yields but 1.9% of dextrose. The non-reducing residue is preformed in the inulin, since polysaccharides related to inulin, soluble in 60-70% alcohol, derived from artichoke and iris yield, under similar hydrolytic conditions, lævulose and dextrose It is considered that these refractory diffuctose alone. anhydrides form an essential part of the molecule, which therefore contains not less than 110 hexose residues, corresponding with M 18,000.

### T. H. MORTON.

Highly-polymerised compounds. XLVIII. Molecular size of cellulose. H. STAUDINGER and O. SCHWEITZER (Ber., 1930, 63, [B], 3132-3154).--Hydrolysis of a series of polytriacetylcelloglucan diacetates, the mol. wt. of which has been determined according to Bergmann and Machemer and by measurement of viscosity (cf. A., 1930, 1415, 1416), yields a polymeric homologous series of polycelloglucan dihydrates. The mol. wt. of the dihydrates is uniformly greater than that of the corresponding acetates owing to removal of the simplest portions of the hydrolysate by the mother-liquors. It may, however, be assumed that the length of the chain of the polycelloglucan diacetates remains intact during conversion into the hydrates and that cellulose derivatives may be subjected to chemical change without altering the degree of polymerisation. The polycelloglucan dihydrates thus obtained are hemicolloids insoluble in water or formamide but soluble in Schweitzer's reagent; they are identical with the socalled cellodextrins or hydrocellulose. The behaviour of solutions of hemicolloidal polycelloglucan dihydrates in Schweitzer's solution is less complicated than expected, provided that the concentration of the reagent is maintained uniform and it is used in excess so that more than 1 atom of copper is present for each glucose residue. Solutions of a 70-polycelloglucan dihydrate do not change with time and obey the Hagen-Poiseuille law. Within the limits imposed by the volatility of the ammonia, the value  $\eta_{sp.}$  is independent of the temperature, so that the hydrates are dissolved as molecules, not micelles. The values  $\eta_{\rm sp.}/C$  for different concentrations are constant for the hemicolloids in quite dilute solution, but increase with the concentration when the degree of polymerisation exceeds 150. The viscosity of the hemicolloidal heteropolar polycelloglucan dihydrate complexes in Schweitzer's solution resembles that of hemicolloidal polystyrenes in benzene or tetrahydronaphthalene. With the simpler dihydrates of degree of polymerisation 30-100 the value  $K_m$  shows relatively little variation. With more complex products the value is less constant, possibly owing to the imperfect applicability of the Bergmann-Machemer method.

The viscosity of solutions of purified cotton in Schweitzer's reagent diminishes with time without becoming constant after 4 weeks. The change depends on the oxidative degradation of the macromolecules of the cellulose by copper oxide. Comparable values can be obtained only by use of solutions which have been preserved for equal intervals at the same temperature. When rapidly observed, the value  $r_{\rm sp.}/C$  at different temperatures is approximately constant; the primary colloid particles are therefore macromolecules, not micelles. The value is also independent of concentration and conditions of flow provided that the solutions are quite dilute (sol solutions). Calculation of the mol. wt. of cellulose from the viscosity of its solutions in Schweitzer's reagent shows that a more or less profound degradation of the molecule occurs according to the method of purification. The highest observed value (190,000) is for purified cotton. Slight degradation accompanies mercerisation. Sulphite-cellulose and copper-silk are more appreciably affected (mol. wt. 80,000-65,000 and 35,000, respectively). The apparent discrepancy between the behaviour of more dilute and concentrated solutions of cellulose in Schweitzer's reagent is explained, as in previous cases, by the consideration that the sphere of influence of dissolved thread molecules is much greater than that corresponding with the actual size of the molecules. About 0.2% solutions of cellulose in Schweitzer's reagent are gel solutions which show deviations from the Hagen-Poiseuille law. The swelling of cellulose in Schweitzer's reagent is not evidence of micellary structure, but is equally reconcilable with the presence of long molecules. The stability of macromolecules in the solid state and in solution is discussed. The highest observed value for the mol. wt. of cellulose can be regarded only as a minimum value for native cellulose, since it is not impossible that degradation occurs during swelling and dissolution. Possibly native cellulose is an aggregated compound the macromolecules of which are capable of existence only in the solid state embedded in the crystal lattice.

# H. WREN.

Action of acids on cellulose. BOUCHONNET, JACQUET, and MATHIEU (Bull. Soc. chim., 1930, [iv], 47, 1265-1270).-Cellulose obtained from lucerne and from linters when purified and boiled (1) with 10% sulphuric acid for (a) 15-20 min. or (b) 2 hrs.; (2) with 2% oxalic acid or treated cold with hydrochloric acid,  $d \cdot 1 \cdot 18$ , for (a) 25 hrs. or (b) 50 hrs., or with 4% sulphuric acid or with acetic acid in presence of sulphuric acid, is converted into hydrocelluloses, the copper numbers of which vary irregularly from 1.82 to 4.42 with the linters cellulose and from 2.96 to 5.5 with the lucerne cellulose. Examination of the hydrocelluloses in polarised light (Röntgen rays) showed no difference in structure from that of the original cellulose and indicated that the crystalline constituent of cellulose is more developed in linters than in lucerne cellulose. Photomicrographs indicate that the copper number of the hydrocellulose increases with the degree of division of the cellulose under the action of acid. It is suggested that cellulose is a mixture of a crystalline phase enveloped in an amorphous skin which is destroyed under more or less drastic conditions, yielding the crystallite constituent the degradation of which yields polysaccharides. The same cellulose thus yields the same crystallite structure under the action of acid media, but the copper number depends on the extent of the degradation of the amorphous form. The variations in copper numbers are not due to adsorption of reducing products, as prolonged washing did not affect the R. BRIGHTMAN. value obtained.

Chemical changes during the dissolution of cellulose in copper oxide-ethylenediamine and -ammonia solutions. W. TRAUBE (Cellulosechem., 1930, 11, 249-254).—A review (cf. Traube, Glaubitt, and Schenck, A., 1930, 1417). T. H. MORTON.

Benzylcellulose. H. OKADA (Cellulosechem., 1931, 12, 11-17).-Benzylcellulose of a high carbon content and viscosity may be made in either a single or a two-stage process by steeping cellulose in aqueous sodium hydroxide, pressing free from excess of alkali, and heating with benzyl chloride at 100°. It forms films of greater extensibility but lower tensile strength than does cellulose nitrate. In the former process alkali concentrations of 30-50% are employed; the use of excessive concentrations reduces the reaction velocity and the viscosity of the product. In general, the products are incompletely soluble in benzene, but readily soluble in benzenc-alcohol mixtures. The use of 17.5% alkali and a weight of benzyl chloride rather greater than of cellulose in a first stage, followed by 50% alkali and three to four times the weight of benzyl chloride in a second, gives a product completely soluble in benzene. Use of benzene or toluene as solvent reduces the reaction velocity, and temperatures below 100° favour depolymerisation rather than benzylation. H. A. PIGGOTT.

Nitration of cellulose with a mixture of nitric and phosphoric acids. E. BERL and G. RUEFF (Ber., 1930, 63, [B], 3212).—Since cellulose nitrates are not hydrolysed by phosphoric acid, it is easily possible by use of suitable mixtures to obtain products with 14.0-13.7% N. The process is accompanied by marked swelling of the fibres which facilitates access of the acid to the interior of the material and thus uniform action. After short boiling the nitrates are completely stable and contain no mixed phosphatenitrate esters. Nitrates with  $11\cdot0-11\cdot5\%$  N cannot be obtained by the process in fibrous form. During esterification the lattice of native cellulose is transformed into that of hydrocellulose. With phosphoric and nitric acids, nitration is relatively slow, the nitric acid mercerising the cellulose before esterification commences. The cellulose trinitrates obtained give a clear point diagram if nitration and washing are effected under tension. H. WREN.

Absorption of bases by Willstätter's lignin, and related swelling phenomena. L. KALB, F. NEVELY, and O. TOURSEL (Cellulosechem., 1931, 12, 1-11).-The absorption of alkali, measured by the decrease in concentration of the solution, from aqueous sodium or potassium hydroxides by Willstätter's lignin (A., 1928, 743) increases rapidly with increasing concentration of the solution to 0.5N, and then remains constant at 0.126 g.-equiv. per 100 g. A higher value (0.168) is obtained by direct determination of alkali in the product. Absorption, measured by the first method, is higher (0.154) in presence of sodium chloride (approx. 3N). Methyl - alcoholic sodium hydroxide gives abnormally high results, with no evidence of a constant value; from sodium carbonate the absorption is inconsiderable. Barium hydroxide gives a value (0.168) which is regarded as approaching the true value, it being considered that the lower values obtained with the alkalis are the result of masking of the true value by the swelling of the lignin. In general, the results for strong bases are parallel to the swelling of the fibre. They do not vary appreciably between 0° and 30°, and are unaffected by the relative amounts of lignin and solution or by short drying of the lignin at 100°. The effects of the presence of carbohydrates and alkali-soluble material are measured and discussed. Gaseous ammonia is absorbed in quantity by dry lignin, the actual amount depending on a number of physical factors, but much of the gas is rapidly lost on keeping, a final value of 0.130 g.-equiv. per 100 g. being reached. Progressive methylation of lignin leads to a decrease in affinity for bases which eventually disappears completely; in view of its behaviour in this respect, the absorption of bases is regarded as conditioned in part by the presence of alcoholic hydroxyl groups.

Absorption of alkali is not a consequence of the chlorine content, and is unaffected by its partial or complete removal. It is shown by measurements of the  $p_{\rm H}$  of aqueous and aqueous potassium chloride extracts that most samples of lignin contain looselybound acid constituents, and it is noteworthy that samples regenerated from the alkali-ligning slowly regain their acidity on keeping.

A standard method is described for determination of the absorption of sodium hydroxide from a 0.5Nsolution, and the values measured for a number of lignin preparations are given. H. A. PIGGOTT.

Beech-wood alkyl-lignins and their fission. A. VON WACEK (Ber., 1930, 63, [B], 2984—2993; cf. A., 1930, 458).—The oil obtained by treatment of primary beech-wood methyl-lignin with sodium ethoxide consists of a neutral portion (oxidised to 3: 5-dimethoxybenzoic acid) and a phenolic fraction con-

verted by successive ethylation and oxidation into 3-methoxy-4-ethoxybenzoic acid. Lignin, isolated from beech wood by Freudenberg's method, gives a methyl-lignin with 36.57% OMe which differs from primary methyl-lignin in its methoxyl content and in its behaviour when treated according to Friedrich. Ethylation of the "Freudenberg" lignin gives a product with 34.17% of alkoxyl (as OMe) which when treated with sodium ethoxide affords an oil partly soluble in ether which is divided into neutral and acidic portions. Oxidation of the portions (after ethylation of the acidic material) gives an acid which does not melt below 300° and 3-methoxy-4-ethoxy-benzoic acid, respectively. The "residual" lignin differs therefore from primary methyl-lignin. Treatment of beech-wood meal, free from resin and gum, with ethyl sulphate at  $60^{\circ}$  yields a product with 27.35% OAlk (as OMe) which gives a primary ethyllignin with 29.10% OAlk. The product is very sensitive towards heat. When treated with sodium ethoxide it affords an oil almost completely soluble in ether and divisible into neutral and acidic portions, yielding on oxidation only a trace of crystalline material and (after ethylation) non-crystalline substances, respectively. Ethylation of beech wood at 25-30° gives a product with 30.15% OAlk yielding a more stable primary ethyl-lignin with 31.27% OAlk which with sodium ethoxide gives an oil completely soluble in ether. Oxidation of the neutral portion thereof affords 3:5-dimethoxybenzoic acid, whereas successive methylation and oxidation of the acidic portion does not yield a crystalline substance. The ethyl groups of the primary ethyl-lignin could not be detected in the phenolic fission products. A free phenolic group does not appear to be present in the phenolic components of genuine beech-wood lignin which contains other groups capable of alkylation. The methoxyl groups are present in genuine lignin. The methoxyl content of isolated beech-wood lignin and methyl-lignin contradicts the hypothesis that lignin contains only the components

 $\cdot \mathring{O} \cdot C_6 H_2(OMe)_2 \cdot CH_2 \cdot CH: CH \cdot The assumption that aliphatic hydroxyl groups are present in the side$ chain necessitates a much higher methoxyl content than that actually found. It is uncertain whether pyrocatechol derivatives are present in the chain in addition to pyrogallol residues or whether a substance of entirely different constitution participates in the structure.

The synthesis of 3-methoxy-5-ethoxybenzoic acid, m. p. 145° (corr.), is recorded. H. WREN.

Reaction between propylene oxide and diethylamine. K. A. KRASUSKI and G. T. PILIUGIN (Ukraine Chem. J., 1930, 5, 135–139).—The product of the interaction of 1 mol. of propylene oxide with 2 mols. of diethylamine either in aqueous solution at the ordinary temperature or on heating in a sealed tube is  $\alpha$ -diethylaminopropan- $\beta$ -ol, b. p. 157:5—159°/ 756 mm.,  $d_0^{29}$  0.8511, which is the only amino-alcohol obtained in aqueous solution. The hydrochloride and picrate are described. E. B. UVAROV.

Reaction of ethylamine and diethylamine with isopropylethylene oxide. F. F. KRIVONOS (Ukraine Chem. J., 1930, 5, 141-146).—The reaction

between isopropylethylene oxide (2 mols.) and ethylamine (1 mol.) gives ethyl- $\beta$ -hydroxy- $\gamma$ -methyl-n-butylamine, b. p. 150—152°/25 mm.,  $d_{2}^{30}$  0.8929. The hydroehloride and picrate were prepared. Using 1.5 mols. of oxide to 1 mol. of ethylamine, ethyldi- $\beta$ -hydroxy- $\gamma$ -methyl-n-butylamine, b. p. 244—247°/20 mm., was obtained. The hydrochloride was prepared. The reaction between isopropylethylene oxide and diethylamine gave diethyl- $\beta$ -hydroxy- $\gamma$ -methyl-n-butylamine, b. p. 151—154°/15 mm.,  $d_{2}^{30}$  0.8512 (picrate and hydrochloride). E. B. UVAROV.

Preparation of dimethylamino-aliphatic acids. V. PRELOG (Coll. Czech. Chem. Comm., 1930, 2, 712-722).—Dimethylammonium hydrogen succinate, m. p. 159-160°, is converted by heating at 160-180° until steam ceases to be evolved, followed by distillation under reduced pressure, into a mixture of the monoand bis-dimethylamides, which is reduced electrolytically, using an activated lead cathode (cf. Tafel, A., 1900, ii, 588). The product is made alkaline with barium hydroxide and ad-tetramethyldiaminobutane (picrate, m. p. 188-189°) removed by distillation in steam; from the residue &-dimethylamino-n-butyric acid, b. p. 145-150°/2 mm., m. p. 102-104° [hydrochloride, m. p. 145—147° (cf. A., 1915, i, 966); ethyl ester, b. p. 78—90°/18 mm.,  $d^{136}$  0.9187,  $n_{\rm D}^{144}$  1.4264]. may be isolated after removal of inorganic matter. Its methiodide gives with silver oxide in aqueous solution a quaternary hydroxide (?), m. p. 77°, converted by prolonged drying at the ordinary temperature into the betaine, m. p. 219° (decomp.) [chloroaurate, m. p. 184-185°; chloroplatinate, m. p. 225-226° (cf. A., 1902, i, 266)]. Similarly, from dimethylammonium hydrogen adipate, m. p. 75°, were prepared : adiptetramethyldiamide, m. p. 85°; an-tetramethyldiaminohexane [picrate, m. p. 163-164°; chloroplatinate, m. p. 222° (decomp.); chloroaurate, m. p. 169°]; ξ-dimethylamino-n-hexoic acid, m. p. 107-109° [hydrochloride, m. p. 97-99°; quaternary (methyl) hydroxide, m. p. 115°; betaine, m. p. 254-255° (chloroaurate, m. p. 149°)]. The betaine is decomposed at temperatures above its m. p. into methyl ξ-dimethylamino-n-hexoate, b. p. 209-210°, trimethylamine, and (probably)  $n - \Delta^{\delta}$ -hexenoic acid.

H. A. PIGGOTT.

Ability of peptides to combine with acid and alkali. E. STIASNY and H. SCOTTI (Ber., 1930, 63, [B], 2977-2983).-Glycine, glycylglycine, di-, tri-, tetra-, and penta-glycylglycine, and glycine anhydride are titrated with sodium hydroxide and hydrochloric acid, respectively, the hydrogen-ion concentration being measured potentiometrically after each addition by aid of the hydrogen electrode. The graphs show that union of hydrochloric acid does not occur with the peptide groups of soluble peptides, which, however, definitely combine with alkali hydroxide. The dissociation constants and the isoelectric points are calculated from the graphs. The introduction of the first peptide group has a more marked effect than that of subsequent peptide groups on the acidic and basic character of the peptides. With increasing number of peptide groups the acidic character steadily increases; the basic properties increase only to the dipeptide. The isoelectric point, confirmed by measurement of the optimal conditions for precipitation with alcohol in the cases of the tri-, tetra-, and pentapeptide and by  $p_{II}$  measurement on solutions of increasing concentration with glycine and dipeptide, wanders into the acidic region with increasing number of peptide groups and in the case of polypeptides attains the value of many proteins. H. WREN.

Synthesis of serine. S. K. MITRA (J. Indian Chem. Soc., 1930, 7, 799-802).—Ethyl sodiophthalimidomalonate and methyl chloromethyl ether react in ether, forming ethyl phthalimidomethoxymethylmalonate, m. p. 127°, hydrolysed to the free acid, m. p. 102° (silver salt), only by hydrobromic acid (d 1.8) at 48°. When this acid is heated with fuming hydrochloric acid in a scaled tube at 100°, the hydrochloride of  $\alpha$ -amino- $\beta$ -hydroxypropionic acid (serine) (phenylcarbimide derivative, m. p. 159°) is obtained in 50% of the theoretical amount. Hydrolysis of the above ester with alcoholic potassium hydroxide affords a tripotassium salt, probably

 $CO_2K \cdot C_6H_4 \cdot CO \cdot NH \cdot C(CH_2 \cdot OMe)(CO_2K)_2$ , which when treated with acid gives carbon dioxide and an oily product (hydrolysed further to serine).

H. BURTON. Ethyl aminomalonate and its derivatives. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1930, [iv], 47, 1274—1279, 1282—1287, 1287—1289).— Reduction of ethyl oximinomalonate with excess of aluminium amalgam gave only 15% of ethyl amino-malonate in place of the 60% yield claimed by Piloty and Neresheimer (A., 1906, i, 146). By using only a slight excess of aluminium (1<sup>2</sup>/<sub>3</sub> atoms per mol. of ester), in the form of 0.3-mm. leaves amalgamated with 4% mercuric chloride solution, covering the amalgam with an ethereal solution of ethyl oximinomalonate, and gradually adding to the boiling ethereal solution water equal in weight to six times the weight of aluminium, the aluminium hydroxide separates in pulverulent form and from the clear liquid ethyl aminomalonate, b. p. 122—123°/16 mm.,  $d_4^{16}$  1·100,  $n_D^{16}$  1·4353, is obtained in 65% yield by direct distillation. It is best isolated for storage as the oxalate, m. p. 138°. The carbamide, NH<sub>2</sub>·CO·NH·CH(CO<sub>2</sub>Et)<sub>2</sub>, m. p. 173°, is obtained in 50-70% yield with potassium cyanate in acetic acid; hydrolysis with 25% hydrochloric acid yields 90% of hydantoin. The phenylcarbamide m. p. 117°, ethyl carbethoxyaminomalonate, m. p. 61-63°, and diamide, m. p. 197° (yield 90%), are also described. R. BRIGHTMAN.

Preparation of ethyl oximinomalonate. V. CERCHEZ (Bull. Soc. chim., 1930, [iv], 47, 1279—1281). —Ethyl oximinomalonate, b. p.  $172^{\circ}/12$  mm.,  $d_4^{18}$ 1·182,  $n_{18}^{18}$  1·4544, is obtained in 90% yield by the action of a slow current of nitrous fumes or of methyl nitrite on ethyl sodiomalonate in alcoholic solution. Yields of 80—90% are obtained by the action of a concentrated aqueous solution of sodium nitrite (3 mols.) on a solution of ethyl malonate (1 mol.) in 3 mols. of glacial acetic acid. Nitrosyl hydrogen sulphate gives only 40% yields. R. BRIGHTMAN.

Action of magnesium phenyl bromide on ethyl  $\alpha$ -cyano- $\alpha$ -ethyl-*n*-butyrate. A. MAVRODIN (Compt. rend., 1930, **191**, 1064—1066).—Magnesium phenyl bromide reacts with ethyl  $\alpha$ -cyano- $\alpha$ -ethyl-*n*-butyrate,

which is incapable of enolisation (cf. A., 1929, 796), thus: CEt<sub>2</sub>(CN)·CO<sub>2</sub>Et + PhMgBr  $\longrightarrow$  PhCN + CEt<sub>2</sub>(MgBr)·CO<sub>2</sub>Et (I); PhCN+PhMgBr $\longrightarrow$ CPh<sub>2</sub>:N·MgBr $\longrightarrow$ CPh<sub>2</sub>:N·H $\longrightarrow$ COPh<sub>2</sub>; 2(I) $\longrightarrow$ CEt<sub>2</sub>(MgBr)·CO·CEt<sub>2</sub>·CO<sub>2</sub>Et $\rightarrow$ CHEt<sub>2</sub>·CO·CEt<sub>2</sub>·CO<sub>2</sub>Et (II), the final products being benzophenone, a small quantity of ethyl a-ethyl-n-butyrate (from I), and ethyl β-keto-aay-triethyl-n-hexoate (II), b.p. 138°/18 mm. The last-named is hydrolysed by alcoholic potassium hydroxide to di-(a-ethyl-n-propyl) ketone, b. p. 90°/15 mm. (Zerner, A., 1911, i, 950). Comparable cases of elimination of a group from a quaternary carbon atom by a Grignard reagent are cited. J. W. BAKER.

Polymerisation and ring formation. VIII. Amides from e-aminohexoic acid. W. H. CARO-THERS and G. J. BERCHET (J. Amer. Chem. Soc., 1930, 52, 5289—5291).—When ε-aminohexoic acid is heated to 210-220°, water is eliminated and a mixture of 20-30% of the corresponding lactam and 70-80% of a polymeric amide, m. p. 212-214°, M 800-1200, is formed. The amide is insoluble in most organic solvents (except hot formamide), is hydrolysed by hydrochloric acid to  $\varepsilon$ -aminohexoic acid, and when heated in a high vacuum does not give any of the lactam. Its formation probably involves at least 10 mols. of the amino-acid. Partial hydrolysis of the amide gives polyaminohexoylaminohexoic acids of lower mol. wt., indicating that the structure of the original material may be represented as  $\cdot$ NH·[CH<sub>2</sub>]<sub>5</sub>·CO·[NH·(CH<sub>2</sub>)<sub>5</sub>·CO]<sub>x</sub>·NH·[CH<sub>2</sub>]<sub>5</sub>·CO·. No evidence of the presence of terminal amino- or carboxyl groups could be obtained. H. BURTON.

Determination of unsaturated nitriles. G. HEIM (Bull. Soc. chim. Belg., 1930, 39, 458-461) .--The rates of addition of iodine to  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated nitriles (cf. Linstead and May, A., 1927, 1167; Kandiah and Linstead, A., 1929, 1294) do not always differ to a marked degree, since cis- (1.7%) and trans- (1.4%)-crotononitriles and vinylacetonitrile (7.0%) absorb the quantities of iodine given in parentheses, under comparable conditions. A method is described in which a standard solution of bromine in potassium bromide is added to a chloroform solution of the nitrile, followed by potassium iodide and titration with thiosulphate. The rate of addition of bromine to the  $\alpha\beta$ -unsaturated nitriles, cis- and trans-crotononitrile (0.9% and 2.1%),  $\alpha$ -methylcrotononitriles (cis- 0.6; trans- 1.2%), and the nitriles of  $\alpha$ -methyl- $\beta$ -ethyl-(cis- 1.8%), a-methyl- (1.2%), a-ethyl- (1.4%), and  $\alpha$ -propyl- (3.0%) -acrylic acids is much less than in the case of the  $\beta\gamma$ -unsaturated vinylacetonitrile (99.8%). The composition of mixtures of  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated nitriles may be determined in this way.

J. D. A. JOHNSON.

Unsaturated nitriles.  $\gamma$ -Methyl- $\Delta^{\alpha}$ -pentenonitriles. P. BRUYLANTS and H. MINETTI (Bull. Acad. roy. Belg., 1930, [v], **16**, 1116—1128).—*iso*-Amyl alcohol (isolated as barium *iso*amyl sulphate from fusel oil), b. p. 131·5—132°/755 mm.,  $d_4^{x_0}$  0·80788, is oxidised to *iso*valeraldehyde, b. p. 91·9—92·1°/ 765·5 mm.,  $d_4^{x_0}$  0·79770. The cyanohydrin, b. p. 107°/9 mm.,  $d_4^{x_0}$  0·91852, of the latter is dehydrated by means of phosphoric oxide; careful fractionation of the product affords cis- $\gamma$ -methyl- $\Delta^{\alpha}$ -pentenonitrile, b. p. 137.5—138°/770 mm.,  $d_4^{30}$  0.80781, n 1.42493, and a fraction, b. p. 160—160.5°/767 mm.,  $d_4^{30}$  0.82491,  $n_{\rm D}$  1.43620, consisting of a mixture of the *trans*isomeride and  $\gamma$ -methyl- $\Delta^{\beta}$ -pentenonitrile (20%), inseparable by distillation. Treatment of the mixture with bromine removes the latter compound (which reacts more readily with halogens), leaving trans- $\gamma$ methyl- $\Delta^{\alpha}$ -pentenonitrile, b. p. 48.5—49°/13.5 mm.,  $d_4^{30}$ 0.82131,  $n_{\rm D}$  1.43418, distillation of which at atmospheric pressure (b. p. 156—157°/761 mm.) causes some re-isomerisation to the  $\Delta^{\beta}$ -compound. The fractions, b. p. above 163°, from the original dehydration appear to contain larger percentages of the  $\Delta^{\beta}$ -nitrile.

Addition of hydrogen chloride to either of the geometrical isomerides of  $\gamma$ -methyl- $\Delta^{\alpha}$ -pentenonitrile affords  $\gamma$ -methyl- $\beta$ -chloropentonitrile, b. p. 90·4— 91·4°/13 mm.,  $d_4^{3\circ}$  1·0186,  $n_a^{3\circ}$  1·44375, from which hydrogen chloride is removed in the usual manner by quinoline leading to a mixture containing the  $\Delta^{\beta}$ -nitrile and the two  $\Delta^{\alpha}$ -nitriles. Sodium phenoxide acts on the two geometrical isomerides, with formation of considerable percentages (particularly with the *cis*-compound) of  $\gamma$ -methyl- $\Delta^{\beta}$ -pentenonitrile.

The corresponding amides—cis-, m. p. 80°, and trans- $\gamma$ -methyl- $\Delta^{\alpha}$ -pentenoamide, m. p. 87.6—88.2°— are prepared by the action of cold sulphuric acid on the nitriles.

New data are given of the molecular refractivities and dispersions of *iso*amyl alcohol, *iso*valeraldehyde and its cyanohydrin, and the new derivatives.

R. CHILD.

Ultra-violet absorption spectra of  $\gamma$ -methyl-A<sup>e</sup>-pentenonitriles and the corresponding amides. A. CASTILLE and E. RUPPOL (Bull. Soc. roy. Belg., 1930, [v], 16, 1129—1133).—As has been observed with other members of the series, the absorption of the *trans*-nitrile is greater than that of the *cis*-isomeride, whilst the reverse is the case with amides.

### R. CHILD.

Alteration in properties of chemical compounds by complex formation. VI. Methylation of alcohols by diazomethane. H. MEERWEIN and G. HINZ (Annalen, 1930, 484, 1-25).—The reactivity of a hydroxyl group towards diazomethane may be increased either by the introduction of polar groups in the  $\alpha$ -position, or by formation of a polar complex by substances capable of addition to the oxygen atom (catalysts). Use of ether as a solvent tends to prevent methylation, and a similar influence is often exerted by the products of methylation.

Saturated aliphatic alcohols are not methylated by diazomethane, but allyl alcohol accelerates its decomposition, and benzyl alcohol gives 13% of methyl ether. The influence of an electronegative group in the  $\alpha$ -position is shown by the methylation of the following: glycol monoacetate;  $\alpha$ -monoacetin (methyl ether, b. p. 126—129°/18 mm., readily methylated to the dimethyl ether); glycol trichloroacetate (methyl ether, m. p. 77—78°); ethylene chlorohydrin;  $\alpha$ -monochlorohydrin (monomethyl ether, b. p. 171—172°;  $d_{0}^{\alpha}$  1·1832; accompanied by the dimethyl ether);  $\alpha\gamma$ -dichlorohydrin; ethylene cyanohydrin [methyl ether, b. p. 162—164°; and a base,

 $C_4H_7ON_3$  (hydrochloride)]; and acetaldehyde cyanohydrin. In the last case the methyl ether is accompanied by dimethylethylene oxide, acetone, and methyl ethyl ketone. Acetyl- and benzoyl-carbinols react abnormally, being converted into propionylcarbinol and *phenacylcarbinol*, b. p. 140—145°/11 mm., respectively.

Methylation of saturated aliphatic alcohols may be effected in presence of halogenated alcohols, e.g., ethylene chlorohydrin, aa'-dichlorohydrin, and trichloroethyl alcohol, or of salts such as zinc, ferric, or magnesium chlorides, or of alkoxides or ortho-esters. Catalysts of the first two types, particularly the chloro-alcohols, which lose their activity on methylation, give poor results, but good yields are obtained with the third class. Thus *n*-butyl and *iso*propyl alcohols are readily methylated in presence of the corresponding aluminium alkoxides, or, in the former case, of n-butyl antimonite. Alkyl borates are rather less active and fail completely in the case of isopropyl and n-butyl alcohols. It is suggested that polyhydric alcohols should readily be methylated in presence of boric or arsenious acid, the complexes here being intramolecular. H. A. PIGGOTT.

Electrolysis of Grignard solutions. H. E. FRENCH and M. DRANE (J. Amer. Chem. Soc., 1930, 52, 4904—4906; cf. A., 1927, 756).—Electrolysis of ethereal magnesium isoamyl chloride, using a platinum cathode and an anode of bismuth, gold, silver, nickel, or tin, causes no loss of anode material; the amount of Grignard reagent decomposed is equivalent to the amount of current for the first three anode metals. An anode of aluminium, zinc, or cadmium is attacked. Aluminium, approximately equivalent to the quantity of current used, is found in the ethereal solution; the other metals are found in the solid residue in the cell. H. BURTON.

Reaction between magnesium phenyl bromide and carbon dioxide at elevated temperatures. H. GILMAN and (MISS) N. B. ST. JOHN (Rec. trav. chim., 1930, 49, 1172-1177).-Since triphenylmethyl peroxide is not formed when the reaction is carried out in phenetole or bromobenzene, its formation when ether is used as the reaction medium is considered possibly due to the presence of diethyl ether peroxide in the latter medium. It is suggested that this might oxidise any triphenylmethyl halide formed by the action of magnesium halide on triphenylcarbinol, produced by hydrolysis of CPh<sub>3</sub>·O·MgBr. When ethereal benzene solutions of the latter are refluxed for several hours, good yields of triphenylmethane are obtained, and the slow addition of carbon dioxide to heated solutions of magnesium phenyl bromide leads to 36.9-46.8% yields of triphenylcarbinol. J. D. A. JOHNSON.

Magnesium dialkyls. Historical note on the first preparation of a magnesium alkyl halide. H. GILMAN and R. E. BROWN (J. Amer. Chem. Soc., 1930, 52, 5045—5048).—The properties of magnesium dimethyl, diethyl, and di-*n*-butyl, prepared from the corresponding mercury dialkyls, are given. Magnesium reacts with ethyl iodide in absence of solvent at  $120-130^{\circ}$  (cf. A., 1930, 1302), forming magnesium ethyl iodide; this observation is recorded by Hall-
wachs and Schafarik (Annalen, 1859, 109, 206). Magnesium does not react with methyl iodide in absence of a solvent at  $140-150^{\circ}$  (cf. Cahours, *ibid.*, 1860, 114, 227, 240); magnesium halides are formed from ethyl bromide and *n*-butyl chloride and bromide. H. BURTON.

Reactivity of halogens in the halogeno-derivatives of cyclohexane. B. V. TRONOV and L. V. LADIGINA (Ber., 1930, 63, [B], 3060-3067).—The rates of reaction of cyclohexyl chloride, bromide, and iodide and of a sec.-hexyl iodide (about 70% of B- and 30% of y-iodohexane from mannitol with hydriodic acid, iodine, and phosphorus) and the corresponding bromide with sodium methoxide, pyridine, and piperidine, respectively, have been measured at 17-19°, the ionised halogen being determined gravimetrically. The halogeno-derivatives of cyclohexane react less readily than the aliphatic halides with amines and potassium iodide, but very energetically with alkoxides. In their reactivity towards amines they very greatly excel the nuclear-substituted aromatic halogeno-compounds. The closure of the six-membered ring does not invariably diminish the readiness with which halogen is lost, but causes a similarity between the halogenated cyclohexanes and the tertiary alkyl halides. In general, the halogen is not replaced but removed mainly, and often exclusively, as hydrogen halide with production of cyclohexene. An electronic interpretation of the course of the reaction is given. H. WREN.

Action of hexahalogenobenzenes on organomagnesium compounds. J. F. DURAND and L. WAI-HSUN (Compt. rend., 1930, **191**, 1460—1463). —Whilst hexachlorobenzene does not react, hexabromobenzene reacts readily and hexa-iodobenzene violently with magnesium methyl iodide and magnesium phenyl bromide to yield, respectively, hexamethylbenzene, m. p. 157—158°, and hexaphenylbenzene, b. p. 418—420°/760 mm., m. p. 266°. Fuming nitric acid converts hexaiodobenzene into a substance, m. p. 330°, converted by prolonged treatment with nitric acid into a substance, m. p. 307—308°, probably  $C_6O_3I_6$ . J. W. BAKER.

Sorption of hydrogen sulphide by potassium benzenesulphonate. W. LANGE and G. LEWIN (Ber., 1930, 63, [B], 2954-2959).—Measurement of the heat of formation of the thiohydrate,

4Ph·SO<sub>3</sub>K,H<sub>2</sub>S (cf. A., 1930, 1423), in the ice calorimeter gives the value  $10.0 \pm 0.2$  kg.-cal. for the dehydrated salt. Differential measurements give the value  $10.5\pm0.3$  kg.-cal. (calc. for 1 mol. of hydrogen sulphide) for the formation of a 1/8 thiohydrate and the value  $9.6 \pm 0.3$  kg.-cal. for subsequent absorption. When the molten salt is employed, 8.5 kg.-cal. are evolved; the difference is accounted for by the greater energy required by the hydrogen sulphide to penetrate the more compact mass. Mathematical expressions have been derived for the relationship between the amount of hydrogen sulphide absorbed, the temperature, and pressure. Irregularities occur corresponding with a thiohydrate, 8Ph·SO<sub>3</sub>K,H<sub>2</sub>S. Since the volume of the hydrogen sulphide molecule is approximately twice that of the water molecule, it appears that the 1/8 mol. of hydrogen sulphide occupies the space of

the 1/4 mol. of water previously present zeolitically and that further penetration of hydrogen sulphide into the lattice requires a definite amount of energy. H. WREN.

Oxidation of organic iodine compounds by organic per-acids. J. BÖESEKEN and G. C. C. C. SCHNEIDER (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 827-829).-Numerous organic compounds containing iodide are oxidised by peracetic or perbenzoic acid to iodoso- and iodoxy-compounds. With peracetic acid an iodoso-compound is always obtained, generally in the form of its acetate. With perbenzoic acid the iodoxy-compound is obtained directly; iodoxy-compounds are also produced when the iodoso-products obtained with peracetic acid are subsequently treated with perbenzoic acid. With o-iodobenzoic acid and p-iodobenzenesulphonic acid the oxidation ceases at the iodoso-stage even when perbenzoic acid is used, probably on account of the pronounced polar character of these compounds. o-Iodobenzoic acid is often supposed to have a ring structure, but the analogous properties of p-iodosobenzenesulphonic acid, m. p. 156.4° (decomp.), suggest that these compounds should be considered as internal E. S. HEDGES. salts without ring structure.

V. N. IPATIEV, B. Preparation of mesitylene. DOLGOV, and J. VOLNOV (Ber., 1930, 63, [B], 3072-3078).-At 175° under an initial pressure of 100 atm. the yield of mesitylene from acetone increases rapidly with increasing concentration of hydrochloric acid until a concentration of 5% by volume is reached; simple, oxygenated condensation products are formed to some extent. With increase of concentration of acid between 5% and 50%, a gradual fall in the yield of mesitylene occurs, and terpene-like products with a higher degree of condensation appear. With rise in temperature the graph showing relationship of temperature to yield of mesitylene calculated on the acetone used shows a sharp inflexion at 140°, whereas a similar break is noted at 170° when the yield of mesitylene is calculated on the basis of acetone taken. At 175-190° the graphs coincide, indicating the complete utilisation of the acetone. The yield of mesityl oxide diminishes with rise of temperature. At  $140-150^{\circ}$  in the presence of 5% of hydrochloric acid the yield of mesitylene is 43% of the weight of acetone which enters into the change; 50% of the acetone remains unaffected and can be used in subsequent operations. At 175-180° almost the whole of the acetone reacts and the yield of mesitylene is 36%. The course of the change is represented by the scheme  $2\text{COMe}_2^{-H_3O}\text{CMe}_2$ :CH·COMe $^{+\text{Me·CO·Me}}$  $C_6H_3Me_3+2H_2O$  or  $CO(CH:CMe_2)_2+H_2O$ .

H. WREN.

Nitration of s-diphenylethane. W. H. RINKEN-BACH and H. A. AARONSON (J. Amer. Chem. Soc., 1930, 52, 5040—5045).—4:4'-Dinitrodiphenylethane, m. p. 180.5° (corr.), is obtained in 95% of the theoretical amount when diphenylethane is heated with nitric acid (d 1.42) at 70—80°. Sulphonation of 2:4:2':4'-tetranitrodiphenylethane, m. p. 170.9° (corr.) (obtained in 90—95% yield from diphenylethane and fuming nitric acid, first below 30°, and then at 70°), with fuming sulphuric acid (103%) at 85° for 4 days and treatment of the reaction mixture with 95% nitric acid at 85° for 2 days affords  $\alpha$ -2 : 4-dinitrophenyl- $\beta$ -2 : 4 : 5-trinitrophenylethyl alcohol, m. p. 187·3° [benzoate, m. p. about 200° (decomp.)]; in one case, a small amount of 2 : 4 : 6 : 2' : 4' : 6'-hexanitrodiphenylethane was isolated. The above alcohol is oxidised by chromic and acetic acids to a mixture of 2 : 4 : 5-trinitrobenzoic acid and (?) 2 : 4-dinitrobenzyl acetate [(?) 2 : 4-dinitrobenzylidene acetate].

H. BURTON.

Alkali-organic compounds. O. BLUM-BERG-MANN (Annalen, 1930, 484, 26—51).—The constitution of 3-phenyl-1-benzhydrylidenehydrindene, assigned by Wieland and Kloss (A., 1929, 1053) to the product of reduction of 2-chloro-3-phenyl-1-benzhydrylideneindene, is confirmed by synthesis; of the isomerides, "m. p. 171° and 131°" (Schlenk and Bergmann, A., 1928, 1031 *et seq.*), the former is shown by synthesis to be 3-phenyl-1-benzhydrylindene, and the latter from its mode of formation must therefore be 1-phenyl-3-benzhydrylindene; this is confirmed by the reduction of 3-phenyl-1-benzhydrylideneindene to a mixture of these (m. p. 174·5—175° and 133— 134·5°) by aluminium amalgam in dioxan and reduction of the last by sodium and amyl alcohol to 3-phenyl-1-benzhydrylhydrindene.

The position of the metal in 1-lithio-3-phenylindenc is proved by its condensation with benzophenone to 3-phenyl-1-benzhydrylideneindene. The interaction of methyl chloroformate and lithio-3-phenylindene gives methyl 3-phenylindene-1: 1-di-carboxylate, m. p. 105-107°, reduced by hydrogen and palladised barium sulphate in propyl alcohol to methyl 3-phenylhydrindene-1: 1-dicarboxylate, m. p. 102-103.5°. The corresponding acid, m. p. 175-177° (decomp.), is decomposed by heating above its m. p. into 3-phenylhydrindene-1-carboxylic acid, m. p. 143-144.5°, b. p. 227-229°/14 mm. (?) (methyl ester, b. p. 204.5-205°/13 mm.). 3-Phenyl-1-z-hydroxybenzhydrylhydrindene, m. p. 122-124°, results from the action of magnesium phenyl bromide on the lastnamed methyl ester, and is dehydrated by acetyl chloride to 3-phenyl-1-benzhydrylidenehydrindene, dimorphic, m. p. 130-131° and 115-117°. It is readily hydrogenated to 3 - phenyl - 1 - benzhydrylhydrindene. Bromodiphenylmethane interacts with lithio-3-phenylindene to give 3-phenyl-1-benzhydrylindene, m. p. 174-5-175°, tetraphenylethane, 3:3'-diphenyl-1:1'-di-indenyl), a dimeride, m. p. 207-209°, of 3-phenylindene, and a hydrocarbon (C28H22), dimorphic, m. p. 166-167° and 162-164.5°, reduced catalytically, or by sodium and amyl alcohol, to a catalytically, of by solutin and any account of hydrocarbon ( $C_{28}H_{24}$ ), m. p. 182—184°. The action of methyl iodide on lithio-3-phenylindene leads to 9-methyl- and 9:9-dimethyl-fluorene; the interaction of bromodiphenylmethane with lithioindene gives 1-benzhydrylindene (A., 1915, i, 392) un-accompanied by isomerides, and with lithio-2-phenylindene, 2-phenyl-1-benzhydrylindene, m. p. 175°, converted by sodium and amyl alcohol into 2-phenyl-

1-benzhydrylhydrindene, m. p. 151°. The "dihydroanthroic acid" of Schlenk and Bergmann is an additive compound of anthroic and tetrahydroanthroic acids, the methyl esters of which may be separated by repeated fractional crystallis-

ation. As a by-product from the action of carbon dioxide on lithioanthracene (Schlenk and Bergmann, loc. cit.), 9:10-dihydroanthracene-9:10:10-tricarboxylic acid (+1Et<sub>2</sub>O), m. p. 289—292° (decomp.) (trimethyl ester, m. p. 147.5—148°), is formed. Its ready decomposition by boiling with acetic acid into  $\alpha$ - and by heating above its m. p. into  $\alpha$ - and  $\beta$ -9:10dihydroanthracene-9:10-dicarboxylic acids is proof of the structure assigned.

The interaction of alkali-organic compounds with carbonic esters leads generally to esters of the corresponding carboxylic acid; e.g., sodiotriphenylmethyl gives esters of triphenylacetic acid, but in many cases further action produces ketones. With disodiotetraphenylethylene, the original hydrocarbon is reformed. Methyl carbonate gives with lithiofluorene methyl fluorenyl-9-carboxylate and difluorenylacetone, m. p. 230-232° (decomp.), with sodiodiphenylmethyl s-tetraphenylacetone, with disodiotetraphenylbutane 1:1:4:4-tetraphenylcyclopentan-5-one in quantitative yield, and with disodio- or dilithioanthracene bisdihydroanthranyl ketone, m. p. 238-240° with decomp. into carbon monoxide, anthracene, and dihydroanthracene. s-Tetraphenylacetone interacts with finely-divided sodium in ether to form an enolic sodio-derivative, decomposed by heat into tetraphenylallene and aayy-tetraphenylpropene.

H. A. PIGGOTT.

Preparation of 2-naphthalene derivatives. A. BARBOT (Bull. Soc. chim., 1930, [iv], 47, 1314-1323). -When treated with alkyl bromides at 120-130° in presence of aluminium bromide tetrahydronaphthalene yields 2-alkyltetrahydronaphthalenes, which on dehydrogenation with sulphur at 215-220° are converted into 2-alkylnaphthalenes. Similarly, in presence of aluminium chloride acyl chlorides yield exclusively the  $\beta$ -tetrahydronaphthyl ketones and on dehydrogenation with sulphur the corresponding β-naphthyl ketones. With the lower members of the series the condensation yields are poor. Thus methyl bromide at 140-150° affords only 14% of 2-methyltetrahydronaphthalene, b. p. 99-101°/13 mm., together with octahydrophenanthrene and octahydroanthracene. 2-Methylnaphthalene, b. p. 110-112°/16 mm. (picrate, m. p. 115°), is obtained in 75% yield on dehydrogenation for 3 hrs. at 210°. The following are also described : 2-ethyltetrahydronaphthalene, b. p. 121-122°/10 mm. (yield 28-35%, together with a 121—122 /10 mm. (yield 23—35%), together with a substance,  $C_{20}H_{24}$ , b. p. 219°/9 mm.), 2-ethylnaphthalene, b. p. 117—118°/10 mm., yield 69%; 2-isopropyl-tetrahydronaphthalene, b. p. 124—126°/13 mm., yield 37%, together with the substance,  $C_{20}H_{24}$ , b. p. 219°/9 mm.; 2-isopropylnaphthalene, b. p. 129— 219<sup>-/9</sup> mm.; 2-isopropyinaphtalene, b. p. 129– 130°/14 mm., yield 72·5%; 2-tert.-butyltetrahydro-naphthalene, b. p. 129°/11 mm., yield 70%; 2-tert.-butylnaphthalene, yield 70%; β-tetrahydronaphthyl methyl ketone (yield 90%), b. p. 161°/16 mm. (semi-carbazone, m. p. 257–258°); β-naphthyl methyl ketone (yield 77%), m. p. 52°, b. p. 171–173°/17 mm. (oxime, m. p. 142°; semicarbazone, m. p. 234–235°); β totrahydronaphthyl thyl ketone (xield 469′) b. p.  $\beta$ -tetrahydronaphthyl ethyl ketone (yield 46%), b. p. 169°/17 mm., d= 1.033, n= 1.55 (semicarbazone, m. p. 224—225°);  $\beta$ -naphthyl ethyl ketone (yield 71·7%), b. p. 181-183°/18 mm., m. p. 58-59°; β-tetrahydronaphthyl propyl ketone (yield 50%), b. p. 178°/18 mm.,

 $d_{m}^{23}$  1.03,  $n_{D}^{23}$  1.546;  $\beta$ -naphthyl propyl ketone, m. p. 52°, b. p. 184-185°/16 mm.; β-tetrahydronaphthyl isopropyl ketone (yield 54%), b. p. 163°/11 mm., dz  $1.025, n_{\rm D}^{22}$   $1.5444; \beta$ -naphthyl isopropyl ketone (yield 71.4%), b. p.  $180-181^{\circ}/18$  mm. The substance,  $C_{20}H_{24}$ , yields benzoic acid on oxidation with permanganate and is probably a-phenyl-8-2-tetrahydronaphthylbutane.

In confirmation of this view, αδ-diphenylbutane, m. p. 52°, is obtained by the condensation of benzene and tetrahydronaphthalene in presence of aluminium bromide and chloride.

With other catalysts substitution in the 2-position does not take place exclusively. R. BRIGHTMAN.

New complex hydrocarbon of the probable formula C16H14. C.S. GIBSON and J. D. A. JOHNSON (J.C.S., 1930, 2785-2787).-When chloro-ββ'-dichlorodivinylarsine is treated with benzene in presence of aluminium chloride at 100° (bath), the resulting product contains a small amount of a hydrocarbon, probably  $C_{16}H_{14}$ , m. p. 179—180° (*dibromo*-derivative, not melted at 310° after darkening at 210°), stable to boiling alkaline permanganate. The yellow solution of the hydrocarbon in alcohol exhibits strong bluishviolet fluorescence.

When chloro-BB'-dichlorodivinylarsine is treated with ethyl sodiomalonate under various conditions, acetylene is produced. H. BURTON.

Polynuclear aromatic hydrocarbons and their derivatives. VII. New class of deeply-coloured radical hydrocarbons and the so-called "pentacene " of Philippi. E. CLAR and F. JOHN (Ber., 1930, 63, [B], 2967-2977; cf. A., 1930, 203).--2:3:6:7-Dibenz-9:10-dihydroanthracene gradually passes at the ordinary temperature into 2:3:6:7dibenz-1: 4-dihydroanthracene, m. p. 300-310° when rapidly heated, oxidised by chromic acid in glacial acetic acid exclusively to the diquinone

 $C_6H_2\left(\langle \begin{array}{c} CO\\ CO \rangle C_6H_4 \right)_2$ . The 9:10-dihydro-compound

is converted by passage over heated copper, by treatment with phenanthraquinone in boiling nitrobenzene, or with chloranil in boiling xylene into 2:3:6:7-dibenzanthracene-9: 10-diyl (I), blue crystals. When dissolved in xylene the hydrocarbon is not affected by dry oxygen, but is converted by moist oxygen or air



into a mixture of the peroxides II, decomp. 335-360°, and III, m. p. 320-330° (decomp.); oxidation is greatly accelerated by light. The suspension of the hydrocarbon in xylene is immediately decolorised by *p*-benzoquinone with production of the quinol ether (IV), decomp. 262°, whereas with chloranil it affords a mixture of the analogously constituted tetrachloroquinyl ether, decomp. 263°, which dissociates into its components in boiling nitrobenzene and the (3)



monoether (V), decomp. 267-268°. The last-named compound is converted by aqueous sodium hydroxide into a colourless substance and by glacial acetic acid into a pale red material,

C28H12O2Cl2, m. p. 370° (decomp.) after darkening at 300°. Under similar conditions the blue hydrocarbon does not react with phenanthraquinone. It reacts readily with halogens, including iodine, yielding very stable, halogenated diradicals and with boiling aniline containing a little aniline hydrochloride. When sublimed in a vacuum in a current of carbon dioxide above 300° it is transformed into 2:3:6:7-dibenz-9:10-dihydroanthracene and a grey residue retaining the crystalline structure of the blue hydrocarbon.

The "lin-pentacene" of Philippi (A., 1929, 1436) is oxidisable to 2:3:6:7-dibenzanthraquinone, is dehydrogenated to the blue hydrocarbon, and suffers rise in m. p. when preserved; it is therefore regarded as 2:3:6:7-dibenz-9:10-dihydroanthracene.

Reply is made to the criticisms of Scholl and Böttger (A., 1930, 1439). H. WREN.

New colour reaction of aromatic amines. I. DE PAOLINI (Gazzetta, 1930, 60, 859-862).-Addition to neutral alcoholic solution of an aromatic amine of benzoyl peroxide in small doses as long as it dissolves results in the formation of a coloured compound, owing to oxidation of the amine to a quinonoid compound (cf. Gambarjan, A., 1925, i, 1260). Thus, with benzylamine:  $3CH_2Ph\cdot NH_2 + Bz_2O_2 \longrightarrow CH_2Ph\cdot NHBz + CHPh\cdot NH + Ph\cdot CO_2NH_3\cdot CH_2Ph +$  $H_2O$ . The benzoylating action of benzoyl peroxide is exerted also on other compounds of the type NH<sub>2</sub>R; thus, with hydroxylamine and hydrazine hydroxide, N-benzoylhydroxylamine and s-dibenzoylhydrazine, These actions are respectively, are obtained. probably due to the intermediate formation of perbenzoic acid. In presence of water and of oxidisable substances, this acid may be formed, not only from primary, but also from secondary and tertiary amines, as the result of a hydrolysis analogous to that caused T. H. POPE. by alkali hydroxides.

Preparation of substituted amides and hydrazides. S. M. MISTRY and P. C. GUHA (J. Indian Chem. Soc., 1930, 7, 793-797).-The following diarylcarbamides are prepared in 70-95% yield from carbamide (1 mol.) and the requisite amine (2 mols.) in boiling isoamyl alcohol: diphenyl-; di-m- and -p-tolyl-; di-m- and -p-nitrophenyl-; di-a- and -β-naphthyl-; di-p-acetamidophenyl-; dibenzyl-; di-m- and -p-hydroxyphenyl-, m. p. 215° (decomp.) and 288° (decomp.), respectively; o- and m-phenylene-, and diphenylene-carbamides. Similarly, carbamide and o-aminobenzoic acid afford 2: 4-diketo-1:2:3:4tetrahydroquinazoline; hydrazine hydrate and carbamide give semicarbazide (78% yield) preferably in presence of ethyl and *iso*amyl alcohols; diphenyl-, pp'-dinitrodiphenyl-, m. p. 361°, and pp'-dibromodiphenyl-carbohydrazides, m. p. 236° (decomp.), are obtained from carbamide and the requisite phenylhydrazine, whilst 4-phenylthiosemicarbazide and carbamide yield a mixture of 2-anilino-5-thiol-1phenyl-1:3:4-triazole, 2:5-endoxy-1:3:4-triazole, and 5-anilino-2-keto-2:3-dihydro-1:3:4-thiodiazole (A., 1927, 784).

Oxanilide, oxphenylhydrazide, and ox-p-acetamidoanilide, m. p. above 370° (ox-p-aminoanilide dihydrochloride is also described), are prepared from oxamide and the requisite amine by the above method. The following are also described : malonanilide; malonphenylhydrazide, m. p. 194—195° (lit. 184° and 187°); malon-p-acetamidoanilide, m. p. 235° (decomp.); succinanilide; succinphenylhydrazide, m. p. 207— 208° [lit. 201° (decomp.)]; succin-p-acetamidoanilide, m. p. 347° (decomp.)]; succin-p-acetamidoanilide, m. p. 347° (decomp.); succin-p-aminoanilide, m. p. 172°. Acetanilide is obtained from aniline and acetamide; p-acetamidodiphenylcarbamide from phenylcarbamide and acetyl-p-phenylenediamine; di-pacetamidophenylthiocarbamide from thiocarbamide and acetyl-p-phenylenediamine; 4-phenylthiosemicarbazide (instead of diphenylthiocarbohydrazide) from phenylhydrazine and thiocarbamide.

o-Nitroamines, hydrazines, and aminobenzenesulphonic acids do not react. Reaction does not occur between arylamines and aromatic acid amides.

H. BURTON.

Influence of strength of aromatic amines on their modes of reaction. E. HERTEL and K. SCHNEIDER (Z. physikal. Chem., 1930, 151, 413-419).—The extent of the reaction  $R \cdot NH_2 + H = R \cdot NH_3$  has been determined by measuring the electrical conductivity of the hydrochlorides of aromatic amines in aqueous acetone in the presence of varying amounts of the free amines. The substances studied were aniline,  $\alpha$ - and  $\beta$ -naphthylamines, 4-bromo(chloro)-a-naphthylamine, and 1-bromotheir (chloro)-β-naphthylamine. From relative capacity for combining with hydrogen ions the first three are strong, the fifth is weak, and the fourth of medium strength, "strength" here signifying a property analogous to, but not identical with, the strength of a base in water. The order of strengths is the same when referred to the combination with picric acid in acetone solution. The character of the crystalline compounds formed with nitrophenols depends both on the strength of the amine and on that of the phenol. Thus, aniline,  $\alpha$ -, and  $\beta$ -naphthylamine form both with pieric acid and with 2:6-dinitrophenol compounds of the type -NO, ... NH,-, whereas the two weaker amines form compounds of this type with picric acid only; with the weaker dinitrophenol the linking takes place between a nitrogroup and a carbon atom of the nucleus of the amine.

F. L. USHER.

Action of thiocarbimides on oximes. A. OBREGIA and C. V. GHEORGHIU (J. pr. Chem., 1930, [ii], **128**, 239—319; cf. Pavlovski, A., 1904, i, 237).— Reaction between arylthiocarbimides and oximes is less general than with arylcarbimides (Goldschmidt, A., 1890, 251). When reaction does occur, the initial products are probably the normal additive compounds NHAr·CS·O·N;CRR', but these are unstable and undergo either autoxidation (particularly ketoximes) or self-decomposition (aldoximes). The nature of the final products of the reaction also depends on temperature. Thus, the following changes probably occur between ketoximes and arylthiocarbinides: 2NHAr·CS·O·N;CRR' heat 2CRR';N·OH + 2[NHAr·CS·OH]  $\longrightarrow$  CS(NHAr)<sub>2</sub> + COS + H<sub>2</sub>O; 2NHAr·CS·O·N;CRR' (ordinary temperature) $\longrightarrow$ 2SH·C(:NAr)·O·N;CRR'  $\stackrel{0}{\longrightarrow}$  [{·S·C(:NAr)·O ·N;CRR'}<sub>2</sub>]  $\xrightarrow{2H_2O+3O}$  2NHAr·CO·O·N;CRR' + H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

An equimolecular mixture of phenylthiocarbimide and acetoxime in ethereal solution at the ordinary temperature forms sulphur (produced by decom-position of the intermediate thiosulphuric acid) and the O-phenylcarbamyl derivative of acetoxime (Goldschmidt, loc. cit.); the corresponding o- and p-tolylcarbamyl derivatives, m. p. 81-82° and 105-106°, respectively, are obtained similarly, using o- and p-tolylthiocarbimides. The O-phenylcarbamyl deriv-ative, m. p. 135°, of methyl ethyl ketoxime (o- and p-tolylcarbamyl derivatives, m. p. 80° and 146-147°, respectively) is obtained from the oxime and phenylthiocarbimide in absence or presence of acetone at the ordinary temperature, or from the oxime and phenylcarbimide. When the reaction is carried out in presence of alcoholic potassium hydroxide, the above phenylcarbamyl derivative and potassium thiosulphate are produced. The separation of sulphur from the reaction mixture of phenylthiocarbimide and methyl ethyl ketoxime is retarded by the absence of air; an attempt to prove the intermediate formation of a disulphide during the autoxidation by Storch's method (A., 1891, 548) was unsuccessful. A small amount of the above carbamyl derivative is formed together with s-diphenylthiocarbamide and carbonyl sulphide when phenylthiocarbimide is heated with methyl ethyl ketoxime. The O-phenylcarbamyl derivatives of diethyl, methyl propyl, and methyl isobutyl ketones, b. p. 175°,  $d_4^{17}$  0.8935,  $n_D^{20}$  1.456 (o-tolylcarbamyl derivative, m. p. 184°), have m. p. 96-98°, 146°, and 117°, respectively. Acetophenone-oxime furnishes O-phenylcarbamyl, m. p. 131.5° (lit. 126°), and O-o- and -p-tolylcarbamyl derivatives, m. p. 109° and 126°, respectively, whilst resacctophenone gives the *phenylcarbamyl* derivative, NHPh·CO·O·N.CMe·C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub>, m. p. 118-120°. In the last case reaction does not occur with the phenolic hydroxyl groups (cf. Goldschmidt, loc. cit.). The O-phenylcarbamyl derivative of p-tolyl methyl ketoxime has m. p. 112°. Benzhydroxamic acid and phenylthiocarbimide do not react at the ordinary temperature; when they are heated together, s-diphenylcarbamide is produced from the decom-position products (phenylcarbimide and water) of the acid. No reaction occurs between thiocarbimides and tetramethyldiaminobenzophenoneoxime, a- and  $\beta$ -benzilmonoximes, diacetylmonoxime, and  $\beta$ -oximinolævulic acid.

Aldoximes react generally with arylthiocarbimides in presence or absence of solvent at the ordinary temperature, forming mainly carbonyl sulphide, s-diarylthiocarbamides, and the nitriles corresponding with the oximes used :  $2NHAr \cdot CS \cdot O \cdot N:CHR \longrightarrow 2R \cdot CN + [2NHAr \cdot CS \cdot OH] \longrightarrow CS(NHAr)_2 + COS + H_2O.$  The following secondary reaction also occurs whereby sulphur is formed :  $2[SH \cdot C(:NAr) \cdot O \cdot N:CHR] \xrightarrow{O} [\cdotS \cdot C(:NAr) \cdot O \cdot N:CHR]_2 \longrightarrow 2R \cdot CN + [\cdotS \cdot C(:NAr) \cdot OH]_2 \longrightarrow CS(NHAr)_2 + S + CO_2 \text{ or }$ 

CO(NHAr),+S+COS. The same products are formed from both syn- and anti-oximes; the reaction thus differs from that with carbinides (Goldschmidt, loc. cit.). Since the nitrile is produced, it follows that the anti-additive compound rearranges into the sunform. When reaction is carried out in presence of alcoholic potassium hydroxide, a-benzaldoxime and anti-furfuraldoxime afford mainly the O-arylcarbamyl derivative of the oxime and potassium thiosulphate; secondary reactions occur as above. a-Anisaldoxime and a-salicylaldoxime undergo the general reactions in presence of alkali. The reactions between phenylthiocarbimide and o- and p-tolylthiocarbimides and  $\alpha$ - and  $\beta$ -benzaldoxime, acetaldoxime, salicylaldoxime (reaction does not occur with the phenolic hydroxyl group), a- and B-anisaldoximes, and syn- and antifurfuraldoximes are studied. The O-o-tolylcarbamyl derivative of a-benzaldoxime has m. p. 124°.

H. BURTON.

New process for preparing tetryl. L. DES-VERGNES (Chim. et Ind., 1930, 24, 785—793, 1304— 1316).—The solubilities of the oxalates of aniline and mono- and di-methylanilines in  $95 \cdot 7\%$  alcohol, 50%alcohol, and water were determined at various temperatures. By fractional crystallisation of the mixed oxalates from water, methylaniline may be separated in a state of purity from a technical mixture with dimethylaniline, but aniline if present is not completely removed. Methylation of aniline by gradual addition of 1 mol. of methyl sulphate gives a mixture containing dimethylamine, and offers no advantage over ordinary methods of alkylation.

A technical method for the preparation of tetryl by a two-stage nitration of methylaniline is described. In the first stage methylaniline sulphate is added to a diluted mixture of nitric and sulphuric acids at 20- $30^{\circ}$ , 2: 4-dinitromethylaniline and a small amount of a new dinitromethylaniline being produced. Further nitration of these with more concentrated acids at 70-75° gives tetryl and an isomeric trinitro-N-nitromethylaniline, m. p. 250-253° (decomp.) [261-262° (decomp.) when pure ?]. From the product of nitration of technical 2:4-dinitromethylaniline with 31% nitric acid on the water-bath, a small amount of a new dinitro-N-nitromethylaniline, m. p. 235-236° (decomp.), converted by further nitration into the above isomeride of tetryl, is isolated. H. A. PIGGOTT.

Behaviour of the phenylenediamines towards aromatic nitro-derivatives. G. B. CRIPPA (Gazzetta, 1930, 60, 644—647; cf. A., 1927, 352, 1205).— The final black product, comparable with anilineblack, obtained by oxidation of *p*-phenylenediamine in presence of nitrobenzene, is derived from an intermediate compound, tetra-aminodiphenyl-*p*-azophenylene. *m*-Nitrotoluene (but not its two isomerides) also condenses with *o*-phenylenediamine, giving 2-m-tolyl-

benziriazole, C<sub>6</sub>H<sub>4</sub><br/>N·C<sub>6</sub>H<sub>4</sub>Me, m. p. 99°, also

obtainable as follows. By condensation of *m*-nitrosotoluene and benzoyl-o-phenylenediamine, m-tolueneazo-o'-benzamidobenzene,

m-CH<sub>3</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NHBz(o), m. p. 100°, is obtained, giving on hydrolysis m-tolueneazo-o'-aminobenzene, m. p. 81°, which is converted by Zincke's method into the triazole. No condensation occurs between nitrobenzene and m-phenylenediamine. T. H. POPE.

Decomposition of benzenediazonium sulphate by aliphatic alcohols. H. H. HODGSON and A. KERSHAW (J.C.S., 1930, 2784—2785).—Dry benzenediazonium sulphate is decomposed by warming with an excess of an alcohol and the amount of aldehyde ( $\equiv$ benzene) produced is determined as the *p*-nitrophenylhydrazone. The amounts of aldehyde (as mol.-%) produced from the following alcohols are: benzyl, 19.5; methyl, 0; ethyl, 9.4; *n*-propyl, 4.7; *iso*propyl, 5; *iso*propyl+water, 3.6; *n*-butyl, 1.25. Ether formation is the main reaction.

H. BURTON.

Mechanism of the production of hydrazones from diazo-compounds and alkyl derivatives of acetoacetic, malonic, and cyanoacetic esters. G. FAVREL (Bull. Soc. chim., 1930, [iv], 47, 1290— 1300).—m-Nitrobenzenediazonium hydroxide in acetic acid solution at 0° couples with ethyl ethylacetoacetate in ethereal solution, yielding ethyl m-nitrobenzeneazoethyl acetoacetate,

NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>·CEtAc·CO<sub>2</sub>Et, m. p. 132-133°, which on reduction in alcoholic solution with acetic acid and sodium amalgam yields *m*-phenylenediamine, and with aqueous alkali isomerises to the *m*-nitrophenylhydrazone, m. p. 77-78°. Ethyl methylacetoacetate similarly gives ethyl m-nitrobenzeneazomethylacetoacetate, m. p. 122-123°, isomerising to the m-nitrophenylhydrazone of ethyl pyruvate, m. p. 102-103°, but the diazonium hydroxides derived from toluidines, chloroanilines, bromoanilines, etc. yield oils which decompose at 110° and could not be purified, but by the action of aqueous alkalis or, more slowly, by water alone are converted into the corresponding hydrazones. With ethyl ethylmalonate or ethyl methylmalonate the condensation product is always an oil. The hydrazones obtained from these compounds by treatment with water or alkalis are identical with those obtained from the same diazo-compounds and alkylacetoacetates and from phenylhydrazine and ethyl pyruvate or its homologue. pp'-Diphenyltetrazonium hydroxide in acetic acid and ethyl ethylmalonate in ether at 0° yield the *dihydrazone*,  $[\cdot C_6H_4 \cdot NEt \cdot N:C(CO_2Et)_2]_2$ , m. p. 112—114° (decomp.), which on reduction with zinc and acetic acid yields NN'-diethylbenzidine. Methyl methylmalonate similarly affords the dihydrazone,  $[\cdot C_6H_4\cdot NMe\cdot N:C(CO_2Me)]_2$ , m. p. 103-104° (decomp.), yielding on reduction NN'-dimethyl-benzidine, m. p. 77-78°. With tetrazotised o-tolidine ethyl ethylmalonate yields the dihydrazone,  $[\cdot C_6H_3Me \cdot NEt \cdot N:C(CO_2Et)_2]$ , m. p. 118—120° (decomp.), and with dianisidine the dihydrazone, [•(OMe)C<sub>6</sub>H<sub>3</sub>•NEt•N:C(CO<sub>2</sub>Et)<sub>2</sub>]<sub>2</sub>, m. p. 115-116° (decomp.).

Ethyl ethylcyanoacetate in ether at 0° with p-bromobenzenediazonium hydroxide yields both the hydrazone,  $C_6H_4Br\cdot NEt\cdot N:C(CN)\cdot CO_2Et$ , m. p. 56— 57°, and the *azo*-compound,

 $C_{6}H_{4}Br\cdot N:N\cdot CEt(CN)\cdot CO_{2}Et$ , m. p. 111—112°, which on reduction yield ethylaniline and *p*-bromoaniline with a little aniline, respectively. The same compounds are obtained from *p*-bromophenylhydrazine and ethyl cyanomalonate. *m*-Nitrobenzenediazonium hydroxide and ethyl methylcyanoacetate yield both the hydrazone,  $NO_{2}\cdot C_{6}H_{4}\cdot NMe\cdot N:C(CN)\cdot CO_{2}Et$ , m. p. 148°, and the *azo*-derivative,

 $NO_2 \cdot C_6H_4 \cdot N: N \cdot CMe(CN) \cdot CO_2Et$ , m. p. 197—198°; benzenediazonium hydroxide and ethyl ethylcyanoacetate give the *hydrazone*, m. p. 72°, and *azo*-compound, m. p. 126°. Ethyl cyanoacetoacetate and benzenediazonium hydroxide yield only the *azo*-compound, Ph·N:N·C(CN)(COMe)·CO\_2Et, m. p. 129—130°. R. BRIGHTMAN.

Labile compound of benzeneazo-3-naphthol and β-naphthol. H. H. HODGSON and W. ROSEN-BERG (J.C.S., 1930, 2787).-When diazotised aniline is coupled with  $\beta$ -naphthol in aqueous sodium hydroxide (1 equiv.) containing an excess of sodium carbonate and the resultant product crystallised from benzene, an additive compound  $(-+C_{c}H_{a})$ , m. p. 62-64°, m. p. (benzene-free) 79-80°, of 1 mol. of benzeneazo- $\beta$ -naphthol and 1 mol. of  $\beta$ -naphthol is frequently produced. Crystallisation of the benzenefree product from acetic acid, pyridine, or alcohol gives benzeneazo-\beta-naphthol, m. p. 133-134° (lit. 131°). When coupling is effected in aqueous sodium hydroxide, hydrogen carbonate, acetate, or borate, only benzeneazo-\beta-naphthol results. Equimolecular amounts of benzenediazonium sulphate and aqueous sodium  $\beta$ -naphthoxide give the double compound, and unchanged diazonium salt remains in solution; with excess of the oxide a quantitative yield results.

H. BURTON.

Preparation of unsaturated ethers from acetals. A. JOHANNISSIAN and E. AKUNIAN (Bull. Univ. Etat R.S.S. Arménie, 1930, No. 5, 245—251; Chem. Zentr., 1930, ii, 552).—Toluene-*p*-sulphonic acid is a good catalyst for the preparation of alkoxycyclohexenes from the corresponding acetals. On long heating the reaction takes place in absence of a catalyst. A. A. ELDRIDGE.

Preparation of *p*-nitrophenol from *p*-chloronitrobenzene. A. M. Porov (Ukraine Chem. J., 1930, 5, [Tech.], 105—111).—The usual method of obtaining *p*-nitrophenol by nitrating phenol and separating the *o*- and *p*-isomerides by steam-distillation is slow and gives a poor yield. By heating *p*-chloronitrobenzene with sodium hydroxide a 93%yield is obtained after 30 min. at 160—162°. Excess of alkali has no influence on the yield, temperature being the chief factor. A theoretical relationship is given connecting temperature and yield. On the semi-technical scale 83% of the theoretical yield was obtained under the same conditions.

E. B. UVAROV.

[Preparation of] picramic acid. E. CLAYTON (J. Soc. Dyers and Col., 1930, 46, 365).—In the preparation of picramic acid by partial reduction of picric acid with sodium sulphide the initial  $p_{\rm H}$  of the reaction mixture is a governing factor; the best

yields are obtained when the concentration of alkali is low. The highest yields (90%) result from reduction of an aqueous solution of sodium picrate with sodium hydrosulphide at 50-66% (details given), and high yields are favoured by the use of a reducing agent the aqueous solution of which has a low hydrolysis constant. Confirmation is obtained of the view that in the reduction of polynitro-compounds the presence of hydroxyl ions in the reaction mixture leads to the production of azoxy-compounds, whilst their absence favours the formation of amino-compounds. The highest yields of picramic acid appear to result when the reaction proceeds thus: picric acid  $\rightarrow$  nitroso-derivative  $\rightarrow$  hydroxylamino-derivative  $\rightarrow$  picramic acid, and it follows that the formation of azoxy-derivatives should be avoided. A. J. HALL.

Syntheses of aceto-*p*-phenetidide. A. Koss and Z. KWIATKOWSKI (Rocz. Farm., 1928, 15-28; Chem. Zentr., 1930, ii, 549).—A criticism.

A. A. ELDRIDGE.

Action of trichloromethyl chloroformate on phenols. N. MELNIKOV (J. pr. Chem., 1930, [ii], 128, 233—238, and J. Russ. Phys. Chem. Soc., 1930, 62, 1671—1675; cf. A., 1930, 738, 1019, 1270).—Trichloromethyl chloroformate (1 mol.) reacts with sodium aryloxides (1 mol.) in aqueous solution, forming aryl trichloromethyl carbonates; with 4 mols. of the aryloxide, diaryl carbonates are produced. The following are new: p-tolyl, b. p. 162°/10 mm., m. p. 47°;  $\beta$ -naphthyl, m. p. 128°; p-chlorophenyl, m. p. 109°, and p-nitrophenyl trichloromethyl carbonates, m. p. 132°. Treatment of these mixed carbonates with aniline in ether affords a mixture of diphenylcarbamide and the appropriate aryl phenylcarbamate. H. BURTON.

Sulphur derivatives of o-methoxytoluene. G. B. KOLHATKAR and K. V. BOKIL (J. Indian Chem. Soc., 1930, 7, 843-850).-The compound, m. p. 138°, obtained by Meldrum and Shah (J.C.S., 1923, 123, 1992) as a by-product during the sulphonation of o-methoxytoluene is also formed from 2-methoxytoluene-5-sulphonyl chloride and o-methoxytoluene in presence of aluminium chloride and 2-methoxytolidele in presence of aluminium chloride and carbon di-sulphide; it is, therefore, 6:6'-dimethoxydi-m-tolyl-sulphone. This is oxidised by alkaline potassium permanganate to 4:4'-dimethoxydiphenylsulphone-3:3'-dicarboxylic acid, m. p. 250° (decomp.) after sintering at 245°, which when heated with calcium oxide gives 4:4'-dimethoxydiphenylsulphone. De-methylation of the above sulphone and acid with methylation of the above sulphone and acid with hydriodic acid (d 1.7) at  $165^{\circ}$  furnishes 6:6'-dihydroxydi-m-tolylsulphone, m. p. 263° (corr.), and 4:4'-dihydroxydiphenylsulphone-3:3'-dicarboxylic acid, m. p. 306-307° (decomp.), respectively. Benzenesulphonyl chloride and o-methoxytoluene react as above, forming 4-methoxy-3-methyldiphenylsulphone, m. p. 112-112.5°, also obtained from benzene and 2-methoxytoluene-5-sulphonyl chloride. This is demethylated to 4-hydroxy-3-methyldiphenylsulphone, m. p. 226°, and oxidised to 4-methoxydiphenylsulphone-3-carboxylic acid, m. p. 176° (the corresponding 4-hydroxy-acid has m. p. 216-217°). p-Toluenesulphonyl chloride and o-methoxytoluene

yield 4-methoxy-3: 4'-dimethyldiphenylsulphone, m. p. 109.5—110°, also formed from toluene and 2-methoxytoluene-5-sulphonyl chloride. 4-Hydroxy-3: 4'-dimethyldiphenylsulphone and 4-methoxydiphenylsulphone-3: 4'-dicarboxylic acid have m. p. 200—201° and 283°, respectively. p-Methoxybenzenesulphonyl chloride and o-methoxytoluene give 4:4'-dimethoxy-3-methyldiphenylsulphone, m. p. 126°, also produced together with an isomeride, m. p. 102°, from anisole and 2-methoxytoluene-5-sulphonyl chloride. 4:4'-Dimethoxydiphenylsulphone-3-carboxylic acid has m. p. 186—187°. o-Anisolesulphonyl chloride and o-methoxytoluene afford (?) 2': 4-dimethoxy-3-methyldiphenylsulphone, m. p. 145°.

Treatment of o-methoxytoluene with sulphur dioxide in presence of aluminium chloride yields a mixture of tri-o-methoxytolylsulphonium chloride (+3H<sub>2</sub>O), m. p. 69-70°, m. p. (anhydrous) 140-141°, and 6:6'-dimethoxydi-m-tolylsulphoxide, m. p. 87-87.5°. This sulphoxide is reduced by zinc dust and acetic acid to 6: 6'-dimethoxydi-m-tolyl sulphide, m. p. 37.5-38°. When 2 - methoxytoluene - 5 - sulphonyl chloride is reduced with alkaline sodium sulphite a mixture of 2-methoxytoluene-5-sulphinic acid (sodium and silver salts) and 6:6'-dimethoxydim-tolyldisulphone, m. p. 206.5° (decomp.), is produced. The sulphinic acid changes spontaneously into 6 : 6'-dimethoxydi-m-tolyldisulphoxide, m. p. 118°, which is prepared by oxidising 6:6'-dimethoxydim-tolyl disulphide, m. p. 44-45°, with hydrogen peroxide in acetic acid. This disulphide is produced when 5-thiol-2-methoxytoluene, b. p. 236-237°, m. p. 42-43°, is oxidised by iodine. H. BURTON.

Preparation of β-*p*-hydroxyphenylethylamine. T. KONDO and Y. SHINOZAKI (J. Pharm. Soc. Japan, 1929, 49, 267—269).—Electrolytic reduction of *p*methoxy-ω-nitrostyrene (obtained by treatment of alcoholic anisaldehyde and nitromethane with methylalcoholic potassium hydroxide) gave β-*p*-methoxyphenylethylamine hydrochloride, m. p. 210° (hydroxycompound, m. p. 268—269°).

CHEMICAL ABSTRACTS. β-Phenylethylamines. I. Mezcaline and substances resembling mezcaline. K. H. SLOTTA and H. HELLER (Ber., 1930, 63, [B], 3029-3044).o-Methoxybenzaldehyde is condensed with malonic acid in pyridine containing piperidine at 100° to o-methoxycinnamic acid, m. p. 183° (yield 80%), which is reduced by sodium amalgam to  $\beta$ -o-methoxyphenylpropionic acid, m. p. 92° (yield 99%), converted by thionyl chloride in chloroform into the corresponding chloride and thence by sodium hydroxide and ammonia into β-o-methoxyphenylpropionamide, m. p. 111° (yield 86.3%). The amide is transformed by successive treatment with sodium hypochlorite and potassium hydroxide into \$-o-methoxyphenylethylamine (yield 35.2%) (hydrochloride, m. p. 143°; sulphate, m. p. 230°). m-Nitrobenzaldehyde is transformed by the usual methods into m-methoxybenzaldehyde, which is converted successively into mmethoxycinnamic acid, m. p. 177°; β-m-methoxyphenylpropionic acid, m. p. 50°, and β-m-methoxy-phenylpropionamide, b. p. 222-225°/12 mm. The amide is converted by sodium hypobromite into

β-m-methoxyphenylethylamine, b. p. 182°/112 mm., in 61% yield, whereas with hypochlorite the yield is only 19%. Anisaldehyde is similarly transformed into  $\beta$ -*p*-anisylpropionamide, transformed by hypochlorite into  $\beta$ -*p*-anisylethylamine hydrochloride, m. p. 210°. in 43% yield. Cuminaldehyde and malonic acid yield successively *p*-isopropylcinnamic acid, m. p. 165°;  $\beta$ -*p*-isopropylphenylpropionic acid, m. p. 73°, and  $\beta$ -p-isopropylphenylpropionamide, m. p. 142°, degraded by hypochlorite at  $65^{\circ}$  to  $\beta$ -p-isopropylphenylethyl-amine hydrochloride, m. p. 270°, in small yield. Vanillin ethyl ether, m. p. 63°, affords successively 3-methoxy-4-ethoxycinnamic acid, m. p. 205° (yield 89%); β-3-methoxy-4-ethoxyphenylpropionic acid, m. p. 130° (yield 79%); β-3-methoxy-4-ethoxyphenyl-propionamide, m. p. 124° (yield 33.9%), and (by sodium hypochlorite, but not hypobromite) \$-3methoxy-4-ethoxyphenylethylamine, b. p. 165°/ 15—18 mm. (hydrochloride, m. p. 120°). 2:4-Dimethoxybenzaldehyde gives 2:4-dimethoxycinnamic acid and  $\beta$ -2 : 4-dimethoxyphenylpropionic acid, m. p. 105°, which could not be transformed into the corresponding amide. Piperonal is converted into  $\beta$ -3:4methylenedioxyphenylethylamine (hydrochloride, m. p. 206°). 2:3:4-Trimethoxybenzaldehyde, b. p. 170°/12 mm., is obtained in 53% yield by the addition of pyrogallol trimethyl ether and hydrogen cyanide to aluminium chloride in benzene and treatment of the product with steam. It affords successively 2:3:4-trimethoxycinnamic acid, m. p. 172° (yield 94%);  $\beta \cdot 2:3:4$ -trimethoxyphenylpropionic acid, m. p. 76° (yield 65%);  $\beta \cdot 2:3:4$ -trimethoxy-phenylpropionamide, m. p. 171° (yield  $63\cdot 5\%$ ), and (by sodium hypobromite)  $\beta - 2:3:4$ -trimethoxyphenylethylamine, b. p. 167°/12 mm. (yield 71.5%) (hydrochloride, m. p. 146°). 3:4:5-Trimethoxybenzoyl chloride is converted by hydrogen in boiling xylene in presence of palladised barium sulphate into 3:4:5-trimethoxybenzaldehyde, m. p. 74° (yield 80%). The aldehyde yields successively 3:4:5-trimethoxycinnamic acid, m. p.  $124^{\circ}$ ;  $\beta$ -3:4:5-tri-methoxyphenylpropionic acid, m. p. 98° (yield 88%);  $\beta$ -3:4:5-trimethoxyphenylpropionamide, m. p. 106° (yield 60%), and (by sodium hypobromite)  $\beta \cdot \overline{3} : 4 : 5$ trimethoxyphenylethylamine (mezcaline), b. p. 180°/ 12 mm. (yield 66%).

Anisole in glacial acetic acid is converted by bromine vapour into p-bromoanisole, b. p.  $120^{\circ}/12$  mm. (yield 82.9%), transformed by successive treatment with activated magnesium in ether and ethylene oxide into  $\beta$ -p-anisylethyl alcohol, in 31.1% yield. With 47.5%hydrobromic acid the alcohol gives  $\beta$ -p-anisylethyl bromide (yield 45%), transformed by successive treatment with phthalimide and potassium carbonate and hydrazine hydrate into  $\beta$ -p-anisylethylamine in 11.8% yield. 4-Bromoveratrole, p-bromophenol, pbromophenyl acetate, o- and p-bromonitrobenzene, and o-dichlorobenzene could not be caused to react with magnesium in ethyl or *iso*amyl ether.

H. WREN.

Derivatives of *m*-xylenols. I. Intermediate products from *m*-5-xylenol (5-hydroxy-1:3dimethylbenzene). F. M. ROWE, S. H. BANNISTER R. R. SETH, and R. C. STOREY (J.S.C.I., 1930, 49, 469-473T).—Direct nitration of *m*-5-xylenol in

acetic acid is accompanied by much resinification, but gives volatile 4-nitro-m-5-xylenol, m. p. 66° (29%), and non-volatile 2-nitro-m-5-xylenol, m. p. 107-108° (18%). Monosulphonation of *m*-5-xylenol under all conditions appears to occur solely in o-position to the hydroxyl group, and m-5-xylenol-4-sulphonic acid is best made with cold monohydrate. There is a confusion in the properties of this acid as described by Raschig (G.P. 283,306). The sulphonic acid is very soluble in water, but does not separate as crystals, m. p. 102-103°, on adding concentrated hydrochloric acid to a concentrated solution. A sulphur-containing by-product, m. p. 111-112°, however, is formed in sulphonations with chlorosulphonic acid at 100°. Nitration of m-5-xylenol-4-sulphonic acid in monohydrate gives a little 4-nitro-m-5-xylenol, but mainly nitrosulphonic acids, from which 4-nitro- (total 38%) and 2-nitro-m-5-xylenol (29%) are obtained by acid hydrolysis. Nitration of 2-nitro-m-5-xylenol in acetic acid gives volatile 2:4-dinitro-m-5-xylenol, m. p. 115-116° (85%), but nitration of 4-nitro-m-5-xylenol in monohydrate gives some non-volatile 2:4:6-trinitro-m-5-xylenol, m. p. 107-108°, and mainly 2:4-dinitro-m-5-xylenol-6-sulphonic acid, from which the sulphonic group is eliminated by boiling with aqueous sulphuric acid. Non-volatile 4 : 6-dinitro-m-5-xylenol, m. p. 126—127°, was obtained only as a byproduct of the nitration of a sulphonation mixture probably containing 4 : 6-disulphonic acid. Toluenep-sulphonyl-m-5-xylenol, m. p. 83°, is nitrated satisfactorily only to a trinitro-derivative, m. p. 148-149° (70%), readily hydrolysed by boiling aqueous-alcoholic potassium hydroxide to 2:4-dinitro-m-5-xylenol (97%).

Diazotised aniline couples with m-5-xylenol under all conditions to give a mixture of mono- (maximum 73%) and dis-azo-compounds, alkaline coupling favouring formation of the latter. Reduction of benzeneazo-m-5-xylenol, m. p. 104—105°, with alkaline sodium hyposulphite gives 2-amino-m-5-xylenol, m. p. 182° (96%), which is obtained also by a similar reduction of 2-nitroso-m-5-xylenol, m. p. 182° (decomp.), and forms a diacetyl derivative, m. p. 182°. Attempts to prepare 2:4-dinitro-4'-hydroxy-2':6'dimethyldiphenylamine always gave its 2'':4''dinitrophenyl ether, m. p. 283—284° (23%).

Reduction of 4-nitro-m-5-xylenol with alkaline sodium hyposulphite gives 4-amino-m-5-xylenol, m. p. 163° (72%) (diacetyl derivative, m. p. 87—88°).

m-5-Xylenol and methyl sulphate give the methyl ether, b. p. 194—195° (87%), which could not be mononitrated. Methyl sulphate with the corresponding nitroxylenols gives the volatile 4-nitro-5-mxylenol methyl ether, m. p. 45—46°, and the nonvolatile 2-nitro-methyl ether, m. p. 53°. Dinitration of m-5-xylenol methyl ether gives the 2:4-dinitroderivative, m. p. 172°, identical with the methylation product of 2:4-dinitro-m-5-xylenol, and some 2:4:6trinitro-derivative, m. p. 124—125°.

Reduction of 4-nitro-m-5-xylenol methyl ether with acid stannous chloride gives volatile 4-aminom-5-xylenol methyl ether, m. p.  $36-37^{\circ}$  ( $80^{\circ}_{0}$ ) (diacetyl derivative, m. p.  $80-81^{\circ}$ ), but reduction with alkaline sodium hyposulphite is accompanied by the introduction of a sulphonic group, giving sodium 4-aminom-5-xylenolsulphonate. Reduction of 2:4-dinitrom-5-xylenol methyl ether with sodium sulphide gives, presumably, 2-nitro-4-amino-m-5-xylenol methyl ether, m. p. 91° (76%).

Alkamine and ether-bases of the tetralin and hydrindene series. J. von BRAUN and K. WEISS-BACH (Ber., 1930, 63, [B], 3052-3059).-When the product of the action of ammonia, methylamine, or dimethylamine on 2-bromo-1-hydroxy-1:2:3:4tetrahydronaphthalene (cf. A., 1923, i, 105) is treated with methyl sulphate and sodium hydroxide and subsequently with potassium iodide it yields 2methoxy-1:2:3:4-tetrahydronaphthyltrimethylammonium iodide, m. p. 168°. When heated at 170° it is decomposed into trimethylamine hydriodide and 2-methoxy-3: 4-dihydronaphthalene, b. p. 136°/15 mm.,  $d_1^{37}$  1.0674, converted by 2N-hydrochloric acid into 2-keto-1:2:3:4-tetrahydronaphthalene, b. p. 132-133°/12 mm. The ether is relatively slowly hydrogenated in presence of palladium to 2-methoxy-1:2:3:4tetrahydronaphthalene, b. p. 123-124°/16 mm.; in carbon disulphide it readily adds bromine and loses hydrogen bromide with production of β-naphthyl methyl ether.

2-Bromo-1-methoxy-1:2:3:4-tetrahydronaphthalene and dimethylamine in benzene at 100° afford 2 - dimethylamino - 1 - methoxy - 1 : 2 : 3 : 4 - tetrahydro naphthalene, b. p. 147—149°/13 mm. (hydrochloride, m. p. 184°; picrate, m. p. 192°; methiodide, m. p. 210°). 2-Methylamino-1-methoxy-1: 2:3:4-tetrahydronaphthalene, b. p. 144—146°/14 mm., yields a hydrochloride, m. p. 228°; a picrate, m. p. 150°, and a methiodide, m. p. 210°. 2-Piperidino-1-methoxy-1:2:3:4-tetrahydronaphthalene, b. p. 191-193°/15 mm., its hydro-chloride, m. p. 230°, and picrate, m. p. 153°, are 1 - Methoxy - 1:2:3:4 - tetrahydro - 2 described. naphthyltrimethylammonium iodide decomposes only to a slight extent when heated about 10° above its m. p., but yields 2-dimethylamino-1-methoxy-1:2:3:4-tetrahydronaphthalene when subjected to dry distillation. 2-Methylamino-1-methoxy-1:2:3:4tetrahydronaphthalene is transformed by 66% hydrobromic acid at 55-60° into 2-methylamino-1-hydroxy-1:2:3:4-tetrahydronaphthalene, m. p. 77-79°, b. p. about 122°/0.2 mm. (hydrochloride, m. p. 206°: picrate); if the treatment with hydrobromic acid is conducted at 100° the product is 2-methylamino-3: 4dihydronaphthalene, b. p. 162-164°/12 mm. (hygroscopic hydrochloride, m. p. 148-150°; picrate, m. p. 149°). Similar treatment of the 2-dimethylaminoand 2-piperidino-derivatives with hydrobromic acid at 40-45° affords, respectively, 2-dimethylamino-3:4dihydronaphthalene, b. p. 102-104°/0.4 mm. (noncrystalline hydrochloride; picrate, m. p. 148°), and 2-piperidino-3: 4-dihydronaphthalene, b. p. 168-170°/ 0.4 mm., m. p. 40° (picrate, m. p. 149°).

1-Methylamino-2-hydroxyhydrindene, m. p. 130° (hydrochloride, m. p. 175°; picrate, m. p. 153°), is prepared by the action of 33% aqueous methylamine on bromohydroxyhydrindene (cf. A., 1923, i, 107). If the product of the action of methylamine, dimethylamine, or ammonia on 2-bromo-1-hydroxyhydrindene is treated with methyl sulphate and, subsequently, potassium iodide, 2-methoxyhydrindyltrimethylammon-

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ium iodide, m. p. 187°, is formed. It decomposes when heated above its m. p. or, preferably, when distilled in a vacuum into 1-dimethylamino-2-methoxyhydrindene, b. p. 132°/14 mm. (picrate, m. p. 159°), hydrolysed by acid to 2-hydrindone. 2-Dimethylamino-1-methoxyhydrindene, b. p. 128-129°/14 mm. (methiodide, m. p. 176°), is obtained by the action of dimethylamine in benzene at 100° on 2-bromo-1-methoxyhydrindene, b. p. 134°/11 mm., prepared by the action of boiling methyl alcohol on 1:2-dibromohydrindene. 2-Methylamino-1-methoxyhydrindene, b. p. 127-128°/14 mm. (picrate, m. p. 118°; hydrochloride, m. p. 173°), is described. Replacement of methoxyl by hydroxyl is more difficult than in the tetrahydronaphthalene series owing to the tendency of the products towards polymerisation, but treatment of the methylamino-base with fuming hydrobromic acid at the ordinary temperature and subsequently at 45-50° affords 2-methylamino-1-hydroxyhydrindene, m. p. 77-79° (picrate, m. p. 171°), in small amount. The base loses water with great readincss, whereby in presence of hydrochloric acid a compound, C<sub>10</sub>H<sub>13</sub>NCl<sub>2</sub>, m. p. 165-166°, is produced. Replacement of methoxyl by hydroxyl does not appear possible in the case of the dimethylamino-base. H. WREN.

Course of substitution reactions. Aromatic and hydroaromatic halogen compounds from β-naphthol. K. FRIES and K. SCHIMMELSCHMIDT (Annalen, 1930, 484, 245-300).-The reaction  $C_{10}H_7 \cdot OH(\beta) + Br_2 \Longrightarrow C_{10}H_6Br \cdot OH + HBr$  is shown to be reversible, since treatment of 1-bromo-\beta-naphthol with 10 parts of a saturated solution of hydrogen bromide in acetic acid in presence of 1 part of potassium iodide (saturated aqueous solution diluted with 3 parts of acetic acid) gives, after some hours at the ordinary temperature or after a few seconds at 100°, β-naphthol. Potassium iodide may be replaced by stannous chloride and hydrogen bromide by hydrogen chloride. 1:6-Dibromo- $\beta$ -naphthol is converted similarly into 6-bromo- $\beta$ -naphthol. 1-Chloro- and 1:4-dichloro- $\beta$ -naphthols afford  $\beta$ -naphthol and 4chloro- $\beta$ -naphthol, respectively, when treated with a solution of hydrogen chloride in acetic acid in presence of stannous chloride at 100°.

Further evidence is now brought forward supporting the formation of ketobromides during the bromination of β-naphthol derivatives. Various discrepancies in the literature are also explained, the chief of which is that bromination of β-naphthol gives successively the 1-bromo-, 1: 6-dibromo-, and 1: 4: 6-tribromo-derivatives (cf. Franzen and Stäuble, A., 1922, i, 450). The tetrabromo-\beta-naphthols, formed by bromination in acetic acid, consist of the 1:3:4:6-, 1:3:5:6-, and 1:3:6:8-derivatives; the last two compounds are not produced by simple substitution processes. Different derivatives are produced when the ketobromides are brominated (and the products then reduced) from those formed when bromo- $\beta$ -naphthols are brominated. Thus, 1:3:6-tribromo-\$-naphthol is produced when 1:1-dibromo-2-keto-1:2-dihydronaphthalene is brominated and the resultant product reduced. Extensions of the changes previously suggested (A., 1924, i, 1187) are given which explain the formation of the polybromo-\beta-naphthols now described.

2:3-Hydroxynaphthoic acid and a large excess of bromine in acetic acid at 100° give the 1:5:6-tribromo-derivative, m. p. 320°, oxidised by boiling nitric acid (d 1.4) to 3:4-dibromophthalic acid, m. p. 196° (decomp.) (anhydride, m. p. 148.5°). When bromination is carried out in cold acetic acid containing sodium acetate, 1:1:3:3-tetrabromo-2-keto-4-acetoxy-1:2:3:4-tetrahydronaphthalene, m. p. 140°, decomp. 155°, is produced; carbon dioxide is eliminated. This is reduced by stannous chloride and alcoholic hydrochloric acid to 1:3-dibromo-2-hydroxy-4-acetoxynaphthalene, m. p. 148° [the 2:4-diacetoxy-derivative, m. p. 122°, is identical with that described by Meyer and Wolfsleben (A., 1911, i, 631)], which is converted by alkaline sodium stannite into 1: 1'-dibromo-2:4:2':4'tetrahydroxy-3: 3'-dinaphthyl, m. p. 242° (decomp.) (tetra-acetate, m. p. 222-223°). Treatment of the above tetrabromo-derivative with hydrogen bromide in acetic acid gives 1:3:6-tribromo-2:4-dihydroxynaphthalene, whilst reduction with zinc dust and acetic acid affords 1:3-dibromo-\$-naphthol, m. p. 75° (acetate, m. p.  $102^{\circ}$ ), which with nitric acid (d 1.52) in cold acetic acid yields 1: 3-dibromo-1-nitro-2-keto-1:2-dihydronaphthalene, m. p. 98° (decomp.). When a solution of this nitro-compound is boiled for a short time, there is obtained 3-bromo-1: 2-naphthaquinone, m. p. 179°, converted by alcoholic hydrochloric acid into 3-bromo-2-hydroxy-1: 4-naphthaquinone, m. p. 202° (lit. 196°) (4-anil, m. p. 233°, prepared by the action of alcoholic aniline on the 1 : 2-quinone), by an excess of aniline into 2-anilino-1: 4-naphthaquinoneanil, and by sulphurous acid into 3-bromo-1:2-dihydroxynaphthalene, m. p. 117° (diacetate, m. p. 160°). Bromination of 1:3-dibromo-β-naphthol in acetic acid and sodium acetate affords 1:1:3-tribromo-2-keto-1:2dihydronaphthalene, m. p. 102-105°, which with hydrogen bromide in acetic acid gives some 1:3:6tribromo-\$-naphthol. Reduction of 1: 3-dibromo-\$naphthol with tin and alcoholic hydrochloric acid furnishes 3-bromo- $\beta$ -naphthol, m. p. 83° (acetate, m. p. 94°; methyl ether, m. p. 77–78°, converted by the Grignard method into 3-methoxy- $\beta$ -naphthoic acid). 4-Bromo-β-naphthol, m. p. 122°, is prepared by the usual method from the bromonaphthylamine.

The sulphate of 4-bromo-2-amino- $\alpha$ -naphthol, m. p. 128° (diacetyl derivative, m. p. 231°), is oxidised by nitric and acetic acids to 4-bromo-1 : 2-naphthaquinone, m. p. 154°. Treatment of 1 : 6-dibromo- $\beta$ -naphthol with nitric and acetic acids yields 1 : 6-dibromo-1-nitro-2-keto-1 : 2-dihydronaphthalene, m. p. 100° (decomp.) after sintering at about 75°, converted by heating in benzene into 6-bromo-1 : 2-naphthaquinone, m. p. 168° (decomp.) after darkening at 145° and sintering at about 150°.

β-Naphthol and a large excess of bromine in acetic acid and sodium acetate give 1:1:3:6-tetrabromo-2keto-1:2-dihydronaphthalene, m. p. 168° (decomp.), reduced by stannous chloride in acetic acid to 1:3:6tribromo-β-naphthol, m. p. 132° (acetate, m. p. 152°), also prepared by brominating 1:3-dibromo-β-naphthol. Reduction of this with tin and hydrochloric acid affords 3:6-dibromo-β-naphthol, m. p. 127° (acetate, m. p. 127°), whilst treatment with nitric and acetic acids yields 1:3:6-tribromo-1-nitro-2-keto-1:2-dihydronaphthalene. When this is heated in benzene, 3:6dibromo-1: 2-naphthaquinone, m. p. 176°, is probrominer in acetic acid at 100% give the 11c 5. beauti

1:4:6-Tribromo-B-naphthol [described as the 1:3:6-derivative by Franzen and Stäuble (loc. cit.)] and nitric acid  $(d \ 1.52)$  in chloroform give 1:4:6tribromo-1-nitro-2-keto-1: 2-dihydronaphthalene, m. p. about 145° after reddening at 110°, convertible into 4:6-dibromo-1:2-naphthaquinone, m. p. 153°. This reacts with aniline (2 mols.) in alcohol, forming 6bromo-2-hydroxy-1: 4-naphthaquinoneanil, m. p. 276° (also obtained similarly from 6-bromo-1: 2-naphthaquinone), and is converted by alcoholic hydrochloric acid into 6-bromo-2-hydroxy-1: 4-naphthaquinone, m. p. 203° (also formed similarly from the 6-bromo-1: 2quinone).

1:3:4:6-Tetrabromo- $\beta$ -naphthol, the main product of bromination of 3-naphthol with 4 mols. of bromine in acetic acid at 100°, is oxidised by nitric and acetic acids to 3:4:6-tribromo-1:2-naphthaquinone, m. p. 191° (quinoxaline derivative, m. p. 250°, from o-phenylenediamine), reduced by stannous chloride and acetic acid to a mixture of 3:6-dibromo-1:2dihydroxynaphthalene and probably 3:6:3':6'-tetrabromo-1:2:1':2'-tetrahydroxy-4:4'-dinaphthyl, m. p. 293°. Treatment of the tribromoquinone with sulphuric acid at 175° gives 3 : 6-dibromo-2-hydroxy-1 : 4naphthaquinone, m. p. 219° (the anil, m. p. 185°, is prepared by the action of alcoholic aniline on the tribromoquinone), whilst with a large excess of aniline 6-bromo-2-anilino-1: 4-naphthaquinoneanil, m. p. 211° (decomp.), results. The tribromoquinone and warm nitric acid (d 1.52) give 3:3:6-tribromo-1:2:4triketo-1:2:3:4-tetrahydronaphthalene (+H,O), m. p. 157°, reduced by stannous chloride and acetic acid to 3:6-dibromo-1:2:4-trihydroxynaphthalene. 1:3:5:6-Tetrabromo-β-naphthol, m. p. 186° (acetate, m. p. 155°), is best prepared by brominating 1:5:6tribromo-2-hydroxy-3-naphthoic acid in acetic acid and sodium acetate, and reducing the 1:1:3:3:5:6hexabromo-2-keto-4-acetoxy-1:2:3:4-tetrahydronaphthalone, m. p. 170-175°, so produced with zinc dust and acetic acid. 1:3:5:6-Tetrabromo-1-nitro-2keto-1: 2-dihydronaphthalene passes at 85° into 3: 5: 6tribromo-1: 2-naphthaquinone, m. p. 184°, and is reduced by stannous chloride and acetic acid to 3:5:6tribrome-1-nitro-B-naphthol, m. p. 159° (decomp.). This quinone is converted by alcoholic aniline (3 mols.) and hydrochloric acid into 5: 6-dibromo-2-anilino-1: 4naphthaquinoneanil, m. p. 221° (decomp.), and 3:5:6tribromo-2-hydroxy-1: 4-naphthaquinone, m. p. 232°, respectively. Oxidation of 1:3:5:6-tetrabromo-βnaphthol with nitric and acetic acids furnishes a mixture of the tribromoquinone and the compound (I) (+Ac·OH), m. p. 115° (decomp.), m. p. (solvent-free)

Br Br

Br ONO<sub>2</sub> 121° (decomp.); I is reduced by stannous chloride and acetic acid  $(OH)_2$  to 3:5:6-tribromo-1:2-dihydr-Br oxynaphthalene, m. p. 181° (di-acetate, m. p. 171°), and con-verted by boiling with alcohol into the tribromoquinone.

1:1-Dibromo-2-keto-1:2-dihydronaphthalene (improved preparation given) (A., 1924, i, 1187) is brominated in chloroform at -15° to 1:1:3:4:6:7hexabromo - 2 - keto-1:2:3:4:6:7-hexahydronaphth-

alene, m. p. 173°, converted by stannous chloride in acetic acid or potassium iodide in aqueous acetic acid into 1:3-dibromo-\beta-naphthol, and acetylated to 1:1:3:4:6:7-hexabromo-1:4:6:7-tetrahydro-3naphthyl acetate, m. p. 178° after previous sintering. This acetate is reduced by zinc dust and acetic acid to 1:3-dibromo-3-naphthyl acetate, and converted by warming with pyridine into the acetate, m. p. 221° of 1:3:6:7-tetrabromo-β-naphthol, m. p. 174° (oxidised by nitric and acetic acids to 4:5-dibromophthalic acid).

Bromination of 1-methyl-3-naphthol in acetic acid gives first the 6-bromo- and then the 4:6-dibromoderivatives [previously described (A., 1906, i, 190) as the 3:6-compound]. Reduction of the product formed by bromination in acetic acid and sodium acetate with zinc dust and acetic acid affords 3-bromo-1methyl-β-naphthol, m. p. 76° (acetate, m. p. 77°), converted further into the 3:6-dibromo-, m. p. 110° (acetate, m. p. 136°), and the 3:4:6-tribromo-derivatives, m. p. 158° (acetate, m. p. 202°); the 3:6dibromo-derivative is also obtained by reduction of the ketobromide from 6-bromo-1-methyl-β-naphthol. 1:4:6-Tribromo-2-keto-1-methyl-1:2-dihydronaphthalene, m. p. 124° (decomp.), prepared from the 3:6and 4:6-dibromo-1-methyl-3-naphthols, reacts with aniline, forming the 6-bromo-1: 4-dianilino-derivative, m. p. 250° (decomp.).

1:1 - Dichloro - 2 - keto - 1:2 - dihydronaphthalene, m. p. 54° (cf. Zincke, A., 1889, 265), is converted by hydrogen chloride and bromide into 1:4-dichloro- and 1-chloro-6-bromo-β-naphthol, respectively. Chlorination of 1-bromo-\beta-naphthol or bromination of 1-chloroβ-naphthol in acetic acid and sodium acetate gives 1-chloro-1-bromo-2-keto-1: 2-dihydronaphthalene, m. p. about 90°, reduced by zinc dust to 1-chloro-B-naphthol and converted by hydrogen chloride or bromide in acetic acid into 1-chloro-6-bromo-β-naphthol. Prolonged treatment of 2: 3-hydroxynaphthoic acid with chlorine in acetic acid yields 1:1:3:3:4-pentachloro-2-keto-1:2:3:4-tetrahydronaphthalene, m. p. 116° (Zincke, loc. cit.), reduced by zinc dust and acetic acid to 1:3-dichloro-\$-naphthol. 1:6-Dibromo-\$naphthol is obtained from 1:1:6-tribromo-2-keto-1:2-dihvdronaphthalene (A., 1924, i, 1187) and hydrogen bromide in acetic acid.

[With B. HEINEMANN.] Treatment of 1:1-dibromo-2-keto-1: 2-dihydronaphthalene with pyridine below 40° gives 1-(6-bromo-2-hydroxy-a-naphthyl)pyridinium bromide, yellow, m. p. 320° (decomp.) after becoming colourless at 310°, converted by sodium acetate solution into the compound (II), orange-red, m. p. 250° (decomp.). Treatment of II with acetic



anhydride and sulphuric acid at the ordinary temperature affords the substance (III), m. p. 330° after blackening at 325°, which when heated with acetic acid passes into 1-(6-bromo-2-hydroxy-a-naphthyl)pyridinium sulphate, m. p. 245° (decomp.); III is converted by aqueous sodium acetate into II.

1-Bromo-2-keto-1-methyl-1 : 2-dihydronaphthalene (A., 1924, i, 1187) and sodium 1-methyl-β-naphthyloxide in benzene give dehydro-1-methyl-β-naphthol (Pummerer and Cherbuliez, A., 1919, i, 440). H. BURTON.

Derivatives of dinaphthylene dioxide. II. A. CORBELLINI and A. PASTURINI (Gazzetta, 1930, 60, 843-851; cf. A., 1929, 193).-Dibromination of  $\beta$ -dinaphthol in acetic acid solution yields 6:6'-dibromo-2: 2'-dihydroxy-1: 1'-dinaphthyl, m. p. 202-203° (not 155°, as given by Fosse, A., 1899, i, 818), which forms a dimethyl derivative, m. p. 239.5° (uncorr.), gives 2-[2-hydroxy-6-bromonaphthoyl(1)]-5bromobenzoic acid, m. p. 346° (uncorr.), when oxidised by alkaline permanganate and 4-bromophthalic acid when oxidised by chromic acid and alkaline permanganate successively, and is obtained also by oxidising 6-bromo- $\beta$ -naphthol by means of ferric chloride. When heated with cupric oxide or when its basic copper salt is heated,  $\vec{6}: 6'$ -dibromo-2:2-di-hydroxy-1:1'.dinaphthyl undergoes cyclisation, giving 2:7-dibromodinaphthylene dioxide, m. p. 361° (uncorr.), and a red compound, m. p. about 421°, of lower bromine content, this being possibly formed from 2 mols. of the preceding compound with loss of two bromine atoms. The m. p. of the dibromoderivative obtained by brominating dinaphthylene dioxide in carbon disulphide (cf. Corbellini and Victti. A., 1929, 193) was given erroneously as 277°; it should be 335°. T. H. POPE.

Halogen derivatives of acyl- and alkyl-resorcinols. C. M. BREWSTER and J. C. HARRIS (J. Amer. Chem. Soc., 1930, 52, 4866-4872).-4-Propionylresorcinol, m. p. 96° (2 : 6-dibromo-. m. p. 151-152°; tribromo-, m. p. 157-158°, and dichloro-, m. p. 146-147°, -derivatives), and 4-butyrylresorcinol, m. p. 68-70° (dichloro-derivative, m. p. 110.5-111°), are obtained when resorcinol, the appropriate fatty acid (technical), and zinc chloride are heated to 160-165° and the mixture is cooled. A substance, m. p. 111-112°, accompanies the butyryl derivative when the mixture is kept at 165° for 2-5 min. Reduction (Clemmensen) of resaccetophenone gives 4-ethyl-resorcinol (2 : 6-dibromo-derivative, m. p.  $73 \cdot 5 - 74 \cdot 5^{\circ}$ , also prepared by the Clemmensen reduction of 2:6-dibromo-4-acetylresorcinol); dichloro-4-ethylresorcinol, m. p. 78-79°, is obtained from dichlororesaceto-phenone, m. p. 190-193°. Bromination of resacetophenone in acetic acid containing a little iodine gives the ωω: 3: 5-tetrabromo-derivative, m. p. 110-110.5°, reduced to 2:6-dibromo-4-ethylresorcinol. Tribromoresacetophenone (Segalle, A., 1896, i, 613) could not be prepared. H. BURTON.

Naphthols. I. Bromination of 1:5-dihydroxynaphthalene. A. S. WHEELER and D. R. ERGLE (J. Amer. Chem. Soc., 1930, 52, 4872-4880).--Bromination of 1:5-dihydroxynaphthalene with 2 mols. of bromine in acetic acid containing a little iodine at 80° gives the 2:6-dibromo-derivative, darkens at 200°, not melted at 300° (diacetate, m. p. 228°; dibenzoate, m. p. 262°; dimethyl ether, m. p. 161°; diethyl ether, m. p. 148°), oxidised by chromic and acetic acids to 2:6-dibromo-5-hydroxy-1:4-naphthaquinone, m. p. 202° (acetate, m. p. 148°), which is not

identical with 2: 3-dibromojuglone (A., 1922, i, 1165). Reduction of the quinone with zinc dust and acetic acid affords 2:6-dibromo-1:4:5-trihydroxynaphthalene, decomp. 157° after darkening at 110°, whilst treatment with alcoholic aniline yields 6-bromo-2. anilino-5-hydroxy-1: 4-naphthaguinone, m. p. 249°. 2:6:8-Tribromo-1:5-dihydroxynaphthalene, m. p. 189° (decomp.) (diacetate, m. p. 174°; dibenzoate, melts at 185° to a turbid liquid which clears at 189°; dimethyl ether, m. p. 149°; diethyl ether, m. p. 125°), is oxidised similarly to a small amount of 2:6:8tribromo-5-hydroxy-1: 4-naphthaquinone, m. p. 196° (acetate, m. p. 234°), which is isomeric with tribromo-juglone (A., 1919, i, 490). This quinone gives a boroacetate, not melted at 300° after evolution of red vapour at 200°, indicating that it is an o-hydroxyquinone (cf. Dimroth, A., 1926, 297); it reacts with aniline in acetic acid forming 6: 8-dibromo-2-anilino-5hydroxy-1: 4-naphthaquinone, m. p. 206°, and is reduced by zinc dust and dilute sulphuric acid in presence of ether to 2:6:8-tribromo-1:4:5-trihydroxynaphthalenc, decomp. about 140° (triacetate, m. p. 185°).

Treatment of 1:5-diacetoxynaphthalene with bromine (6 mols.) in chloroform containing iodine gives 2:4:6:8-tetrabromo-1:5-dihydroxynaphthalene, not melted at 300° (dimethyl ether, m. p. 226°; dibenzoate, m. p. 268°), oxidised by chromic and acetic acids to 2:6:8-tribromo-5-hydroxy-1:4-naphthaquinone. Bromination with 5 mols. of bromine in acetic acid at the ordinary temperature gives a mixture of 2:6-dibromo-5-acetoxy- $\alpha$ -naphthol, m. p. 173° (benzoate, m. p. 164°), and the above tetrabromo-compound.

H. BURTON.

Condensation products of methylolamides with phenolic ethers. L. MONTI (Gazzetta, 1930, 60, 777-786; cf. A., 1930, 598).-Interaction of chloroacetamide with formaldehyde in presence of potassium carbonate yields hydroxymethylchloroacetamide, m. p. 102° (cf. Einhorn, A., 1905, i, 344), which condenses with veratrole in presence of zinc chloride to form (1) 3:4-dimethoxy-N-chloroacetylbenzylamine, m. p. 116-118° (Jacobs and Heidelberger, A., 1915, i, 667, gave m. p. 117-117.5°), which gives 3:4-dimethoxybenzylamine hydrochloride, m. p. 246° (decomp.) (Douetteau, A., 1911, i, 973, gave m. p. 257°), when heated with 20% hydrochloric acid, and ωω'-dichloroacetamido-4: 5-dimethoxy-o-xylene, (2)·  $C_6H_2(OMe)_2(CH_2\cdot NH\cdot CO\cdot CH_2Cl)_2$ , m. p. 169–170°, which gives ωω'-diamino-4 : 5-dimethoxy-o-xylene [picrate, m. p. 216-218° (decomp.) (anhydrous)] when boiled with 20% hydrochloric acid. Condensation of hydroxymethylchloroacetamide with pyrogallol trimethyl ether yields 2:3:4-trimethoxychloroacetyl-benzylamine, m. p. 98–99°, which gives 2:3:4-tri-methoxybenzylamine [picrate, m. p. 208–210° (decomp.); chloroplatinate, blackening at 200° and not melting at 300°] when boiled with 20% hydrochloric acid. Hydroxymethylbenzamide (cf. Einhorn, A., 1905, i, 344) and pyrogallol trimethyl ether condense in presence of zine chloride to form (1) 2:3:4-trimethoxybenzoylbenzylamine, m. p. 125-126°, which yields 2:3:4-trimethoxybenzylamine (see above) when boiled with alcoholic potassium hydroxide, and (2) ωω'-dibenzamido-2:3:4-trimethoxy-o-xylene, m. p.

189—190°, which gives  $\omega\omega'$ -diamino-2:3:4-trimethoxyxylene (picrate, m. p. 215—217°) with alcoholic potassium hydroxide. Condensation of hydroxymethylchloroacetamide and hydroxyquinol trimethyl ether yields 2:4:5-trimethoxychloroacetylbenzylamine, m. p. 115—116°, this giving 2:4:5-trimethoxybenzylamine (picrate, m. p. 200—202°) with 20% hydrochloric acid. 3:4:5-Trimethoxy-2-chloroacetylbenzylamine-1-carboxylic acid, m. p. 189—190°, formed by condensing hydroxymethylchloroacetamide with trimethylgallic acid, gives 3:4:5-trimethoxy-2-benzylamine-1-carboxylic acid [hydrochloride, m. p. 153—154° (decomp.); picrate, m. p. 150—152°] on hydrolysis with 20% hydrochloric acid. T. H. POPE.

Aliphatic diazo-compounds. II. A. SCHÖN-BERG and T. STOLFP (Ber., 1930, 63, [B], 3102-3116; cf. this vol., 84).—Gradual addition of o-nitrochlorothiolbenzene to an ethereal solution of diazomethane yields o-nitrophenylthiolmethyl chloride,

NO2. C6H4. S. CH2Cl, m. p. about 95°. Diazodiphenylmethane and o-nitrobromothiolbenzene yield o-nitrophenylthioldiphenylmethyl bromide, m. p. (indef.) 108°. p-Chloro-o-nitrophenylthioldiphenylmethyl chloride, m. p. 121°, is prepared analogously. Phenylthioldiphenylmethyl chloride in ether is transformed by silver benzoate into phenylthioldiphenylmethyl benzoate, m. p. 148—149°; o-nitrophenylthioldiphenylmethyl benzoate. m. p. 132°, and phenylthioldiphenylenemethyl benzoate, m. p. (indef.) 132° (from 9-chloro-9-phenylthiolfluorene), are described. p-Nitrophenylthioldiphenylmethyl chloride is converted by water at the ordinary temperature into benzophenone and di-o-nitrophenylthioldiphenylmethane, m. p. 146°; 9-chloro-9-o-nitrophenylthiolfluorene similarly yields fluorenone and di-o-nitrophenylthioldiphenylenemethane, m. p. 159°. With ammonia in ether at the ordinary temperature phenylthioldiphenylmethyl chloride affords benzophenoneimine and diphenylthioldiphenylmethane, m. p. 173°. In benzene under similar conditions o-nitrophenylthioldiphenylmethyl chloride gives benzophenone and di-o-nitrophenylthioldiphenylmethane, whilst 9-phloro-9-phenylthiolfluorene yields fluorenoneimine and diphenylthioldiphenylenemethane.

Di-o-anisyl thioketone and mercuric chloride in ether give the compound  $C_{15}H_{14}O_2S$ ,  $HgCl_2$ , whilst xanthione and silver perchlorate in benzene afford the substance,  $C_{13}H_8O_5ClSAg$ . The complex compounds from xanthione and silver nitrate and from di-oanisyl thioketone and cadmium iodide are too unstable to permit analysis.

Diphenyldiazomethane and phenyl o-nitrophenyl disulphide in boiling benzene in the absence of light and in an atmosphere of carbon dioxide afford *phenylthiol-o-nitrophenylthioldiphenylmethane*, m. p. 134°, and benzophenoneketazine. Di-o-nitrophenylthioldiphenylmethane, m. p. 146°, di-β-naphthylthioldiphenylmethane, m. p. 133°, and *diphenylthioldi-βnaphthylmethane*, m. p. 160°, are prepared similarly. The methane derivatives from di-p-tolyldiazomethane and diphenyl disulphide and from diphenyldiazomethane and di-p-tolyl disulphide could not be obtained pure.

Xanthione is converted by hydrazine hydrate

in alcohol into xanthonehydrazone, m. p. 128-130°, which is oxidised by mercuric oxide to xanthoneketazine, m. p. 285°, prepared also from xanthione and hydrazine hydrate or, preferably, by the action of xanthone dichloride on xanthonehydrazone. Thioxanthione is converted by hydrazine hydrate in alcoholic benzene into thioxanthonehydrazone, m. p. 115°, oxidised by mercuric oxide in presence of light petroleum at 12° to diazothioxanthen, m. p. 105°. Thioxanthoneketazine, m. p. 284°, is prepared from thioxanthone dichloride and thioxanthonehydrazone. The preparation of chromonehydrazone, m. p. 96°, from chromone or 4-thiochromone is recorded.

H. WREN.

Organic compounds of selenium. I. S. KEIMATSU and K. YOKOTA (J. Pharm. Soc. Japan, 1930, 50, 531-539).-Diazotisation of p-anisidine, followed by addition of selenophenol, sodium hydroxide, and copper powder, and keeping the mixture at 0-5° in an atmosphere of carbon dioxide, affords p-methoxyphenyl selenide, m. p. 46.3° (corr.), in 70% theoretical yield; o-methoxyphenyl selenide, from o-anisidine, was also prepared. p-Acetoxyphenyl selenide has m. p. 55°, and the selenocyanate has m. p. 67°. Selenoquinol, m. p. 56-57°, from alcoholic p-acetoxyphenyl selenocyanate, dextrose, and aqueous sodium hydroxide at 100° in hydrogen, affords on oxidation pp'-dihydroxydiphenyl diselenide, m. p. 134° (diacetoxycompound, m. p. 90.5°). Treatment of selenophenol in alcoholic potassium hydroxide with chloropicrin gave diphenyl diselenide, m. p. 63.5°.

CHEMICAL ABSTRACTS.

Preparation of α-p-methoxyphenyl-β-aminoethyl alcohol. Y. SHINOZAKI (J. Pharm. Soc. Japan, 1930, 50, 666—667).—Catalytic reduction of p-methoxyphenylnitroethanol (from anisaldehyde, nitromethane, and potassium hydrogen carbonate) gave α-p-methoxyphenyl-β-aminoethyl alcohol hydrochloride, m. p. 171—172°. Electrolytic reduction also afforded an amine. CHEMICAL ABSTRACTS.

Optically active diphenylhydroxyethylamines IV. Di-p-methoxyand isohydrobenzoins. phenylhydroxyethylamine and di-3:4-methylenedioxyphenylhydroxyethylamine. V. β-Hydroxy-\beta-phenylethylamine and some derivatives. J. READ and (MISS) I. G. M. CAMPBELL (J.C.S., 1930, 2674-2681, 2682-2685) .- IV. Aminoacetic acid reacts with anisaldehyde in presence of aqueous-alcoholic sodium hydroxide at 50° (cf. Erlenmeyer, A., 1905, i, 131), forming the anisylidene derivative, m. p. 116°, of dl-di-p-methoxyphenylhydroxyethylamine, m. p. 135.5° [chlcroplatinate, m. p. 171° (decomp.); mono-acetyl derivative, m. p. 145-147°; diacetyl derivative, m. p. 169-171°: benzylidene derivative, m. p. 125-126°; salicylidene derivative, m. p. 134-135°]. Treatment of the amino-alcohol with d-tartaric acid in alcoholic ethyl acetate gives the hydrogen d-tartrate  $(+H_2O)$ , m. p. 110-111°,  $[M]_D$  -294° in water, of 1-di-p-methoxyphenylhydroxyethylamine, m. p. 111-112°,  $[\alpha]_{\rm D}$  —150° in alcohol (hydrochloride,  $[M]_{\rm D}$  –307° in water; monoacetyl derivative, m. p. 128–  $129^{\circ}$ ,  $[\alpha]_{D} - 16.9^{\circ}$  in alcohol : *diacetyl* derivative, m. p. 160-161°,  $[\alpha]_{D}$  +44.6° in alcohol: benzylidene derivative, m. p. 136°,  $[\alpha]_{D}$  -88·1° in alcohol). Treatment

of the l-base with nitrous acid affords a 30% yield of cis-aβ-di-p-methoxyphenylethylene oxide, m. p. 142-143°, and oily material which appears to contain some hydroanisoin. The oxide is also obtained when I-, m. p. 145° (decomp.),  $[\alpha]_{D} - 34.6^{\circ}$  in methyl alcohol, or dl - di-p-methoxyphenylhydroxyethyltrimethylammonium iodide, m. p. 155° (decomp.), is treated with silver oxide (A., 1930, 1576). Aminoacetic acid and piper-onal react as above, forming the *piperonylidene* derivative, m. p. 177°, of dl-di-3: 4-methylenedioxyphenylhydroxyethylamine, m. p. 159° [chloroplatinate, m. p. 184° (decomp.)], resolved by tartaric acid into the d-amino-alcohol, m. p.  $164^{\circ}$ ,  $[\alpha]_{p} + 196^{\circ}$  in alcohol (hydrogen d-tartrate  $+H_{2}O$ , m. p.  $145^{\circ}$ ,  $[M]_{p} + 549^{\circ}$  in water), and the l-amino-alcohol, m. p. 164°, [a] -196° in alcohol {hydrogen d-tartrate, m. p. 208° (decomp.),  $[M]_{\rm p} - 470^{\circ}$  in water; hydrochloride,  $[M]_{\rm p} - 442^{\circ}$  in water; diacetyl derivative, m. p. 222-224° (decomp.),  $[\alpha]_n - 38.5^\circ$  in alcohol}. V. In the preparation of dl- $\beta$ -hydroxy- $\beta$ -phenyl-

ethylamine {hydrochloride, m. p. 213° (decomp.); benzoyl derivative, m. p. 148°; benzylidene derivative, m. p. 111–112°; the d-methylenecamphor derivative, m. p. 106–108°,  $[\alpha]_{\rm p}$  +230° in alcohol, and the d-camphor-10-sulphonate, m. p. 125-126°, [M]o  $+52.8^{\circ}$  in water, are partly racemic compounds) from styrene by the method previously described (A., 1928, 866), a small amount of a base, C8H-N, m. p. 191-193°, is produced : when a specimen of styrene containing cinnamyl alcohol was used, a small amount of basic substance, C9H12O2N2, m. p. 192°, was formed. The above dl-amino-alcohol absorbs carbon dioxide, yielding a carbamate. It is resolved by tartaric acid into the d-base (d-tartrate, m. p.  $210^{\circ}$ ,  $[M]_{p} + 195^{\circ}$  in water), which with methyl iodide and methyl-alcoholic sodium methoxide (cf. loc. cit.) gives d-B-hydroxy-Bphenylethyltrimethylammonium iodide, m. p. 223- $224^{\circ}$ ,  $[\alpha]_{\rm D} + 4.5^{\circ}$  in methyl alcohol. Treatment of this with silver oxide furnishes a small amount of acetophenone and a dextrorotatory oil, which appears to consist mainly of d-phenylethylene oxide (or a polymeride) together with a little phenylethylene glycol.

H. BURTON. Manufacture of optically active  $\beta$ -aralkylmethylamino- and  $\beta$ -methylamino- $\pi$ -hydroxyn-propylbenzenes. I. G. FARBENIND. A.-G.—See B., 1931, 13.

Manufacture of β-methylamino-α-phenylpropyl alcohol ("diephedrine"). KNOLL A.-G. CHEM. FABR. and W. KLAVEHN.—See B., 1931, 58.

Esters of phenyltribromomethylcarbinol. J. W. Howard (J. Amer. Chem. Soc., 1930, 52, 5059– 5060).—Phenyltribromomethylcarbinol, m. p.  $72 \cdot 5$ – 73°, is obtained when powdered potassium hydroxide (4 g.) is added with constant stirring to a mixture of benzaldehyde (37 g.) and dry bromoform (130 g.), the reaction mixture diluted with ether, filtered, distilled up to 155°/680 mm., and the residue distilled with steam. The yield is 16–18 g. The following esters were prepared : acetate, m. p. 133°; propionate, m. p. 70.5°; butyrate, b. p. 205–207°/220 mm., d<sup>20</sup> 1.779, and benzoate, m. p. 146°. H. BURTON.

Di- $\alpha\beta$ -diphenylethyl ether and di- $\beta$ -phenyl- $\alpha$ -anisylethyl ether. C. R. KINNEY and W. G.

BYWATER (J. Amer. Chem. Soc., 1930, 52, 4893-4895).-Di-β-phenyl-α-anisylethyl ether, m. p. 148-149°, isolated during the attempted oxidation of β-phenyl-α-anisylethyl alcohol with nitrogen trioxide in ether, is also formed (in small amount) when the alcohol is treated with hydrochloric acid in presence of ether and calcium chloride, and when the product from magnesium benzyl chloride and anisaldehyde is decomposed with ice and concentrated hydrochloric acid. In the last case none of the above alcohol is produced. 4-Methoxystilbene is obtained when the alcohol is treated with ethereal hydrogen chloride. Distillation of the ether gives a substance, m. p. 107-108°. Diaß-diphenylethyl ether, m. p. 129.5-130.5°, is formed in small amount when  $\alpha\beta$ -diphenylethyl alcohol is treated with nitrogen trioxide or concentrated hydrochloric acid in ether; it is not obtained when the product from magnesium benzyl chloride and benzaldehyde is decomposed. H. BURTON.

Action of chloral and trichloroacetic acid on cholesterol. E. MONTIGNIE (Bull. Soc. chim., 1930, [iv], 47, 1323—1325).—When heated with chloral at 100° cholesterol is partly isomerised to metacholesterol [acetate, m. p. 110°; bromide, m. p. 105° (decomp.)]. Trichloroacetic acid at 60—70° and at 100° affords two fractions, m. p. 121° and 140°, mixtures of isomeric cholesteryl trichloroacetates, the latter fraction being anhydrous. Attempts to condense cholesterol with  $\alpha$ - or  $\beta$ -penta-acetylglucose in chloroform solution in presence of hydrogen chloride did not yield a glucoside. R. BRIGHTMAN.

Sterol group. X. Relationship of the fully saturated derivatives of ergosterol and sitosterol. F. S. SPRING (J.C.S., 1930, 2664-2667).-Hydrogenation of ergosterol, m. p. 160°,  $[\alpha]_{\rm p}^{22}$  -131° (all rotations are in chloroform), in presence of palladiumblack and ethyl acetate at  $40-50^{\circ}$  affords, in addition to a-ergostenol, some y-ergostenol, m. p. 129-130°,  $[\alpha]_{0}^{\alpha}$  +5.1°. The new sterol gives a green colour with the Tortelli-Jaffé reagent and resists further hydrogenation. Fractionation of the ergosterol from alcoholbenzene (2:1) and hydrogenation of the less and more soluble fractions shows that more  $\gamma$ -ergostenol is obtained from the latter fraction. The ergosterol used is probably a mixture of isomerides.  $\gamma$ -Ergostenyl acetate, m. p. 140°, is isomerised by treatment with hydrogen chloride in chloroform into iso-y-ergostenyl acetate, m. p. 103—104°,  $[\alpha]_{D}^{22} + 4.05°$ . iso- $\gamma$ -Ergo-stenol, m. p. 129°,  $[\alpha]_{D}^{22} + 3.7°$ , is reduced catalytically (palladium-black) in ether to  $\gamma$ -ergostanol, m. p. 137°,  $[\alpha]_{D}^{23} + 29°$ , which gives no Liebermann-Burchard reaction, is isomeric with allo-z-ergostanol (Reindel and Walter, A., 1928, 295), and appears to be identical with the sitostanol, m. p. 136°,  $[\alpha]_{D}^{\circ} - 26^{\circ}$ , obtained from sitosterol, m. p.  $137-137\cdot5^{\circ}$ ,  $[\alpha]_{n} + 38^{\circ}$ , from soften seed oil H. BURTON.

Carbithioic acids. II. cycloHexylcarbithioic [cyclohexanedithiocarboxylic] acid. R. W. Bosr and W. W. WILLIAMS (J. Amer. Chem. Soc., 1930, 52. 4991—4992).—cycloHexanedithiocarboxylicacid, an oil [silver salt, m. p. 163°; methyl, b. p. 90°/3 mm., and ethyl, b. p. 106°/5 mm., esters (both prepared from the sodium salt and the alkyl sulphate); n-propyl, b. p. 106°/3 mm., and n-butyl, b. p. 145°/5 mm., esters (from the sodium salt and the alkyl bromide); p-toluidide, m. p. 160°], is obtained from magnesium cyclohexyl bromide and carbon disulphide by the method previously described (A., 1930, 340). The acid decomposes when distilled or exposed to air, does not give an acid chloride or amide, and when treated with nitric acid in ether is oxidised to hexahydrobenzoic acid. H. BURTON.

Preparation of benzamide. C. H. KAO and S. MA (J.C.S., 1930, 2788).—A mixture of benzoic acid (200 g.), ammonium carbonate (180 g.), and 95% acetic acid (300 c.c.) is heated gradually to boiling and then distilled through a column of glass tubing ( $160 \times 2$  cm.) at 100 c.c. per hr. until the temperature at the head of the column is  $150^{\circ}$ . The residue is poured into water (2 vols.), neutralised with ammonia, and crystallised. Two crystallisations from water give 96—98 g. of benzamide. About half the benzoic acid is recovered. H. BURTON.

Decomposition of benzoyl peroxide by ultraviolet light. F. FICHTER and A. SCHNIDER (Helv. Chim. Acta, 1930, 13, 1428—1433).—Ultra-violet irradiation of benzoyl peroxide in a quartz vessel gives as much as 70% of the theoretical amount of diphenyl:  $(\cdot CO_2 Ph)_2 \longrightarrow 2CO_2 + Ph \cdot Ph$ . Resinous material is also produced. Decomposition also occurs in chloroform solution. H. BURTON,

Formation of a complex mixture of RMgX compounds from the reaction between a simple RX compound and magnesium. H. GILMAN and N. B. ST. JOHN (J. Amer. Chem. Soc., 1930, 52, 5017—5023).—Treatment of the reaction product from magnesium and brono- or chloro-benzene (prepared in absence of solvent) with carbon dioxide gives 30-33% of benzoic acid and small amounts of diphenyl-4-carboxylic acid. The last-named acid probably arises owing to intermediate formation of free phenyl radicals; it could not be isolated when the Grignard reagent was prepared in ether. The various reactions which can occur as the result of radical formation are discussed. H. BURTON.

Configuration of norvaline. P. KARRER and H. SCHNEIDER (Helv. Chim. Acta, 1930, 13, 1281-1291).—dl-Allylhippuric ( $\alpha$ -benzamido- $\Delta \gamma$ -pentenoic) acid, prepared by Sörensen's method (A., 1908, i, 981 1917, i, 89), is resolved by brucine into d(-)-, m. p. 89° (potassium salt,  $[\alpha]_{\mathbb{B}}^{\infty} - 32 \cdot 11^{\circ}$  in water), and l(+)-allylhippurie acids, m. p. 90° (potassium salt,  $[\alpha]_{\mathbb{B}}^{\infty} + 32 \cdot 9^{\circ}$  in water). Oxidation of these active acids by potassium permanganate gives d(-)-, m. p. 175°, and l(+)- $\alpha$ -benzamidosuccinic acids, m. p. 176° (potassium salt,  $[\alpha]_{D}^{19} + 22.4^{\circ}$  in water) (cf. Fischer, A., 1899, i, 888), respectively.  $d(-)-\alpha$ -Benzamidosuccinic acid is also obtained by benzoylating d- $\alpha$ -aminosuccinic acid. Oxidation of *dl*-allylhippuric acid with potassium permanganate or ozone furnishes dl-a-benzamidosuccinic acid (+H,O), m. p. 119° after sintering at 70°. N-(aa-Dicarboxy-Dy-butenyl)phthalamic acid, m. p. 156° (decomp.), is a by-product in the preparation of *dl*-allylhippuric acid

Reduction of d(-)- and l(+)-allylhippuric acids with hydrogen in presence of platinum and the theoretical amount of N-potassium hydroxide affords

d(-)-, m. p. 97° (potassium salt,  $[\alpha]_{19}^{19} - 13\cdot1^{\circ}$  in water), and l(+)-benzoylnorvalines ( $\alpha$ -benzamido-nvaleric acids), m. p. 95° (hydrate, m. p. 64° after sintering at 40-50°; potassium salt,  $[\alpha]_{19}^{19} + 14\cdot0^{\circ}$  in water), respectively. Benzoylation of the ethyl ester of d(-)-norvaline in pyridine gives ethyl  $\alpha$ -benzamidon-valerate, m. p. 59°  $[\alpha]_{19}^{19} + 7\cdot98^{\circ}$  in alcohol, hydrolysed by aqueous-alcoholic sodium hydroxide to the above d(-)-benzoylnorvaline. H. BURTON.

Derivatives of anesthesin [ethyl p-aminobenzoate]. L. CONIGLIO (Rend. Accad. Sci. Fis. Mat. Napoli, 1930, [iii], 36, 56-60).—The action of  $\alpha$ -bromoisovaleryl chloride on anesthesin in presence of 2% sodium potassium hydroxide solution yields ethyl p- $\alpha$ -bromoisovaleramidobenzoate,

 $CO_2Et \cdot C_6H_4$ ·NH·CO·CHPr<sup> $\beta$ </sup>Br, m. p. 115°. Similarly, the action of benzoyl chloride gives *ethyl* p-*benzamidobenzoate*, m. p. 15°; that of phthalyl chloride, *ethyl phthalidobenzoate*, m. p. 152°, and that of acetyl chloride, *ethyl* p-*acetamidobenzoate*, m. p. 181°. T. H. POPE.

Electrochemical oxidation of *p*-toluenesulphonic acid. M. YOKOYAMA (Helv. Chim. Acta, 1930, 13, 1257—1264; cf. Sebor, A., 1903, i, 554).— Oxidation of a *M*-solution of *p*-toluenesulphonic acid at a lead dioxide or platinum anode (current density 0.05 amp./cm.<sup>2</sup>) at 70—75° gives a small amount of a quinone together with formic, mesaconic, *p*-sulphobenzoic, and 4-sulpho-2:3-dihydroxybenzoic acids. Similar oxidation of *o*-cresol-4-sulphonic acid (0.66*N*solution; lead dioxide anode) affords mesaconic and 4-sulpho-2:3-dihydroxybenzoic acids. Various mechanisms are suggested (cf. A., 1929, 1052) to explain the formation of the above compounds.

H. BURTON.

3-Chloro- $\alpha$ -hydroxyphthalide. L. F. LEVY and H. STEPHEN (J.C.S., 1930, 2788).—3-Chloro- $\alpha$ -hydroxyphthalide. d. F. LEVY and H. STEPHEN (J.C.S., 1930, 2788).—3-Chloro- $\alpha$ -toluic acid, m. p. 91-5°, prepared by the usual method from 3-amino-o-toluic acid, is treated with bromine in the fused state and the resultant product warmed with dilute sodium hydroxide solution; 3-chloro- $\alpha$ -hydroxyphthalide, m. p. 138°, is thereby produced.

H. BURTON.

Stereochemistry of diphenyl compounds. XI. Preparation and resolution of 6-nitro-2-methyldiphenyl-2'-carboxylic acid. R. W. STOUGHTON and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 5263-5267).—A mixture of methyl o-iodobenzoate and 2-bromo-3-nitrotoluene is treated with copper-bronze at 270-280° (bath), the resulting mixture heated at 300°, and then hydrolysed with 10% sodium hydroxide solution, whereby 27% of the theoretical amount of 6-nitro-2-methyldiphenyl-2'-carboxylic acid, m. p. 171-172°, is obtained. This is resolved by brucine into the d-, m. p. 171-173° after softening at 167°, [a]<sup>30</sup>  $+63.1^{\circ}$  in methyl alcohol [brucine salt ( $+1.5H_2O$ ), m. p. (anhydrous)  $172^{\circ}$  after softening at  $145^{\circ}$ ,  $[\alpha]_{D}^{\infty}$ -57.3° in chloroform], and l-modifications, m. p. 174—175° after softening at 168°,  $[\alpha]_{D}^{20}$  —67.7° in methyl alcohol [brucine salt (+H<sub>2</sub>O), m. p. (anhydrous) 173-175°,  $[\alpha]_{10}^{\infty}$  +30.4° in chloroform]. The active acids racemise slowly in boiling alkali and more slowly in boiling butyl alcohol or acetic acid. H. BURTON.

Fulminic acid. XI. Triphenylmethyl chloride and silver fulminate. H. WIELAND and B. ROSENFELD (Annalen, 1930, 484, 236-245).---When triphenylmethyl chloride is treated with silver fulminate in benzene with complete exclusion of moisture, an intense vellow coloration is produced owing to the formation of the halochromic additive compound of silver and triphenylmethyl chlorides; this disappears during the reaction provided an excess of the chloride is not used. The main product of the reaction is triphenylacetonitrile oxide (I), CPh<sub>3</sub>·C:N:O, m. p. 153—154°, probably formed thus : CNOAg+CPh<sub>3</sub>CI  $\longrightarrow$  CPh<sub>3</sub>·CCI:N·OAg  $\longrightarrow$  AgCl+I. Treatment of I with alcoholic hydrochloric acid gives triphenylacethydroxamyl chloride, CPh3. CCI.N.OH, m. p. 178-180° (decomp.), which when heated at 190° passes into I, and with methyl-alcoholic potassium hydroxide yields triphenylacethydroxamic acid, m. p. 165-167° (lit. 175-176°), and its methyl ester, m. p. 204°. Reduction of I with tin and alcoholic hydrochloric acid affords triphenylacetonitrile, m. p. 129°, whilst treatment with magnesium phenyl bromide furnishes phenyl triphenylmethyl ketoxime, m. p. 210° (benzoyl derivative, m. p. 175°). Treatment of the oxime with sulphuric acid at 100° gives benzamide and triphenylcarbinol (formed from the intermediate benztriphenylmethylamide). Nitrous acid converts the oxime into the nitroimine, CPh. CPh.N.NO., m. p. 160° (decomp.), which when heated at 160-180° in an atmosphere of carbon dioxide decomposes to nitric oxide, benzonitrile, and triphenylcarbinol. The nitroimine is reduced by 2% sodium amalgam and 96% alcohol to the hydrazone, m. p. 189° (isopropylidene derivative, m. p. 144-145°), of phenyl triphenylmethyl ketone, which is converted by treatment with mercuric oxide in boiling xylene (by way of the unstable, red diazo-derivative) into tetraphenylothylene. Reduction of the nitroimine with tin and aqueous alcoholic hydrochloric acid gives phenyl triphenylmethyl ketimine, m. p. 165°.

When silver fulminate reacts with an excess of triphenylmethyl chloride, a mixture of I and triphenylacethydroxamyl chloride triphenylmethyl ether (II),  $CPh_3 \cdot CCl: N \cdot O \cdot CPh_3$ , m. p.  $174 - 175^\circ$ , is formed:  $CPh_3 \cdot CCl: NOAg + CPh_3Cl \rightarrow AgCl + II$ . This ether is reduced by tin and alcoholic hydrochloric acid to a mixture of triphenylacetonitrile and triphenylmethane. H. BURTON.

New halogenated sulphonephthaleins. W. C. BOYD [with A. W. ROWE] (J. Amer. Chem. Soc., 1930, 52, 4954-4959).-Phenols are condensed with tetrabromo- and tetraiodo-o-sulphobenzoic anhydrides, prepared by the method of Pratt and Shupp (A., 1918, i, 177), in presence of stannic chloride, whereby phenol-tetrahalogenosulphonephthaleins are produced. The following are described : phenoltetraiodosulphonephthalein (tetrabromo-, tetraiodo-, tetranitro-, and diacetyl, m. p. 136°, derivatives), o-cresoltetraiodosulphonephthalein, resorcinoltetraiodosulphonephthalein (tetraiodosulphonefluorescein), o-carboxyphenoltetraiodosulphonephthalein, phenoltetrabromosulphonephthalein (tetrabromo-derivative), resorcinolietrabromosulphonephthalein, and o-cresoltetrabromosulphonephthalein; these decompose gradually at high temperatures. The  $p_{\mu}$  ranges of these compounds are given.

Tetraiodo-o-benzoicsulphinide, not melted at 345°, is also described. H. BURTON.

Preparation of salicylyl chloride. A. KIRPAL (Ber., 1930, 63, [B], 3190).—Salicylic acid (10 g.) mixed with thionyl chloride (7 c.c.) and aluminium chloride (0.02 g.) is warmed at 45—50° until dissolution is complete. Excess of thionyl chloride is removed in a vacuum, leaving crystalline salicylyl chloride, m. p. 18°. H. WREN.

Manufacture of arylamides of 4-arylaminosalicylic acids. I. G. FARBENIND. A.-G.—See B., 1931, 58.

Manufacture of 5-arylaminosalicylic acids. I. G. FARBENIND. A.-G.—See B., 1931, 58.

Stability of magnesium r-mandelate. A. FIND-LAY and A. N. CAMPBELL (J.C.S., 1930, 2721-2724).-Determinations of the solubility of magnesium *l*- and r-mandelates in water at  $0-40^{\circ}$  by the method previously described (A., 1930, 406) show that the solubility curve for the *l*-salt is simple and it ascends rapidly above about  $30^\circ$ ; the r-salt gives a threebranched solubility curve, indicating the existence of a monohydrate (stable up to about 12°), a semihydrate (stable at 12-29°), and, above 29°, an anhydrous salt. The composition of the hydrates is confirmed by vapour-pressure measurements. The composition of the solution in equilibrium with the l- and r-salts as solid phases was determined polarimetrically and plotted in rectangular co-ordinates. The r-salt exists as a stable, solid phase throughout the range of temperature used. H. BURTON.

Benzylidenepyruvic acid. L. MUSAJO (Gazzetta, 1930, 60, 669—672).—The m. p. of the dibromide of benzylidenepyruvic acid ( $\beta\gamma$ -dibromo- $\alpha$ -keto- $\gamma$ -phenyl*n*-butyric acid), for which various values are given in the literature, is 124° for the product crystallised from a concentrated solution in benzene. If the substance is kept for some time in a vacuum it then melts at 142—143°. By crystallising from benzene, fractions which melt at 147—150° can also be obtained. A preliminary study has been made of the action of bromine on the oily variety of benzylidenepyruvic acid, which has also been obtained as a solid amorphous product. O. J. WALKER.

Lichen substances. VI. Gyrophoric acid. Y. ASAHINA and M. WATANABE (Ber., 1930, 63, [B], 3044-3048; cf. A., 1929, 818).—Gryophoric acid (I, X=H), m. p. about 220° (decomp.), is obtained in  $1\cdot4\%$  yield by successive extraction of *Gryophora* 



esculenta with ether and acetone. It is converted by acetic anhydride containing a trace of concentrated sulphuric acid into the corresponding *tetra-acetate*, m. p. 228°, and by chloroacetyl chloride in presence of chloroacetic acid and pyridine into the *tetrachloroacetate* ( $+2H_2O$ ), m. p. 163–164°. It affords a

characteristic quinine salt,  $C_{44}H_{44}O_{12}N_2,H_2O$ , m. p. 162°. With diazomethane it gives methyl tetramethylgyrophorate, m. p. 196—197°. Analysis and determinations of mol. wt. of the acid and its derivatives confirm the structure I. Umbilicaric acid has the similar constitution (X = Me). H. WREN.

Reaction between the binary system magnesium+magnesium iodide and aromatic aldehydes. M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1930, 52, 4967—4972).—When benzaldehyde (3 mols.) is treated with magnesium (1 atom) and magnesium iodide in ethereal benzene and the resulting solution hydrolysed with dilute acid, a mixture of unchanged aldehyde, benzyl alcohol, benzoin, and resinous material is obtained. The use of an excess of magnesium leads to the consumption of 1.5 atoms per 3 mols. of aldehyde; benzyl alcohol and resinous material are the sole products of the reaction. The changes taking place are probably: (a) 2Ph·CHO+Mg+MgI<sub>2</sub>  $\longrightarrow$  2[CHPh·OMgI]—> (CHPh·OMgI)<sub>2</sub> (I); (b) (CHPh·OMgI)<sub>2</sub>+Ph·CHO—> CHPhBz·OMgI (II) + CH<sub>2</sub>Ph·OMgI;

(c) 2CHPhBz·OMgI+Mg+MgI<sub>2</sub> $\longrightarrow$ 

[CHPh(OMgI)·ČPh(OMgI)]<sub>2</sub>. Magnesium methyl iodide (2 mols.) and hydrobenzoin (1 mol.) afford I, which reacts with benzaldehyde, forming (after hydrolysis) benzoin and benzyl alcohol; the presence of II in the reaction mixture is established by treatment with magnesium phenyl bromide, whereby triphenylethylene glycol is produced. These results support change b. Treatment of II, prepared from benzoin (1 mol.) and magnesium ethyl iodide (1 mol.), with a mixture of magnesium and magnesium iodide in ethereal benzene gives, after hydrolysis, a small amount of  $\alpha\beta\gamma\delta$ -tetraphenylerythritol and much resinous material which is apparently identical with that obtained from benzaldehyde. These results support equation c.

 $\alpha$ -Naphthaldehyde, p-tolualdehyde, anisaldehyde, and p-chloro- and p-bromo-benzaldehydes react with the system magnesium-magnesium iodide in essentially the same manner. H. BURTON.

Reducing action of compounds containing the group >CH.OMgI. R. V. SHANKLAND and M. GOMBERG (J. Amer. Chem. Soc., 1930, 52, 4973-4978).—Treatment of 18 aldehydes (mainly aromatic) with magnesium iodohydrobenzoinate, (CHPh·OMgI), in ethereal benzene gives, after hydrolysis of the reaction mixture, benzoin and the primary alcohol formed by reduction of the aldehyde : R·CHO+  $(CHPh \cdot OMgI)_2 \longrightarrow CH_2R \cdot OMgI + CHPhBz \cdot OMgI.$ Substituted hydrobenzoinates can be used and the yields of benzoin and alcohol are usually good. The corresponding magnesium derivatives from benzhydrol, benzopinacolin, isopropyl, benzyl, and chloro-benzyl alcohols may also be used. The hydrobenzoin derivatives are the most effective. The results favour Marshall's explanation (J.C.S., 1914, 105, 527; 1915, 107, 509; A., 1925, i, 1428) of the production of primary alcohols and ketones during the interaction of aldehydes and Grignard reagents. H. BURTON.

Beckmann rearrangement. V. Substituted cinnamaldoximes and cinnamonitriles. K. von AUWERS and M. SEYFRIED (Annalen, 1930, 484, 212-235).-When a-bromocinnamaldoxime, m. p. 144°, previously described as probably the syn-oxime (A., 1925, i, 1428), is treated with phosphorus pentachloride in ether, trans- $\alpha$ -bromocinnamonitrile, b. p. 148—150°/12 mm., m. p. 33—35°,  $d_{1}^{20}$  1.476,  $n_{10}^{20}$ 1.6308, is produced. Treatment with boiling acetic anhydride gives cis-a-bromocinnamonitrile, b. p.  $143 - 145^{\circ}/15$  mm.,  $d_4^{20}$  1.461,  $n_{H_0}^{20}$  1.6294 (cf. loc. cit.). These results are understandable when  $\alpha$ -bromocinnamaldehyde, m. p. 73°, is regarded as the cisderivative; oximation causes no change in configuration. cis-a-Bromocinnamamide, prepared from the cis-chloride and ammonia (unless precautions are taken, the trans-amide results), is dehydrated by phosphoryl chloride at 100° (bath) to the cis-nitrile, also formed from  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionitrile, m. p. 92-93°, and cold alcoholic potassium hydroxide (1 mol.). trans-a-Bromocinnamamide is dehydrated by phosphorus pentachloride and oxychloride at 100° to the above trans-nitrile. Treatment of the cis- and trans-a-bromocinnamonitriles with alcoholic potassium hydroxide causes considerably more elimination of bromine from the trans-form; under suitable conditions both modifications yield the same  $\beta$ ethoxycinnamonitrile, b. p. 152-154°/12 mm., d<sup>20</sup> 1.056,  $n_{\rm He}^{20}$  1.5666, hydrolysed by very dilute sulphuric acid to benzoylacetonitrile. The B-ethoxycinnamonitrile, b. p. 163-165°/11 mm., d4 1.052, nito 1.5507, prepared from phenylpropiolonitrile and alcohol by Moureu and Lazennec's method (A., 1906, i, 240) is a stereoisomeric form. Both forms show no difference in the rates of hydrolysis or reaction with bromine.

Treatment of phenylpropiolaldehyde with hydrogen bromide in cold acetic acid gives the unstable  $\beta$ bromocinnamaldehyde, b. p. 138—140°/11 mm.,  $d_4^{13}$ 1·492,  $n_{\text{He}}^{21}$  1·6383, which with hydroxylanine hydrochloride yields a mixture, m. p. 81°, of oximes, m. p. 63—66° and 103°, separable through the differing solubilities of their sodium salts. The elimination of bromine (by treatment with alcoholic potassium hydroxide) from the aldehyde occurs much more readily than from the oxime mixture. Acetylation of the mixture of oximes gives the acetyl derivative, m. p. 68—69°, of the form of m. p. 103°.

Oxidation of cis- $\alpha$ -bromocinnamaklehyde with silver oxide in presence of aqueous-alcoholic sodium hydroxide affords trans- $\alpha$ -bromocinnamic acid, also formed (in one case only) when the aldehyde is shaken with oxygen in chloroform.

Spectrochemical data are given for most of the above compounds. H. BURTON.

Condensation of aldehydes with hydrazones. II. Condensation of anisaldehyde and salicylaldehyde with the respective phenylhydrazones. III. Condensation of salicylaldehyde, anisaldehyde, and *p*-nitrobenzaldehyde with benzaldehydephenylhydrazone. A. GIACALONE (Gazzetta, 1930, 60, 818-821, 821-824; cf. A., 1930, 213).—II. In presence of zinc chloride, anisaldehyde (3 mols.) condenses with its phenylhydrazone (2 mols.) to form pp'-4: 4'-dimethoxybenzylidenedihydrazino-p''methoxytriphenylmethane,

 $OMe \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NH \cdot N: CH \cdot C_6H_4 \cdot OMe)_2$ , m. p. 215—216°. Similarly, salicylaldehyde and its phenylhydrazone give pp'-2:2'-dihydroxybenzylidenedihydrazino-o''-hydroxytriphenylmethane,

 $\check{OH} \cdot C_6 H_4 \cdot CH(\check{C}_6 H_4 \cdot \check{NH} \cdot \check{N:} \check{CH} \cdot C_6 H_4 \cdot OH)_2$ , m. p. 240° (decomp.).

III. When condensed with benzaldehydephenylhydrazone in presence of zinc chloride, (1) salicylaldehyde yields pp'-dibenzylidenedihydrazino-o''hydroxytriphenylmethane,

 $OH \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NH \cdot N: CHPh)_2$ , m. p. 185°, which forms a triacetyl derivative, m. p. 109—110°; (2) anisaldehyde gives pp'-dibenzylidenedihydrazino-p''methoxytriphenylmethane, m. p. about 125°, and (3) p-nitrobenzaldehyde gives pp'-dibenzylidenedihydrazino-p''-nitrotriphenylmethane, m. p. 213— 214°. T. H. POPE.

Dioximes. LXIX. LXX. G. PONZIO (Gazzetta, 1930, 60, 825-832, 886-893; cf. A., 1930, 1409).—LXIX. The extension to the glyoximes of the differentiation, proposed by Hantzsch for the monoximes, into forms stable towards acid and those stable towards alkali has resulted only in the supposed discovery of new forms of glyoximes which have no actual existence. The methods of Scholl (A., 1891, 315), Russanoff (A., 1892, 321), and Wieland and Semper (A., 1908, i, 108) yield, not  $\alpha$ -phenylglyoxime, but mixtures of this with the  $\beta$ -form, and the three phenylglyoximes described by Russanoff represent one and the same compound in more or less impure condition. With regard to the action of ethereal hydrogen chloride solution on glyoximes, it is now established that this reagent isomerises a form of benzildioxime that does not give a complex nickel salt into one that does, a form of chloroglyoxime giving no such salt into another also giving none, a form of phenylglyoxime giving a nickel salt into one giving no salt, a form of *p*-tolylglyoxime giving no nickel salt into one giving such salt, and the form of ptolylglyoxime giving a nickel salt into a form giving no nickel salt. These results are not in accord with the configurations which would be attributed to the two forms of these glyoximes on the basis of Hantzsch and Werner's thery.

LXX. Experimental results show that replacement of one or both oximinic hydrogen atoms of a glyoxime by one or two acyl groups does not necessarily yield an acyl derivative of the original glyoxime form, even although this may be obtained by subsequent hydrolysis of the acyl derivative. Hantzsch and Werner's hypothesis is found to be inapplicable to the acyl derivatives of chloro- and amino-glyoxime. Thus, when treated with chlorine,  $\alpha$ - and  $\beta$ -phenylglyoximes yield one and the same phenylchloroglyoxime, from which, by conversion into the 2-benzoyl or the dibenzoyl derivative, followed by the action of ammonia, both  $\alpha$ - and  $\beta$ -phenylaminoglyoximes are obtained. 2-Benzoyl- $\alpha$ -phenylchloroglyoxime,

NOBz:CPh·CCI:NOH, m. p. 177—178° (slight decomp.); dibenzoylphenylchloroglyoxime, NOBz:CPh·CCI·NOBz, m. p. 148—149°; 2-benzoyl-α-phenylaminoglyoxime, m. p. 171—172° (slight decomp.), and 2-benzoyl-αphenylacetamidoglyoxime, NOBz.CPh·C(NOH)·NHAc, m. p. 190—191° (slight decomp.), were prepared. T. H. POPE.

[Aromatic thioketones.] E. BERGMANN (Ber., 1930, 63, [B], 3225).—The reaction of aromatic thioketones with sodium (A., 1930, 1584) has been observed previously by Schönberg (A., 1925, i, 1300). H. WREN.

Behaviour of stereoisomeric oximes of ab-unsaturated ketones when hydrogenated. K. W. MERZ (Ber., 1930, 63, [B], 2951-2953).-3-Hydroxy-4-methoxystyryl methyl ketone is converted by hydroxylamine hydrochloride in 50% methyl alcohol into 3-hydroxy-4-methoxystyryl syn-ketoxime hydro-chloride, m. p. 174° (decomp.). The free syn-oxime, m. p. 168-169°, is transformed in hot glacial acetic acid into the anti-oxime, m. p. 142-143°. Both forms yield the same dibenzoyl derivative, m. p. 148-149°, hydrolysed by alcoholic sodium hydroxide to the anti-variety. Hydrogenation of the syn-oxime in presence of palladised charcoal gives a mixture of  $\beta$ -3-hydroxy-4-methoxyphenylethyl methyl ketone, itsoxime, and y-amino-a-3-hydroxy-4-methoxyphenylbutane, whereas the anti-oxime is unchanged under these conditions. Phenyl styryl syn-ketoxime is converted into ay-diphenylpropylamine and phenyl β-methylstyryl syn-ketoxime into αy-diphenylbutylamine, whereas the corresponding anti-oximes are unaffected. H. WREN.

Beckmann rearrangement. IV. Unsaturated ketoximes. K. VON AUWERS and M. SEYFRIED (Annalen, 1930, 484, 178-211).-Hydroxylamine reacts with various phenyl styryl ketones in alkaline solution, forming isooxazolines or isooxazoles, whereas in acidic solution the corresponding oximes are produced. Thus, phenyl styryl ketone and hydroxylamine react in alkaline solution, yielding a mixture of 3:5-diphenylisooxazoline, m. p. 75°, and alkali-soluble hydroxylamino-oximes (cf. Claus, A., 1897, i, 189); with hydroxylamine hydrochloride (cf. Henrich, A., 1907, i, 324), phenyl styryl ketoxime, m. p. 115-116° (lit. 107-108°), results. This oxime is unaffected by boiling alkali; it adds bromine in chloroform, forming phenyl aβ-dibromo-β-phenylethyl ketoxime, m. p. 156°, which when heated at 160° gives hydrogen bromide and 3:5-diphenylisooxazole, and with phosphorus pentachloride in ether undergoes rearrangement to  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionanilide, m. p. 179°. Phenyl a-bromostyryl ketoxime (A., 1929, 816) undergoes the Beckmann rearrangement, yielding an impure substituted benzamide (hydrolysis product benzoic acid). Anisyl styryl ketone furnishes an oxime, m. p. about 140° (acetyl derivative, m. p. 134-135°), rearranged to cinnam-p-anisidide, m. p. 152-153°; in alkaline solution, 5-phenyl-3-anisylisooxazoline, m. p. 104.5-105.5°, results (cf. Stockhausen and Gattermann, A., 1893, 163). Oxidation of this isooxazoline with chromic and acetic acids gives 5-phenyl-3-anisylisooxazole, m. p. 121°, also formed from anisoylphenylacetylene and hydroxylamine (cf. Weygand and Bauer, A., 1928, 187). 1:5-Diphenyl-3-anisylpyrazoline, m. p. 140.5-141.5°, is prepared from anisyl styryl ketone and phenylhydrazine in alcohol containing a little acetic acid.

Anisyl a-bromostyryl ketone, b. p. 250-253°/13 mm. (cf. Weygand and Bauer, loc. cit.), is converted into 5-phenyl-3-anisylisooxazole or the corresponding arime, m. p. 153°, which undergoes the Beckmann rearrangement, yielding resinous material (hydrolysed to anisic acid). Treatment of anisoylphenylacetylene with hydrogen bromide in acetic acid gives anisyl β-bromostyryl ketone, m. p. 65-66°, also convertible into 5-phenyl-3-anisylisooxazole; the oxime, m. p. 115-116°, is converted by phosphorus pentachloride in ether into trans-\$-bromocinnam-p-anisidide, m. p. 144°. Whilst the above (syn) oxime, m. p. 153°, is readily decomposed by aqueous-alcoholic sodium hydroxide to the phenylanisylisooxazole, the oxime of m. p. 115-116° is only partly hydrolysed under the same conditions (the isooxazole is also produced), indicating that it is an anti-derivative. p-Ethoxyphenyl aB-dibromo-B-phenylethyl ketone has m. p. 151-152°.

The mechanism of the formation of the *iso*oxazole derivatives is discussed; they are formed presumably through the *syn*-oximes. The addition of hydroxyl-amine to aryl  $\alpha$ -methoxystyryl ketones (Weygand and Bauer, *loc. cit.*) is considered to give oximinoketones and not hydroxylaminoketones. Meisenheimer's views on the Beckmann rearrangement are criticised and it is considered that the rearrangement is not a method for determining configuration.

H. BURTON.

 $\omega$ -Alkoxyalkylaminopropiophenones. R. T. MAJOR (J. Amer. Chem. Soc., 1930, 52, 5294).— $\omega$ -Methoxymethylamino-, b. p. 159°/23 mm. (hydrochloride, m. p. 155°), and  $\omega$ -ethoxyethylamino-propiophenones, b. p. 151—153°/9 mm., are prepared in 50% and 18% yield, respectively, from acetophenone, the requisite ON-dialkylhydroxylammonium chloride, and trioxymethylene by Mannich's method (A., 1917, i, 634). These compounds have only a slight anæsthetic action. H. BURTON.

Synthesis of aromatic hydroxyketones. I. and p-Acylphenols with normal chains of four to nine carbon atoms. G. SANDULESCO and A. GIRARD (Bull. Soc. chim., 1930, [iv], 47, 1300-1314).-Mixtures of o- and p-hydroxyaryl ketones are obtained in yields of 80-90% of theory when the reaction product ArO·AlCl2(?) from equimolecular proportions of aluminium chloride and a phenol is treated with an acyl chloride at 120-140° in the absence of a solvent. In presence of nitrobenzene or other solvent, the yields are lower and operating difficulties are greater, heptoyl chloride and phenol in nitrobenzene affording 33% of o- and 46% of p-hydroxyphenyl hexyl ketone. In the absence of solvent about 45-60% of o- and 30-40% of pderivative are formed, together with a little op-disubstituted derivative. The o-hydroxyaryl ketones are liquids or easily fusible solids, readily soluble in light petroleum and volatile in steam, the p-isomerides being non-volatile solids and sparingly soluble. In contrast to the p-compounds, the o-hydroxyaryl ketones have little tendency to form alkali derivatives and only o-butyrylphenol is completely soluble in the equivalent amount of N-sodium hydroxide. The o-compounds are benzoylated only with difficulty in presence of

pyridine, and attempts at methylation with methyl iodide or methyl sulphate failed. The o-hydroxyaryl ketones are reduced with difficulty, increasing with the mol. wt., whilst the p-compounds with zinc and hydrochloric acid readily give the alkylphenols in 75-90% yields; the o-compounds require the presence of acetic acid.

The following are described, the yields being indicated in parentheses : o- (45%), m. p. 10.5-10.6°, b. p. 119°/9 mm., d<sup>24</sup> 1.0683, n<sup>23'3</sup> 1.5375 (semicarbazone, m. p. 192-193°), and p-hydroxyphenyl n-propyl ketone (30%), m. p. 91-91.5°, b. p. 187-188°/9 mm. (benzoate, m. p. 107-107.5°), o- (56%), b. p. 130°/10 mm., dai 1.0435, np 1.5309 (semicarbazone, m. p.  $204-204\cdot5^{\circ}$ ), and p-hydroxyphenyl n-butyl ketone (29%), m. p. 63°, b. p. 197.5-198.5°/10 mm. (benzoate, m. p. 92°); o- (56%), b. p. 142-143°/10 mm., m. p. 17·2-17·4°, d<sup>21</sup> 1·026, n<sub>0</sub><sup>25</sup> 1·5254 (semicarbazone, m. p. 179°), and p-hydroxyphenyl n-amyl ketone (34%), m. p. 61°, b. p. 207—208°/10 mm. (benzoate, m. p. 105.5°); o. (48%), m. p. 9.8°, b. p. 155—156°/10 mm., d<sup>24</sup> 1.011, n<sup>25.5</sup> 1.5209 (semicarbazone, m. p. 162°), and p-hydroxyphenyl n-hexyl ketone (41%), m. p. 91-91.5° (benzoate, m. p. 96.5-97°; acetate, m. p. 46.5°, b. p. 194-195°/9 mm.); o- (45%), m. p. 22.3°. b. p. 169-170°/11 mm., d<sup>24</sup> 0.9989, np<sup>235</sup> 1.5169 (semicarbazone, m. p. 157-158°), and p-hydroxyphenyl n-heptyl ketone (38%), m. p. 62°, b. p. 224-225°/10 mm. (benzoate, m. p. 107-108°); o- (55%), m. p. 18.4°, b. p. 180°/10 mm.,  $d^{24}$  0.9887,  $n_{\rm p}^{25.5}$  1.5139 (semicarbazone, m. p. 164°), and p-hydroxyphenyl n-octyl ketone (35%), m. p. 54.5°, b. p. 232°/10 mm. (benzoate, m. p. 99.8°); o-n-butylphenol (83%), b. p. 109.5-110°/10 mm., d<sup>23</sup> 0.9774, n<sup>25 5</sup> 1.518 (phenoxyacetic acid, m. p. 105.5°), p-n-butylphenol (86%), m. p. 22°, n<sub>D</sub><sup>23</sup> 1.5165, n<sub>D</sub><sup>43</sup> 1.5082 (benzoate, m. p. 27°), o-n-amylphenol (72%), b. p. 122-124°/10 mm., d<sup>23</sup> 0.9635, np3 1.5132 (o-n-amylphenoxyacetic acid, m. p. 77-77.5°), p-n-amylphenol (79%), m. p. 23°, b. p. 134-136°/10 mm.,  $n_{\rm D}^{25.5}$  1.5119,  $n_{\rm D}^{45.5}$  1.5038 (benzoate, m. p. 51-51.5°); o-n-hexylphenol (80%), m. p. -2°. b. p.  $135-136^{\circ}/10$  mm.,  $d^{23}$  0.9524,  $n_{\rm p}^{23.5}$  1.5089 (o-n-hexylphenoxyacetic acid, m. p. 89.5-90°), p-nhexylphenol (77%), m. p. 28°, b. p. 146-147°/10 mm., n<sup>455</sup> 1.4996 (benzoate, m. p. 26.5°); o-n-heptylphenol (90%), m. p. 3°, b. p. 147-148°/10 mm., d<sup>23</sup> 0.9432,  $n_{\rm p}^{253}$  1.5058 (o-n-heptylphenoxyacetic acid, m. p. 71.5°); p-n-heptylphenol (73%), m. p. 26°, b. p. 157°/9 mm.,  $n_{1}^{45.5}$  1.4969 (benzoate, m. p. 40.5–41°); o-n-octylphenol (79%), m. p. 18–18.5°, b. p. 160–162°/11 mm.,  $d^{23}$ 0.9362, n; 1.5029 (0-n-octylphenoxyacetic acid, m. p. 88-88.5°); p-n-octylphenol (85%), m. p. 41-42°, b. p. 169°/10 mm., n<sup>455</sup> 1.4938 (benzoate, m. p. 40.5°); o-n-nonylphenol (85%), m. p. 19.5°, b. p. 176-177°/ 13 mm., d<sup>21</sup> 0.9309, n<sup>25'5</sup> 1.5005 (o-n-nonylphenoxyacetic acid, m. p. 75.5°); and p-n-nonylphenol (80%), m. p. 42.5°, b. p. 180-181°, np. 1.4920 (benzoate, m. p. 36.2°). R. BRIGHTMAN.

Structure of *p*-dimethylaminobenzoin. S. S. JENKINS [with L. A. BIGELOW and J. S. BUCK] (J. Amer. Chem. Soc., 1930, 52, 5198—5204).—*p*-Dimethylaminomandelonitrile, prepared from *p*-dimethylaminobenzaldehyde and dry hydrogen cyanide in presence of a small amount of calcium oxide, is hydrolysed by sulphuric acid at the ordinary temperature to *p*-dimethylaminomandelamide, m. p. 184-186°, which reacts with ethereal magnesium phenyl bromide, forming *benzoyl*-p-*dimethylaminophenylcarbinol* ( $\alpha$ -p-*dimethylaminobenzoin*), m. p. 159-160° (corr.). This is oxidised by Fehling's solution to 4-dimethylaminobenzil and reduced by tin and alcoholic hydrochloric acid containing a little copper sulphate to  $\alpha$ -p-dimethylaminodeoxybenzoin, m. p. 127-128° (this vol., 92).

p-Dimethylaminobenzoylphenylearbinol ( $\beta$ -p-dimethylaminobenzoin), m. p. 161—162° (corr.), prepared from mandelamide and magnesium p-dimethylaminophenyl bromide, is identical with the supposed  $\alpha$ -derivative, m. p. 163—164°, of Staudinger (A., 1913, i, 1353). It is reduced as above to a mixture of  $\alpha$ - and  $\beta$ -p-dimethylaminodeoxybenzoins (cf. loc. cit.). Similar reduction of p-dimethylaminohydrobenzoin gives 4-dimethylaminostilbene. H. BURTON.

Dioximes. LXXI. G. PONZIO and G. LONGO (Gazzetta, 1930, 60, 893-899).—The action of Grignard's reagent on isomeric arylmethylglyoxime peroxides confirms the view, deduced from the action of phosphorus pentachloride or sodium ethoxide and from physico-chemical investigations (cf. A., 1929, 334, 1316; 1930, 226, 581, 621), that the peroxides with the higher m. p. are furoxans, whilst those with the lower m. p. are dioxdiazines. T. H. POPE.

Anthrone series. I. Condensation of phthalide with aromatic compounds. II. Synthesis of hydroxymethylanthrones. A. STEYERMARK [with J. H. GARDNER] (J. Amer. Chem. Soc., 1930, 52, 4884-4887, 4887-4892).-I. The Friedel-Crafts reaction between benzene and phthalide gives 28% of the theoretical amount of anthrone (cf. King, A., 1927, 358). The oily product obtained similarly, using toluene, is oxidised by chromic and acetic acids to 2-methylanthraquinone; it forms some 2-methylbenzanthrone when treated with glycerol and 82% sulphuric acid, indicating that 2-methyl-10-anthrone is formed in the original condensation. 2-Chloroanthraquinone is obtained when the product from chlorobenzene and phthalide is oxidised; no benz-anthrone derivative could be isolated. The above method is not suitable for synthesising anthrones of definite structure.

II. The following benzylbenzoic acids are prepared by reducing the corresponding benzoylbenzoic acids with zinc dust and animonia: o-2'-hydroxybenzyl-, m. p. 133·8—134·5°; o-2'-hydroxy-3'-methylbenzyl-, m. p. 158·2—159°: o-2'-hydroxy-4'-methylbenzylbenzoic acids, m. p. 129—130°. These are converted by dissolution in sulphuric acid at the ordinary temperature into 1-hydroxy-; 1-hydroxy-2-methyl-, m. p. 207·2—208°; 1-hydroxy-3-methyl-, m. p. 258-259°, and 1-hydroxy-4-methyl-10-anthrones, m. p. 226·2—227°, respectively. Reduction of 1-hydroxyanthraquinones, prepared from the corresponding o-benzoylbenzoic acids, with tin and hydrochloric acid in acetic acid gives 1-hydroxy-9-anthrones in agreement with the work of Cross and Perkin (A., 1930, 607). The following are described : 1-hydroxy-; 1-hydroxy-2-methyl-, m. p. 136·2—137°; 1-hydroxy-3-methyl-, m. p.  $158\cdot2-159^{\circ}$ , and 1-hydroxy-4-methyl-9-anthrones, m. p.  $167\cdot4-168\cdot2^{\circ}$ . These anthrones are bright yellow (? benzenoid-quinonoid tautomerism), whilst their isomerides are colourless. The main product formed when 2-methylanthraquinone is reduced by Barnett and Goodway's method (A., 1929, 1171) is 2-methyl-10-anthrone (cf. loc. cit.). H. BURTON.

**Munjisthin.** II. P. C. MITTER and H. BISWAS (J. Indian Chem. Soc., 1930, 7, 839—841).—6-Methoxy-o-toluidine is converted by the usual method into 2-hydroxy-6-methoxytoluene, b. p.  $242-244^{\circ}$ , and thence into 2:6-dimethoxytoluene, m. p.  $35^{\circ}$ , which reacts with phthalic anhydride in presence of aluminium chloride and carbon disulphide, forming o-2:4-dimethoxy-m-toluoylbenzoic acid, m. p.  $180^{\circ}$ . When this is heated with a mixture of concentrated (1 part) and fuming sulphuric acid ( $20^{\circ}_{0}$  SO<sub>3</sub>; 5 parts) at  $100^{\circ}$ (bath), rubiadin methyl ether, m. p.  $188-189^{\circ}$ , is produced. This is demethylated by aluminium chloride at 200° to rubiadin. The above acid could not be oxidised to the corresponding benzophenonedicarboxylic acid, which, on ring closure, should yield munjisthin. The above methyl ether may be identical with the 3-O-methylrubiadin of Jones and Robertson (A., 1930, 1167). H. BURTON.

Synthesis of munjisthin. P. C. MITTER and H. BISWAS (Nature, 1930, 126, 761; 1931, 127, 166).— The synthesis of munjisthin, a dihydroxyanthraquinonecarboxylic acid occurring in *Rubia munjistha*, starting with 2-chloro-6-methoxytoluene and phthalic anhydride, is recorded. L. S. THEOBALD.

Anthracene derivatives. II. E. DE B. BARNETT and N. F. GOODWAY (Ber., 1930, 63, [B], 3048-3051). -1: 5-Dimethoxyanthraquinone, m. p. 241°, prepared by the action of boiling methyl-alcoholic sodium hydroxide on sodium anthraquinone-1:5 disulphonate, could not be reduced to the corresponding anthrone. 1:5-Diphenoxyanthraquinone is transformed by stannous chloride and concentrated hydrochloric acid in boiling glacial acetic acid into 1:5-diphenoxyanthrone,  $X <_{CH}^{CO} > X$  or  $X <_{CH}^{C(OH)} > X$ ,  $(X = C_6H_3 \cdot OPh)$ , m. p. 166°, which is recovered unchanged after treatment with magnesium methyl iodide or magnesium benzyl chloride and does not afford a mono- or di-benzylanthrone when boiled with benzyl chloride and sodium hydroxide. 1:5-Diphenoxyanthranyl acetate has m. p. 165°. Bromine in carbon disulphide converts the anthrone into 10bromo-1: 5-diphenoxyanthrone, m. p. about 180-183° (decomp.), from which the following compounds are derived by the usual methods: 1:5-diphenoxy-10ethoxyanthrone, m. p. 148° (whence the corresponding acetate, m. p. 238°); 10-piperidino-1:5-diphenoxy-anthrone, m. p. 136°; 10-anilino-1:5-diphenoxy-anthrone, m. p. 159° (decomp.); 10-methylanilino-1:5-diphenoxyanthrone, m. p. 159° after softening; 1:5diphenoxy-10-p-dimethylaminophenylanthrone, m. p. 250° (decomp.). Phthalic anhydride is converted by diphenyl ether in presence of aluminium chloride and carbon disulphide into 0-4'-phenoxybenzoylbenzoic acid, m. p. 162°, which is not transformed into the corresponding anthraquinone by sulphuric acid; it is reduced by zinc dust and ammonia to 0-4'-phenoxybenzylbenzoic acid, m. p. 128°, which could not be converted into the corresponding anthrone.

H. WREN. Derivatives of hydroxyaminomethylanthraquinones and dihydroxydianthraquinonylethylenes. III. H. DE DIESBACH, P. GUBSER, and H. SPOORENBERG (Helv. Chim. Acta, 1930, 13, 1265-1274; cf. A., 1929, 70; 1930, 607).-1-Chloro-2aminoanthraquinone is converted by short treatment with nitrosyl sulphate at 180-200° into 1-chloro-2hydroxyanthraquinone, m. p. 224°, which reacts with N-methyloltrichloroacetamide in cold sulphuric acid, forming 1-chloro-2-hydroxy-3-trichloroacetamidomethylanthraquinone, m. p. 204°. Hydrolysis of this with boiling 10% sodium hydroxide solution gives, instead of the expected amine (or its oxidation product) (cf. loc. cit.), probably impure \$-amino-a\$-di-(1-chloro-2hydroxy-3-anthraquinonyl)ethyl alcohol, m. p. about 250°; ammonia is evolved during the hydrolysis. Alizarin reacts with dimethylolcarbamide and Nmethylolphthalimide, forming  $\alpha$ -(1:2-dihydroxy-3-anthraquinonyl)methyl -  $\gamma$  - hydroxymethylcarbamide, m. p. 204°, and 1: 2-dihydroxy-3-phthalimidomethylanthraquinone, m. p. 310°, respectively. Hydrolysis of the former of these with 65% sulphuric acid at 160° gives 1: 2-dihydroxy-3-aminomethylanthraquinone (the acetate is formed by hydrolysis of the carbamide with a saturated solution of hydrogen chloride in acetic acid at 170° and partial neutralisation of the resulting product), whilst treatment of the latter first with boiling 23% sodium hydroxide solution and then with 90%acetic acid at 170° furnishes \$-amino-a\$-di-(1:2-dihydroxy-3-anthraquinonyl)ethyl alcohol.

2-Hydroxyanthraquinone condenses with dimethylolcarbamide, forming s-di-(a-2-hydroxyanthraquinonyl)methylcarbamide, m. p. 250°, which is stable towards alkaline hydrolysis, but is converted by hydrochloric acid at 150° into a mixture of the reduced form of s-di-(a-2-hydroxyanthraquinonyl)ethylenediamine and the corresponding glycol (cf. loc. cit.). s-Di-(a-2-hydroxy-3-carboxyanthraquinonyl)methylcarbamide, decomp. 318°, is hydrolysed by boiling hydrochloric acid to a mixture of 2-hydroxy-1:9(N)-isopyrroleanthrone-3-carboxylic acid and 2hydroxy-1-aminomethylanthraquinone-3-carboxylic acid. The former of these is obtained when the latter is heated. Neither of these substances is oxidised to the corresponding ethylene derivative by nitrous acid or oxygen in alkaline solution (cf. loc. cit.).

3-Chloroalizarin, anthragallol, and 1-hydroxynaphthacenequinone condense normally with Nmethylolamides (no details given); the resulting products could not be hydrolysed. H. BURTON.

Derivatives of veratrole and of methylvanillin. III. 2:3:6:7-Tetramethoxyanthraquinone. B. L. VANZETTI and A. OLIVERIO (Gazzetta, 1930, 60, 620-632; cf. A., 1927, 462).—Contrary to von Konek and Szamák's statement (A., 1922, i, 458), the preparation of *m*-hemipinic acid from methylvanillin (veratraldehyde) by Perkin and Robinson's method (J.C.S., 1907, 91, 1073) does not give good results. A more satisfactory procedure consists in converting veratraldehyde, by treatment with sodium in ethyl acetate solution, into 3:4-dimethoxycinnamic acid,

reducing this with sodium amalgam to obtain 3:4dimethoxydihydrocinnamic acid, condensing the latter by means of phosphoric anhydride to hydrindone, and oxidising the hydrindone with dilute nitric acid (1:3). Condensation of *m*-hemipinic anhydride with veratrole in carbon disulphide solution in presence of aluminium chloride yields 4:5:3':4'-tetramethoxy-2benzoylbenzoic acid, m. p. 217-218° (uncorr.), which (1) 4:5-dimethoxy-2-(3:4-dimethoxyphenyl)gives phthalide, m. p. 238°, when reduced with zinc dust in sodium hydroxide solution, (2) 4:5:3':4'-tetramethoxy-2-benzylbenzoic acid, m. p. 165-166°, when reduced with zinc dust in acetic acid solution, and (3) 2:3:6:7-tetramethoxy-9-anthrone, m. p. 282-284° (decomp.), when treated with concentrated sulphuric acid at a low temperature. Oxidation of the anthrone by either chromic acid or hydrogen peroxide yields 2:3:6:7-tetramethoxyanthraquinone, m. p. 345°, which may also be obtained, in small yield, by oxidising 2:3:6:7-tetramethoxydihydroanthracene with sodium dichromate in acetic acid solution. Demethylation of 2:3:6:7-tetramethoxyanthraquinone by treatment with hydrobromic acid gives  $\hat{2}: 3: 6: 7$ -tetrahydroxyanthraquinone, decomp. above 360°, which forms a tetra-acetyl derivative, m. p. 300° (decomp.). T. H. POPE.

5:6:5':6'-Dibenzo-NN'-dihydro-1:2:1':2'anthraquinoneazine. E. SCHWENK and H. WALD-MANN (J. pr. Chem., 1930, [ii], 128, 320—326).— Treatment of 4-chloro-2- $\alpha$ -naphthoylbenzoic acid with sulphuric acid at 58—60° gives 2-chloro-5:6-benzanthraquinone, m. p. 222—223°, converted by ammonia and cuprous chloride at 180° mainly into 2-amino-5:6benzanthraquinone, m. p. 283—285°, together with a small amount of probably the 2-amino-1-hydroxyderivative. Fusion with potassium hydroxide of a mixture of the amino-derivative and potassium acetate at 250—270° affords 5:6:5':6'-dibenzo-NN'-dihydro-1:2:1':2'-anthraquinoneazine. This gives a deep blue vat with alkaline hyposulphite, which passes readily, on further reduction, into a dirty brownishviolet; cotton is dved blue.

The Friedel-Crafts reaction with naphthalene-2:3dicarboxylic anhydride and chlorobenzene yields 3-*p*-chlorobenzoyl- $\beta$ -naphthoic acid, m. p. 215—220°, converted by treatment with zinc chloride and a little acetic acid at 200—250° into 2-chloro-6:7-benzanthraquinone; ring closure can be effected by *p*-toluenesulphonyl chloride at 180°. This chloro-compound gives a green vat with alkaline hyposulphite.

H. BURTON.

Monosubstitution derivatives of retene. G. KOMPPA and E. WAHLFORSS (J. Amer. Chem. Soc., 1930, 52, 5009–5017).—Treatment of retene with chlorine in cold carbon tetrachloride containing a little iodine gives a mixture, b. p. 195–205°/10 mm., of chloro-derivatives, part of which distils at 350–351°/747.6 mm. (the remainder resinifies), oxidised by chromic and acetic acids to retenequinone. Introduction of a carboxyl group into retene by Liebermann and Zsuffa's method (A., 1911, i, 202, 387) affords a retenecarboxylic acid, m. p. 229–231° (cf. loc. cit.) [sodium salt (+5H<sub>2</sub>O); methyl ester, m. p. 96–97°; amide, m. p. 224–226°], oxidised to retenequinone-

carboxylic acid, m. p. 237-240°; the carboxyl group does not enter the 9- or 10-position, whereas chlorine does. Addition of sulphuric acid  $(d \ 1.84)$ , with vigorous stirring, to retene at 99° (bath) gives a retenesulphonic acid, m. p. 188-189° (methyl ester, m. p. 164-166°, prepared from the potassium salt and methyl sulphate; ammonium salt); when sulphonation is effected at 200°, an isomeric retenesulphonic acid, m. p. 121-123° [ammonium, sodium (+3H<sub>2</sub>O), potassium, barium  $(+2H_2O)$ , strontium  $(+4H_2O)$ , calcium  $(+4H_2O)$ , and copper  $(+5H_2O)$  salts; sulphonyl chloride, m. p. 146.5—148°; sulphonamide, m. p. 206—207.5°; methyl ester, m. p. 117—119°], results. Mixtures of the acids are separable through the differing solubilities of their ammonium, potassium, or sodium salts in water. Both acids are oxidised by chromic and acetic acids to retenequinonesulphonic acids (potassium salts). Potassium hydroxide fusion of the less fusible acid gives a retenol, m. p. 200-202° (picrate, m. p. 151-152°); the more fusible acid yields a retenol, m. p. 158.5-159° (picrate, m. p. 145-146°; acetate, m. p. 132-134°), which couples with diazobenzenesulphonic acid. H. BURTON.

Solutions of gallic acid and tannin; influence of colloids on the crystal form and solubility of gallic acid. L. E. STEENHUISEN (Pharm. Weekblad, 1930, 67, 1269—1281).—The inhibition of crystallisation of solutions containing 2% of gallic acid, and variations in form of crystals obtained from solutions containing 3% of the acid, as a consequence of the presence in varying quantities of different colloids, are described. When tannin is present, the separated crystals contain very much smaller proportions than correspond with the ratios of tannic to gallic acid in the solution. A modification of Fleck's copper acetate method suitable for determination of tannin and gallic acid together in solution is described. S. I. LEVY.

Rotenone. IX. Alkali fusion of derivatives of rotenone. H. L. HALLER and F. B. LAFORGE. X. Cleavage of derritol and rotenol. L. E. SMITH and F. B. LAFORGE (J. Amer. Chem. Soc., 1930, 52, 4505-4509, 4595-4598).-IX. Fusion of derritol, isoderritol, dehydrorotenone, rotenol, dihydroxyrotenonic acid, or isodihydroxyrotenonic acid with potassium hydroxide at 200-210°, gives, in each case, isotubaic acid (cf. A., 1930, 1043). All the above compounds and dihydroderritol methyl ether (potassium hydroxide fusion product dihydrotubaic acid) contain either the lactone group or its hydrolysis group ; cleavage does not occur at the keto-group. Similar fusion of dehydrodihydrorotenonic and dihydrorotenolic acids affords unidentified phenolic acids, m. p. about 175° and about 159°, respectively, whilst rotenonic and dihydrorotenonic acids give non-crystalline products.

 $\dot{X}$ . Oxidation of methylderritolic acid (A., 1930, 781) with alkaline hydrogen peroxide affords a trimethoxyphenylacetic acid, m. p. 93°, oxidised further by alkaline potassium permanganate to a trimethoxybenzoic acid, m. p. 78-80° (amide, m. p. 173°). These results make probable Butenandt's suggestion (A., 1928, 1017) that derritol contains the 2-hydroxy-5: 6dimethoxyphenylacetyl group. Oxidation of dihydrorotenolic acid (loc. cit.) with alkaline hydrogen peroxide furnishes a dimethoxy-acid,  $C_{12}H_{14}O_5$ , m. p. 91-92°. H. BURTON.

Constitution of santonin. III. Proof of positions of methyl groups. G. R. CLEMO and R. D. HAWORTH (J.C.S., 1930, 2579—2582; cf. A., 1930, 919; Ruzicka and Eichenberger, A., 1930, 1442).— Reduction of tetrahydrosantonin by Clemmensen's method gives *deoxytetrahydrosantonin*, m. p. 141— 142°, which is further reduced by hydrogen iodide and red phosphorus to an iodine-containing oil, which, after treatment with sodium amalgam and alcohol, followed by distillation over soda-lime, gives 1: 4(a)*dimethyl-7-ethyldecahydronaphthalene* (annexed for-MeHC CH, mula), b. p. 120—125°/20 mm.

MeHC CH<sub>2</sub> H<sub>2</sub>C CH CHE H<sub>2</sub>C CH CHE H<sub>2</sub>C CH<sub>2</sub> H<sub>2</sub>C CH<sub>2</sub>

 $\begin{array}{rcl} H_2 & \text{mula}, \text{ b. p. } 120 & -125^\circ/20 \text{ mm.} \\ H_2 & \text{This could not be successfully} \\ \text{CHEt dehydrogenated by selenium,} \\ \text{CH}_2 & \text{but deoxytetrahydrosantonin is} \\ \text{H}_2 & \text{readily dehydrogenated to 1-} \\ \text{methyl-7-ethylnaphthalene (A., 1930, 593), the 5-methyl group} \end{array}$ 

Me 1930, 593), the 5-methyl group being thereby removed. The location of the second methyl group in the 5-position is therefore proved, and the structure previously assigned (*loc. cit.*) confirmed. H. A. PIGGOTT.

Oxidation of abietic acid with mercuric acetate. G. ROUIN (Bull. Inst. Pin, 1930, 155— 157).—Abietic acid,  $[\alpha]_{\rm p}$ —92°, when heated under reflux with 3 mols. of mercuric oxide in acetic acid, gives a monocarboxylic acid,  $C_{20}H_{28}O_4$ , m. p. 198— 200°,  $[\alpha]_{\rm p}$  +29.8°, probably diketonic but yielding no oxime, phenylhydrazone, semicarbazone, or quinoxaline. C. HOLLINS.

Fungus dyes. X. Xylindein, the dye of the green mould of decayed wood. F. KögL, H. ERXLEBEN, and (in part) G. DE Voss (Annalen, 1930, 484, 65-84; cf. A., 1925, i, 1440).-Xylindein is converted by aqueous sodium hydroxide into the tetrasodium salt of xylindeic acid, which, with silver nitrate, even in excess, gives a disilver salt, convertible by methyl iodide into a dimethyl ester. This forms a tetra-acetyl derivative and a disemicarbazone, and is reduced by zinc dust in presence of sodium acetate and acetic anhydride to a hexa-acetyltetrahydroleucodimethyl ester which no longer forms a semicarbazone. As xylindein itself gives a tetra-acetyl derivative, but has no free carbonyl groups, the occurrence of such in xylindeic acid, which still contains only four hydroxyl groups, may be explained by the presence in xylindein of two lactonic systems derived from enolic structures:  $C_{28}H_{29}O_3(OH)_4(CO \cdot O \cdot O \cdot C \cdot C <)_2$ +2H<sub>2</sub>O $\longrightarrow$ C<sub>28</sub>H<sub>22</sub>O<sub>3</sub>(OH)<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>(CO \cdot CH <)<sub>2</sub> This is supported by the catalytic hydrogenation of xylindein, the product of which, when treated with sodium hydroxide, gives the sodium salt of tetra-hydroxylindeic acid which contains two carboxylic and two secondary alcoholic groups; thus the crude sodium salt gives a tetrasilver salt, which with methyl iodide forms a dimethyl ether dimethyl ester (tetra-acetyl derivative, not reduced by zinc dust).

Reduction of xylindein with sodium hyposulphite gives a yellow leuco-compound by addition of 1 mol. of hydrogen, the *tetra-acetyl* derivative of which, like the hexa-acetyltetrahydroleuco-ester, shows two reactive hydrogen atoms by Zerewitinov's method. Quantitative oxidation with potassium permanganate of the sodium salt of xylindeic acid occurs with absorption of 36 atoms of oxygen, and yet catalytic reduction of its methyl ester at  $80-120^{\circ}$  and 120-180 atm. of hydrogen leads only to a hexahydro-compound (isolated as *tetramethyl cther*, m. p. 247°). The hexaacetyl-leuco-ester, alone among the derivatives tried, is degraded to phenanthrene by distillation with zinc dust, and it is suggested that the colour of the dye is due to a 2 : 7-phenanthraquinone structure, the failure to acetylate the hydroxyl groups produced by reduction being ascribed to steric hindrance, probably by *ortho*-substituents.

An acid,  $C_{32}H_{26}O_{12}Cl_4$ , decomp. 225–230° without melting, of unknown constitution, results from the action of hydrogen peroxide and hydrochloric acid on xylindein. Fission of xylindein by heating with alcoholic potassium hydroxide of b. p. 175° gives an acid,  $C_{13}H_8O_{10}$  or  $C_{13}H_{10}O_{10}$ , m. p. 216° [the diacetyl derivative, m. p. 199° (trimethyl ester, m. p. 165°), is converted by catalytic reduction into a substance of m. p. 180–184°], n-butyric, and acetic acids.

## H. A. PIGGOTT.

**Chondridin**. V. V. SAVJALOV and P. P. MILO-VANOV (Jahrb. Univ. Sofia Med. Fak., 1928, 7, 14; Chem. Zentr., 1930, ii, 249—250).—When a solution of chondrosin is heated with barium hydroxide solution barium chitonate and lutidine are formed. The hydrolytic products of chondrosin afford with benzoyl chloride chitose tribenzoate; when heated under pressure with dilute oxalic acid solution they yield hydroxymethylfurfuraldehyde. Dry distillation of chondroitinsulphuric acid or dried cartilage with calcium oxide affords lutidine. The formula  $C_{14}H_{17}O_6N$  is attributed to chondrosin. Chondridin was obtained from tracheal cartilage chondrosin syrup by treatment, after dilution, with ammonium oxalate, evaporation, and extraction with alcohol aud ether, followed by decolorisation and crystallisation at 40°. The composition of the chondridin crystals indicated the formula  $C_{12}H_{19}O_{10}N,H_2O$ . Chondridin is not considered to be a lactone. Chondrosin is regarded as a lutidinecarboxylic ester of chitose.

A. A. ELDRIDGE.

Isoprene and caoutchouc. XXIV. Reduction of caoutchouc with hydriodic acid. H. STAUDIN-GER and J. R. SENIOR. XXV. Polymeric homologous hydrocaoutchoucs. H. STAUDINGER. XXVI. Hemicolloidal hydrocaoutchouc. H. STAUDINGER, E. GEIGER, E. HUBER, W. SCHAAL, and A. SCHWALBACH. XXVII. Relation between viscosity and mol. wt. for hydrocaoutchoucs. H. STAUDINGER and R. NODZU. XXVIII. Fractionation and cracking of hydrocaoutchouc. H. STAUDINGER and W. SCHAAL. XXIX. High molecular hydrocaoutchouc. H. STAUDINGER and W. FEISST. XXX. Hydromethylcaoutchouc. H. STAUDINGER, M. BRUNNER, and E. GEIGER (Helv. Chim. Acta, 1930, 13, 1321-1324, 1324-1334, 1334-1349, 1350-1354, 1355-1360, 1361-1367, 1368-1374) .- XXIV. When caoutchoue is heated with red phosphorus and hydriodic acid (d 1.96) at 245-250° and 280°, the products formed are saturated hydrocarbons with M = 1760 and 1220, respectively. These products cannot be distilled (cf. Berthelot,

Bull. Soc. chim., 1868, [ii], 10, 436; 1869, [ii], 11, 33). They are probably formed by reduction of partly cyclised fragments of the original caoutchoue molecule which result from the cracking process; cyclisation occurs under the influence of the acid.

XXV. The physical properties of the various hydrocaoutchoucs described in the literature and the following papers are discussed. Hydrocaoutchoucs prepared by hydrogenation in absence of solvents at relatively high temperatures are hemicolloids (a 5% solution in carbon tetrachloride is a sol); at lower temperatures in presence of solvents eucolloidal hydrocaoutchoucs are produced (5% solutions in carbon tetrachloride are gels).

XXVI. Hydrogenation of caoutchouc in presence of varying amounts of different catalysts at 275-285° by the method previously described (A., 1922, i, 1043) gives products of widely differing character according to the amount and the activity of the catalyst used. Thus the hydrocaoutchouc obtained with only a small amount of an active nickel (or cobalt) catalyst is much less complex than that formed using equal parts of caoutchouc and catalyst. In the last case reduction occurs at a greater rate than thermal fission of the caoutchouc molecule. Platinum catalysts (cf. loc. cit.) give the simpler products, but with copper catalysts abnormal reduction occurs. The products formed during abnormal reduction are hydropolycyclocaoutchoucs; cyclisation of the hemicolloidal polyprene chains occurs before reduction. Reduction of a caoutchouc which has been allowed to swell in cyclohexane (the solvent is removed before reduction) in presence of half its weight of a very active nickel catalyst at 270°/55 atm. affords a hydrocaoutchouc of very high mol. wt., which is stable at 270°. In this case, reduction occurs before any fission. Guttapercha and balata are reduced in presence of equal amounts of nickel catalysts to products similar to the hydrocaoutchouc obtained under the same conditions.

XXVII. The same relationship exists between the viscosity and mol. wt. of pure hydrocaoutchoucs (prepared by rapid reduction on a small scale) as for polyprenes (A., 1930, 609, 782). With technical products (obtained by large-scale processes using little catalyst), it is found that the mol. wt. calcuated from the expressions  $M=\gamma_{\rm sp.}/cK_{\rm m}$  and  $M=K_{\rm c}K_{\rm cm}$  (cf. loc. cit.) are much greater than those determined in benzene.

XXVIII. An ether-soluble hydrocaoutchouc (M = 14,000) is fractionally precipitated from its ethereal solution by alcohol. Viscosity determinations of the 5 fractions obtained show that the original product is a mixture of polymeric homologues (M = 5000 - 21,000); the viscosity of 0.5*M*-solutions in carbon tetrachloride increases with rise in mol. wt.

Contrary to the statement of Pummerer and Koch (A., 1924, i, 1214), unsaturated compounds are obtained when hydrocaoutchoue is distilled in a high vacuum. The various fractions obtained from a hydrocaoutchoue of M=16,000 have b. p. below  $100^{\circ}/0.1$  mm. to above  $300^{\circ}/0.1$  mm., and the corresponding mol. wt. vary from about 180 to 960. Iodine chloride titration of the various fractions shows that they contain 2.6-13.7 isoprene units per double linking.

XXIX. Reduction of the ether-soluble caoutchoue of Pummerer and Koch (*loc. cit.*) with hydrogen in presence of platinum oxide and hexahydrotoluene in the cold gives a hydrocaoutchoue with a mol. wt. of about 30,000. A similar product is obtained from a caoutchoue (M=70,000) using an active nickel catalyst at  $180-200^{\circ}/100$  atm. The hydrocaoutchoues are purified by precipitation from solutions in hexahydrotoluene by methyl alcohol. The specific viscosity of 0.1M-solutions of these products in tetrahydronaphthalene is the same at  $20^{\circ}$  and  $60^{\circ}$ ; with 0.5M-solutions the specific viscosity is greater at the lower temperature owing to strong association. Solutions of the high-molecular hydrocaoutchoues show only slight deviations from the Hagen-Poiseuille law.

XXX. Hydrogenation of methylcaoutchouc  $\cdot$  in presence of an active nickel catalyst at  $260-270^{\circ}/90$ atm. gives a hemicolloidal hydromethylcaoutchouc with a mean mol. wt. of only 1600. Reduction in presence of 0.025 part of platinum-black at 270- $280^{\circ}/80-100$  atm. gives a mixture of products separable by ether-alcohol and distillation into fractions with M=168-1000; the fraction of lowest mol. wt. is probably a tetramethyloctane. The ease of fission of methylcaoutchouc, caoutchouc, and butadiene caoutchouc during reduction under the same conditions is in the order quoted. H. BURTON.

Synthesis of menthyl hydrogen phosphates. K. P. JACOBSOHN and J. TAPADINHAS (Compt. rend. Soc. Biol., 1930, 104, 432–434, 434–436; Chem. Zentr., 1930, ii, 1221).—The preparation of the esters  $C_{10}H_{19}$ ·O·PO(OH)<sub>2</sub>, ( $C_{10}H_{19}$ ·O·)<sub>2</sub>PO·OH, and  $C_{10}H_{19}$ ·O·PO(OH)·O·PO(OH)·O·C<sub>10</sub>H<sub>19</sub> is described. A. A. ELDRIDCE.

Menthone series. VIII. Characterisation of the optically active menthylamines. J. READ and R. A. STOREY (J.C.S., 1930, 2761-2769),-The four stereoisomeric menthylamines have been prepared in quantity and various physical properties of the free bases and of a large number of their acyl derivatives (prepared by the action of the appropriate acid chloride or anhydride in dry benzene) have been determined. The following new or revised physical data are recorded, the values for  $[\alpha]_n$  being for the homogeneous state and in chloroform, respectively: *l*-, b. p. 81-82°/12 mm.,  $d_4^{25}$  (corr.) 0.8525,  $\hat{n}_{11}^{25}$  1.4600, [x]<sup>25</sup> -44.53°, -38.2°; d-neo-, b. p. 84°/13 mm., d<sup>25</sup> (corr.) 0.8551,  $n_{\rm D}^{25}$  1.4614,  $\lceil \alpha \rceil_{\rm D}^{25}$  +  $15.12^{\circ}$ , +  $8.7^{\circ}$ ; d-iso-, b. p.  $87^{\circ}/13.5$  mm.,  $d_4^{25}$  (corr.) 0.8632,  $n_D^{25}$  1.4659,  $[\alpha]_D$ +28.96°, +29.4°; and d-neoiso-, b. p. 89°/14.5 mm.,  $d_4^{23}$  (corr.) 0.8636,  $n_D^{25}$  1.4670,  $[\alpha]_D$  +2.32°, +10.7°, -menthylamines. The density and refractive index are higher for the iso-bases than for the others, thus supporting the supposed derivation of the former from the cis-ketone, d-isomenthone. Striking alterations in rotatory power occur when the bases are dissolved in chloroform, decreases of 14% and 42% being shown by the l- and d-neo-base, respectively, and increases of 1.6% and 360% for the d-iso- and d-neviso-base, respectively. The following acyl derivatives are described, all rotations being in chloroform at 25°: formyl-, m. p. 102-103°,  $[\alpha]_{\nu}^{25}$  -83.8°; acetyl-, m. p.  $145^{\circ}$ ,  $[\alpha]_{0}^{25} - 81.7^{\circ}$ ; propionyl., m. p. 88°,  $[\alpha]_{0}^{25} - 76.6^{\circ}$ ; n-butyryl-, m. p. 73°, [a]<sup>25</sup><sub>p</sub> -70.9°; isobutyryl-, m. p.

 $128^{\circ}, [\alpha]_{D}^{25} - 66.5^{\circ}; isovaleryl., m. p. 110^{\circ}, [\alpha]_{D}^{25} - 64.7^{\circ};$ *n*-hexoyl-, m. p. 60°,  $[\alpha]_D^{21} - 71 \cdot 2^\circ$ ; *n*-octoyl-, m. p. 57°,  $[\alpha]_{D}^{25}$  -53·2°; chloroacetyl-, m. p. 76°,  $[\alpha]_{D}^{25}$  -71·9°; bromoacetyl-, m. p. 103°, [a] -61.6°; benzoyl-, m. p. 157°,  $[\alpha]_{15}^{\alpha}$  -62.8°; phenylacetyl-, m. p. 106°,  $[\alpha]_{15}^{\alpha}$ -60.4°; 2-naphthalenesulphonyl-, m. p. 135°,  $[\alpha]_{15}^{\alpha}$ -53.3°; and anisoyl-, m. p. 183°,  $[\alpha]_{15}^{\alpha}$  -57.7°, -1-menthyl-amine; formyl-, m. p. 117—118°,  $[\alpha]_{15}^{\alpha}$  +53.8°; acetyl-, m. p. 169–170°,  $[\alpha]_0^{25}$  +53.0°; propionyl-, m. p. 149°,  $[\alpha]_{p}^{25} + 48.3^{\circ}; n$ -butyryl-, m. p.  $104^{\circ}, [\alpha]_{p}^{25} + 46.8^{\circ}; iso-$ butyryl-, m. p.  $160 - 161^{\circ}, [\alpha]_{p}^{25} + 47.5^{\circ}; isovaleryl-, m. p.$  $132^{\circ}, [\alpha]_{0}^{23} + 42.8^{\circ}; n-hexoyl-, m. p. 65^{\circ}, [\alpha]_{0}^{23} + 40.0^{\circ}; n-hexoyl-, m. p. 65^{\circ}; n-hexoyl-,$ octoyl-, m. p. 78°, [a]<sup>35</sup> +36-7°; chloroacetyl-, m. p. 150°,  $[\alpha]_{D}^{m}$  +50.7°; bromoacetyl-, m. p. 160°,  $[\alpha]_{D}^{m}$  +40.9°; benzoyl-, m. p. 121.5°;  $[\alpha]_{D}^{m}$  +22.7°; phenylacetyl-, m. p.  $120^{\circ}$ ,  $[\alpha]_{0}^{25} + 34.5^{\circ}$ ; 2-naphthalenesulphonyl-, m. p.  $208^{\circ}$ ,  $[\alpha]_{D}^{25} + 43.7^{\circ}$ ; and anisoyl-, m. p. 130°,  $[\alpha]_{D}^{25} + 21.1^{\circ}$ , -dneomenthylamine; formyl-, m. p.  $45-46^\circ$ ,  $[\alpha]_D^{23}+31\cdot3^\circ$ ; acetyl-, m. p. 77-79°, [a]<sup>25</sup> +30.7°; propionyl-, m. p. 83°,  $[\alpha]_{11}^{25} + 27.7^{\circ}$ ; *n*-butyryl-,  $[\alpha]_{15}^{25} + 23.9^{\circ}$ ; isobutyryl-, m. p. 116°,  $[\alpha]_{D}^{25} + 22 \cdot 8^{\circ}$ ; isovaleryl-, m. p. 82°,  $[\alpha]_{D}^{25}$ +27.0°; n-hexoyl-,  $[\alpha]_{D}^{ss}$ +24.9°; n-octoyl-,  $[\alpha]_{D}^{ss}$ +23.3°; chloroacetyl-, m. p. 82°,  $[\alpha]_{D}^{ss}$ +30.0°; bromoacetyl-, m. p. 80°,  $[\alpha]_0^{25} + 30.3^\circ$ ; benzoyl-, m. p. 97–98°,  $[\alpha]_0^{25}$ +18.3°; phenylacetyl-, m. p. 103°,  $[\alpha]_{D}^{a_{3}}$  +33.3°; 2-naphthalenesulphonyl-, m. p. 80–81°,  $[\alpha]_{D}^{a_{3}}$  -2.8°; and anisoyl-, m. p. 121°,  $[\alpha]_{D}^{23}$  +25·3°, -d-isomenthylamine; formyl-,  $[\alpha]_{D}^{25}$  -3·9°; acetyl-, m. p. 99-100°,  $[\alpha]_{D}^{25}$ -2.6°; propionyl-, m. p. 103°,  $[\alpha]_{11}^{23}$  0°; n-butyryl-,  $[\alpha]_{12}^{23}$ -1.0°; isobutyryl-, m. p. 128°,  $[\alpha]_{25}^{25}$  -3.7°; isovaleryl-, m. p. 99°,  $[\alpha]_{D}^{25} - 4 \cdot 1^{\circ}$ ; *n*-hexoyl-, m. p. 50°,  $[\alpha]_{D}^{25} = 0^{\circ}$ ; *n*-octoyl-, m. p. 55°,  $[\alpha]_{1}^{25} - 1 \cdot 2^{\circ}$ ; chloroacetyl-, m. p. 80°,  $[\alpha]_{\mathbb{B}}^{\mathbb{B}} = 9.8^{\circ}$ ; bromoacetyl-, m. p. 100°,  $[\alpha]_{\mathbb{B}}^{\mathbb{B}} = 7.5^{\circ}$ ; benzoyl-, m. p. 151°,  $[\alpha]_{\mathbb{B}}^{\mathbb{B}} = -10.4^{\circ}$ ; phenyl-acetyl-, m. p. 109°,  $[\alpha]_{\mathbb{B}}^{\mathbb{B}} = -3.4^{\circ}$ ; 2-naphthalenesulphonyl-, m. p.  $120^{\circ}$ ,  $[\alpha]_{23}^{23}$   $-10.7^{\circ}$ ; and anisoyl-, m. p.  $156^{\circ}$ ,  $[\alpha]_{23}^{23}$   $-9.5^{\circ}$ , -d-neoiso-menthylamine. The rotatory powers of these derivatives conform in general to the numerical relationship  $l \rightarrow l - iso > l - nco$ >l-neoiso, whilst the m. p. observe the sequence d-nco>l->d-neoiso>d-iso. The comparative velocity of reaction of the stereoisomeric bases with various acid chlorides, anhydrides, and aldchydes, has been determined by allowing equimolecular mixtures of pairs of the bases to react with an insufficient quantity of the reagent, and determination of the composition of the product by its rotatory power. The results indicate the sequences d-neo, d-iso, and d-neoiso>l-; and d-neo, and d-neoiso>d-iso. Condensation of the menthylamines with d-, l-, and dl-camphor-10sulphonyl chloride indicates that the reaction is more rapid between molecules which display rotation in opposite senses. Thus are obtained : d-camphor-10sulphonyl-1-menthylamine, m. p.  $139^{\circ}$ ,  $[\alpha]_{D} -28 \cdot 0^{\circ}$ , -d-neomenthylamine, m. p.  $113^{\circ}$ ,  $[\alpha]_{D} +33 \cdot 1^{\circ}$ , and -d-isomenthylamine, m. p.  $169^{\circ}$ ,  $[\alpha]_{D} + 29 \cdot 7^{\circ}$ ; 1-cam-phor-10-sulphonyl-1-, m. p.  $143^{\circ}$ ,  $[\alpha]_{D} - 60 \cdot 9^{\circ}$ , -d-neo-, m. p.  $115^{\circ}$ ,  $[\alpha]_{D} + 7 \cdot 3^{\circ}$ , and -d-iso-, m. p.  $140^{\circ}$ ,  $[\alpha]_{o} = 15.8^{\circ}$ , -menthylamine (all rotations in benzene at about 16°); and dl-camphor-10-sulphonyl-d-neomenthylamine, m. p.  $115^{\circ}$ ,  $[\alpha]_{\rm p} + 21.3^{\circ}$ . The rotations of the products obtained by the interaction of active with dl-reagents and of the hydrochlorides of the unchanged base in such reactions are recorded. J. W. BAKER.

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Piperitone. XI. Synthesis of optically inactive and active piperitylamines, piperitols, and a-phellandrenes. J. READ and R. A. STOREY (J.C.S., 1930, 2770-2783).-Interaction of l-piperitone and hydrazine under appropriate conditions affords a syrupy product,  $[\alpha]_D + 201 \cdot 1^\circ$ , possibly a hydrated azine, which is reduced by zinc and glacial acetic acid to dl-piperitylamine, b. p.  $97.5-98.5^{\circ}/16$  mm.,  $n_{\rm b}^{15}$ 1.4802,  $d_4^{25}$  (vac.) 0.8801 (hydrochloride, m. p. 191°), exhibiting only feeble optical activity and yielding inactive acetyl, m. p. 108°, benzoyl, m. p. 130°, and anisoyl, m. p. 161°, derivatives. Fractional crystallisation of the hydrogen tartrate obtained with d-tartaric acid affords 1-piperitylamine hydrogen d-tartrate, m. p. 217°,  $[\alpha]_{\rm p} -43.0^{\circ}$  in water, from which *l*-piperitylamine, b. p. 101-102°/19 mm.,  $d_4^{35}$  (vac.) 0.8789,  $n_{\rm D}^{25}$  1.4770,  $[\alpha]_{\rm D}^{35}$  -80.35 (homogeneous) and -70.0° in chloroform [hydrochloride, m. p. 213° (decomp.),  $[\alpha]_D^{**} - 83 \cdot 5^\circ$ ; acetyl, m. p. 102-103°,  $[\alpha]_D^{**} - 153^\circ$  in chloroform; benzoyl, m. p. 102-103°,  $[\alpha]_D^{**} - 173^\circ$  in chloroform; anisoyl, m. p. 142-143°,  $[\alpha]_D^{**} - 175^\circ$  in chloroform; and phenylacetyl, m. p.  $89-90^{\circ}$ ,  $[\alpha]_{0}^{25}$  -130.5° in chloroform, derivatives], is obtained. Its cis- or trans-configuration has not yet been ascertained. Methylation of dl-piperitylamine with methyl iodide and sodium methoxide under conditions precluding decomposition of the quaternary salt affords dl-piperityltrimethylammonium iodide, m. p. 88° with decomp. to dl-a-phellandrene and  $\alpha$ -terpinene, separated and characterised as their nitrosites. From the products obtained when the dl-iodide is steam-distilled with silver oxide (trimethylamine being evolved) can be isolated dl-neopiperitol, b. p. 94-96°/15.5 mm., np 193 1.4740 (oxidised by Beckmann's reagent to piperitone), dl-piperitol, b. p. 100- $106^{\circ}/19.5$  mm.,  $n_{\rm D}^{18}$  1.4769 (also obtained by the action of nitrous acid on dl-piperitylamine), and dl- $\alpha$ phellandrene, b. p.  $63-65^{\circ}/15\cdot5$  mm.,  $n_{\rm D}^{195}$  1.4772, identified as its  $\alpha$ -nitrosite :  $\alpha$ -terpinene could not be detected. Similarly methylation of l-piperitylamine and degradation of the quaternary hydroxide affords d-neopiperitol, b. p.  $96\cdot5-98\cdot5^{\circ}/15\cdot5$  mm.,  $n_{15}^{25}$  1·4729,  $d_{45}^{25}$  (vac.) 0·9119,  $[\alpha]_{15}^{16}$  +21·22°, d-piperitol, b. p.  $101-104^{\circ}/16$  mm.,  $n_{15}^{16}$  1·4770,  $d_{45}^{25}$  (vac.) 0·9200,  $[\alpha]_{b}^{16}$  +40.22° (both oxidised to *d*-piperitone), and almost pure d-a-phellandrene, b. p. 66-68°/16 mm.,  $n_{1}^{25}$  1.4777,  $d_4^{25}$  (vac.) 0.8463,  $[\alpha]_{10}^{16}$  +86.4<sup>6</sup>. These degradations afford a ready passage directly from a  $\Delta^{1}$ - to a conjugated  $\Delta^{2:6}$ -derivative and establish a chemical and stereochemical connexion between d-piperitol, d-piperitone, and  $d-\alpha$ -phellandrene, and nake it possible to proceed from *l*-piperitone of *Eucalyptus* oils to *d*-piperitol and *d*-piperitone of Andropogon species by the stages l-piperitone  $\longrightarrow$ dl-piperitylamine  $\longrightarrow l$ -piperitylamine  $\longrightarrow d$ - $\alpha$ -phellandrene+d-piperitols  $\rightarrow d$ -piperitone. The stereochemical relationships of the piperitols are discussed and the relative molecular configurations I and II

-Jin	HOH	HO-4-H	
(I.)	$H_{4}$ $Pr^{\beta}$	H-3-Pr <sup>β</sup>	(II.)

are assigned to d(or l)- and d(or l)-neo-piperitol, respectively, on the basis of physical properties. J. W. BAKER.

Pinene and nopinene. G. BRUS (Bull. Inst. Pin, 1929, 271–276, 293–300; 1930, 7–16, 33–38, 63–68, 87–96, 109–112, 131–136, 151–157, 175– 178, 199-205, 225-228, 244-247, 270-274).-A comprehensive review of pinene, nopinene, and their derivatives, with details of preferred practical methods. d-Nopinene probably does not occur in conifer essences, but has been found (Rutovski and Vinogradova, A., 1928, 1377) in Ferula galbaniflora, Boiss., and has b. p. 162–163°,  $d_0^{15}$  0.8702,  $n_D^{20}$  1.4755,  $[\alpha]_{\rm r}$  +24.01°. Pure *l*-nopinene (Darmois, Diss., Paris, 1910) has  $d_0^{15}$  0.8740,  $n_{578}^{15}$  1.4874,  $[\alpha]_{578}$  -22.44°. The poor yield of crystallisable pinonic acids from oxidation of pinene with neutral permanganate is due largely to racemisation; the presence of d-pinonic acid greatly diminishes the rate of crystallisation of the racemic acid, and conversely. The use of an inactive pinene, produced by mixing the calculated quantities of l- (Bordeaux) and d- (Aleppo) -pinene fractions, leads to a 50% yield of crystalline r-pinonic acid. Racemisation is largely prevented and a good yield (50%) of *d*-pinonic acid, m. p. 69°,  $[\alpha]_v + 116.45^\circ$ , is obtained by neutralising the d-pinene oxidation liquors with acetic acid before concentration. A similar effect results from the removal of hydroxyl ions by means of ammonium chloride or magnesium

sulphate present during oxidation; the latter reagent retards oxidation, and heating at 40° is necessary. The yield of nopinic acid by oxidation of pure nopinene is more than doubled by using neutral in place of alkaline permanganate, and neutralising with carbon dioxide the caustic alkali formed. Purified *l*-nopinic acid has m. p. 127° and  $[\alpha]_v -17.51°$  in chloroform; it yields a nopinone, m. p. 0—1°,  $d^{15}$ 0.9815,  $n_D^{15}$  1.47785,  $[\alpha]_{378} + 19.6°$  (semicarbazone, m. p. 188°; trihydrochloride, decomp. 148°; dihydrochloride, m. p. 125°). Compounds of nopinic acid with 0.5C<sub>6</sub>H<sub>6</sub>, 0.5C<sub>6</sub>H<sub>5</sub>Me, 0.5C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>, and 0.5H<sub>2</sub>O are described, with crystallographic data.

The ozonisation of pinene and nopinene in chloroform is followed by determinations of unabsorbed ozone in every sixth litre of gas passed. The resulting curves show a period of complete absorption (formation of ozonide), followed by a sudden fall, and finally a slowly decreasing absorption by the solvent. Nopinene ozonide provides the best route to nopinone, the yield on decomposition with boiling 5% potassium hydroxide being 50%, together with formaldehyde and a compound,  $C_9H_{14}O_2$ , m. p. 126–127°, which is probably a lactone (annexed formula) and gives CH--CO-0 on hydrolysis an acid not obtained -CMe2 crystalline. Nopinene is readily de-CH<sub>2</sub> tected in mixtures by the production of  $CH_2$ nopinone from the ozonide, and may be CH-CH<sub>2</sub> approximately determined by measure-

ment of the carbon dioxide produced by oxidation of the formaldehyde formed with mercuric oxide. Pinene yields a small amount of carbon dioxide on ozonisation and causes an error in this method when applied to mixtures of nopinene and pinene. Pinane gives about 3% of its molecule as carbon dioxide on ozonisation, but is otherwise unaffected.

Fractional crystallisation of solid pinene hydrochloride fails to show any trace of *iso*bornyl chloride of m. p. 161°, and capillary experiments prove the absence of a racemic compound. By sublimation at 15° over a period of two years pinene hydrochloride is obtained in cubic octahedra, m. p. 132°. Fractional distillation of commercial liquid pinene hydrochloride, from Bordeaux turpentine, yields about 40% of solid pinene hydrochloride, 8—10% of dipentene dihydrochloride, m. p. 49°, about 2% of terpenes (pinene, dipentene, and terpinolene), a little limonene monohydrochloride, and a mixture of fenchyl, bornyl, and isobornyl chlorides. The tertiary hydrochloride of pinene (or nopinene) appears to be a similar mixture, decomposing, however, at 10°; removal of hydrogen chloride by sodium ethoxide yields  $\gamma$ -pinene, nopinene,  $\alpha$ -pinene, limonene, dipentene, and terpinolene.

The camphene problem is discussed. By careful fractionation at 10 mm. of distilled *d*-camphene, b. p. 156-161°, obtained in 77% yield by Reychler's method from *d*-pinene hydrochloride and potassium phenoxide, a series of fractions is obtained which increase, at first rapidly and then more slowly, in m. p.  $(15\cdot6-45\cdot1^{\circ})$ , b. p.  $(148-161^{\circ} \text{ or } 47-52^{\circ}/10 \text{ mm.})$ , rotatory power ([ $\alpha$ ],  $+5\cdot25^{\circ}$  to  $+35\cdot05^{\circ}$ ), and mol. refraction ( $42\cdot72-44\cdot10$ ), the density remaining almost constant. *l*-Camphene shows similar variations. In both cases this is due to the presence of a low-boiling ( $148-153^{\circ}$ ), inactive, liquid constituent, apparently *s*-tricyclene (m. p.  $65^{\circ}$ ) kept liquid by a little fenchene (?). *l*-Pinene hydrochloride is conveniently converted by sodium resinate at 160° into *l*-camphene, m. p.  $43-45^{\circ}$ ,  $[\alpha]_{\circ} -66^{\circ}$  (see also Gammay, F.P. 595,036; B., 1927, 156). By the action of 1 mol. of chlorine on dry *d*-pinene at  $-15^{\circ}$  to  $-20^{\circ}$  there is obtained a mixture of bornyl chloride, 2: 6-dichlorocamphane (by isomeris-

By the action of 1 mol. of chlorine on dry *d*-pinene at  $-15^{\circ}$  to  $-20^{\circ}$  there is obtained a mixture of bornyl chloride, 2 : 6-dichlorocamphane (by isomerisation of 1 : 2-dichloropinane), and liquid di- and polychloro-compounds. 2 : 6-Dichlorocamphane is converted by sodium in ether into tricyclene, m. p. 65°, and is reduced by sodium and alcohol to *i*-camphane, m. p. 150—151°, b. p. 159—160°; potassium phenoxide at 160—170° yields *p*-cymene and a chlorocamphene. Bromine reacts similarly, giving as main product 2 : 6-dibromocamphane, m. p. 169° [crystallographic data by DUFFOUR], from which are obtained tricyclene by the action of sodium, camphor by action of sodium and alcohol, *p*-cymene and a bromocamphene, b. p. 195—200°, by action of potassium phenoxide. Under similar conditions the chlorination of nopinene yields bornyl chloride and liquid products ; bromination also fails to give crystalline products except bornyl bromide. The liquids probably contain  $\omega$  : 2-dichloro- and -dibromo-camphanes, respectively. C. HOLLINS.

Derivatives of pinene. G. GALLAS and J. M. MONTAÑÉS (Anal. Fis. Quím., 1930, 28, 1163—1213).— Unsuccessful attempts have been made to convert pinene into camphene by passing the vapour over various catalysts. A considerable amount of dipentene is found in the products.

Pinene dichloride, m. p.  $170^{\circ}$ , is obtained in 18%yield by shaking an emulsion of pinene and water in a flask containing chlorine and distilling the product in steam. Addition of acid to a mixture of pinene with a solution of sodium bromide and bromate yields a mixture of two forms of pinene dibromide, m. p.  $150^{\circ}$ and  $169^{\circ}$ ; the first is converted into the second by

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heating at 120°. Attempts to isolate a di-iodide, either by direct action of iodine or from the chloride by the action of magnesium or aluminium iodides, were unsuccessful.

Unsuccessful attempts were made to oxidise bornyl iodide to an iodoso-compound by the action of hydrogen peroxide.

The oxime of pinonic acid is reduced by sodium and amyl alcohol to the corresponding *amine*, separated as the *hydrochloride*, m. p. 260° (decomp.). The *benzoyl* derivative, m. p. 210°, yields with acetic anhydride, by dehydration and ring-closure, the *acetate*, m. p. 151°, of an *amino-ketone* (hydrochloride, m. p. 78°; oxime, m. p. 120°).

A preliminary investigation of the conversion of pinene into esters of borneol indicates that the reaction with acids does not proceed in this direction in the absence of catalysts.

Oxidation of bornyl chloride with benzoyl peroxide, hydrogen peroxide, barium peroxide, or permanganate in alkaline solution gives complex mixtures. With benzoyl peroxide, camphoric and ketopinic acids are formed. R. K. CALLOW.

Dependence of optical rotatory power on chemical constitution. IX. (a) Rotatory dispersion of the stereoisomeric oxymethylenecamphors, p-phenylene- and 1:4-naphthylenebisaminomethylenecamphors. (b) Structure of oxymethylenecamphor and the kinetics of its mutarotation. B. K. SINGH and B. BHADURI (J. Indian Chem. Soc., 1930, 7, 771-791).-The rotatory powers of d- and l-oxymethylenecamphor and their condensation products with p-phenyleneand 1:4-naphthylene-diamine have been measured in various solvents for different wave-lengths at 35°. The molecular rotations of the condensation products are lower than those of the analogous compounds from camphorquinone (A., 1930, 1441); this is ascribed to the difference in conjugation. The dispersion data can be expressed by a simple equation of the Drude type. d-, m. p. 269-271°, and l-, m. p. 269-271°, -p-Phenylenebisaminomethylenecamphor (the dl-isomeride has m. p. 273-275°) do not exhibit mutarotation; d-, m. p. 203-204°, and l-, m. p. 203--1: 4-naphthylenebisaminomethylenecamphor 204°, (the dl-isomeride has m. p. 220-222°) show slight mutarotation in chloroform but not in acetone, alcohol, benzene, or pyridine.

The (unimolecular) velocity coefficient for the mutarotation of d- and l-oxymethylenecamphor in benzene at 35° is almost identical with that ded ced by the progressive determination of the amount of enol form under the same conditions, using Meyer's method (A., 1911, i, 832). The chemical change involved in the mutarotation is of the keto-enol type; the keto-form is unstable in benzene solution. Mutarotation is very rapid in benzene at 45°.

H. BURTON.

Higher terpene compounds. XLII. Dehydrogenation and isomerisation of agathicdicarboxylic acid. L. RUZICKA and J. R. HOSKING (Helv. Chim. Acta, 1930, 13, 1402—1423).—Agathicdicarboxylic acid (A., 1929, 572) is isomerised when heated with 95% formic acid at 120—130° to the tricyclic BRITISH CHEMICAL ABSTRACTS .--- A.

isoagathicdicarboxylic acid, m. p. 287-288° (decomp.),  $[\alpha]_{\rm p}$  +12.84° (all rotations are in alcohol) (dimethyl ester, m. p. 121–122°,  $[\alpha]_{\rm p}$  +6.09°, prepared either by the silver salt method or from the sodium salt and methyl sulphate; *diethyl* ester, m. p. 102–103°,  $d_4^{\text{in}}$  1.014,  $n_D^{104}$  1.483,  $[\alpha]_D$  +9.67°). This is reduced catalytically (Adams) in acetic acid or ethyl acetate at 60° to dihydroisoagathicdicarboxylic acid, m. p. 308–310° (decomp.),  $[\alpha]_{\rm D}$  +16.03° (dimethyl ester, m. p. 110–111°,  $d_4^{131}$  1.027,  $n_{\rm D}^{120}$  1.477,  $[\alpha]_{\rm D}$  +9.11°), and when heated at 290°/12 mm., eliminates carbon dioxide forming isonoragathic acid, b. p.  $181-184^{\circ}/$ 0·2 mm., m. p.  $177-178^{\circ}$ ,  $[\alpha]_{\rm b} + 2\cdot13^{\circ}$  (methyl ester, m. p. 98-99°,  $d_4^{\rm H^2}$  0·978,  $n_{\rm b}^{\rm H^2}$  1·4864,  $[\alpha]_{\rm b}$  +2·65°). Catalytic reduction (Adams) of the last-named acid gives an amorphous dihydro-acid (methyl ester, m. p.  $80-81^{\circ}, d_{4}^{111} 0.9714, n_{D}^{102} 1.4793, [\alpha]_{D} +35.34^{\circ}).$ Dehydrogenation of isoagathicdicarboxylic acid with selenium at 250-340° affords pimanthrene and a small amount of a hydrocarbon (unstable picrate, m. p. 163-164°). Agathicdicarboxylic acid is dehydrogenated by sulphur at 180-250° to pimanthrene and 1:2:5-trimethylnaphthalene [previously described (loc. cit.) as a methylethylnaphthalene]; the same products are also obtained similarly from the amorphous resin acid from Manila copal (cf. A., 1927, 60). When agathicdicarboxylic acid is dehydrogenated with selenium at 290-340°, small amounts of the hydrocarbon  $C_{17}H_{20}$  (I) (cf. loc. cit.) and an impure hydrocarbon (II) (unstable picrate, m. p. 210°) are formed in addition to pimanthrene and the trimethylnaphthalene. A mixture of the last-named substance, 1, and II is obtained by dehydrogenating tetrahydroagathicdicarboxylic acid with selenium at  $250-340^{\circ}$ ; in this case, pimanthrene is not produced.

Energetic oxidation of 1:2:5-trimethylnaphthalene, m. p.  $31-32^{\circ}$  (when regenerated from its pure pierate), with alkaline potassium ferricyanide affords some naphthalene-1:2:5-tricarboxylic acid (*methyl* ester, m. p. 90-91°) (cf. Heilbron and Wilkinson, this vol., 80).

The hydrocarbon  $C_{17}H_{20}$  (loc. cit.), m. p. 42°,  $d_1^{*0}$ 0·992,  $u_1^{*0}$  1·5847 (crystallographic data by NANNINGA), is reduced catalytically (Adams) in acetic acid (not in ethyl acetate) to a *tetrahydro*-derivative, m. p. 70— 72°, dehydrogenated by selenium to the original compound. Oxidation of the hydrocarbon (which probably contains a naphthalene ring and a third saturated ring) with alkaline potassium ferricyanide at 60°, affords a *ketodicarboxylic acid*,  $C_{16}H_{12}O_5$ , m. p. 304—305° (decomp.) (oxime, m. p. 240°) when regenerated from its dimethyl ester, m. p. 155—156°. The hydrocarbon could not be dehydrogenated further with selenium at 340°.

[With L. EHMANN, P. JENSEN, and O. T. LIEN.]  $\beta$ -o-Tolylethyl bromide reacts with ethyl sodiomethylmalonate in benzene forming ethyl  $\beta$ -o-tolylethylmethylmalonate, b. p. 192—193°/16 mm., converted by the usual procedure into  $\gamma$ -o-tolyl- $\alpha$ -methylbutyric acid, b. p. 179—180°/16 mm. The chloride, b. p. 146—147°/16 mm., of this, when treated with aluminium chloride in light petroleum, gives 5-keto-1:6dimethyl-5:6:7:8-tetrahydronaphthalene, b. p. 153—155°/16 mm., m. p. 41—42° (semicarbazone, m. p. 194—195°). This is treated with magnesium

methyl iodide, water is eliminated from the resulting carbinol by distillation, and the 1:5:6-trimethyl-7:8-dihydronaphthalene, b. p.  $130-131^{\circ}/11$  mm.,  $d_4^{20}$  0.9760,  $n_{10}^{20}$  1.5672, so obtained dehydrogenated by selenium at 280-340° to 1:2:5-trimethylnaphthalene. H. BURTON.

Furan derivatives. II. I. J. RINKES (Rec. trav. chim., 1930, 49, 1169).—'The "3-nitrofuran" obtained by Marquis (A., 1905, i, 224) is shown to be 2-nitrofuran, and the dinitrofuran obtained therefrom the 2 : 5-derivative. Direct substitution in the furan nucleus yields 2- or 5-derivatives, if these positions are vacant or filled by labile groups. Nitration of pyromucic acid yields 2-nitrofuran and 5-nitropyromucic (5-nitrofuran-2-carboxylic) acid.

J. D. A. JOHNSON.

Unsaturated compounds. XII. Action of hydroxylamine on furfurylidenehippuric acid and its esters and on furylacrylic esters. T. POSNER and I. SICHERT [nee MODROV] (Ber., 1930, 63, [B], 3078—3088).—In comparison with the phenyl residue, the furyl group enhances the dissociation of acids and very considerably increases the difficulty of addition. Towards hydroxylamine, cinnamic acid, furylacrylic acid, and furfurylidenehippuric acid are placed in order of diminishing activity. The products of the reaction are the hydroxylamino-acid,  $R\cdot CH(NH\cdot OH)\cdot CH_2\cdot CO_2H$ , which is gradually oxidised

to the oxime,  $\mathbb{R} \cdot \mathbb{C}\mathbb{M}c: \mathbb{N} \cdot \mathbb{O}H$ . The formation of *iso*oxazolone,  $\mathbb{R} \cdot \mathbb{C} \ll_{\mathbb{N}}^{\mathbb{C}H_2} \cdot \mathbb{O}O$ , and of the amino-acid,  $\mathbb{R} \cdot \mathbb{C}H(\mathbb{N}H_2) \cdot \mathbb{C}H_2 \cdot \mathbb{C}O_2H$ , is irregular. The esters add hydroxylamine more readily than the corresponding

acids, the methyl compounds being usually more reactive than the ethyl analogues. In contrast to the acids they add more than 1 mol. of hydroxylamine, this ability increasing with decreasing acidity of the parent acid. The yields of oxime and *iso*oxazolone increase with increasing dissociation constant of the parent acid, and, generally, the amino-acids are produced in greater amount with the weaker acids.

The following compounds are incidentally described : furfurylidenehippuric acid (cf. Erlenmeyer and Stadlin, A., 1905, i, 238); methyl furfurylidenehippurate, m. p. 141°; furylacrylic acid, m. p. 139—140°; benzimidodiacetic acid, NBz(CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, m. p. 68° (obtained as by-product of the preparation of hippuric acid by the successive action of ammonia and benzoyl chloride on chloroacetic acid);  $\beta$ -amino- $\beta$ -2-furylpropionic acid, m. p. 206°; 2-furyl methyl ketoxime, m. p. 102°; furylisooxazolone,  $O - N \gg C \cdot C_4 H_3 O$ , decomp. 147°;  $\beta$ -amino- $\beta$ -2-furylpropionyl chloride hydrochloride;  $\beta$ -amino- $\beta$ -2-furylpropionic acid, m. p. 173·5°; benzamido- $\beta$ -2-furylpropionic acid, m. p. 173·5°; benzamido- $\beta$ -2-furylpropionic acid, m. p. 173·5°; benzamido- $\alpha$ -benzamido- $\beta$ -2-furylpropionic acid, m. p. 203°; 2-furyl benzamidomethyl ketoxime, m. p. 157°;  $\beta$ -carbamido- $\alpha$ -benzamido- $\beta$ -2-furylpropionic acid, m. p. 196°. H. WREN.

Coumaryl-2-aldehyde [2-aldehydocoumarone] and coumarone derivatives. T. REICHSTEIN and I. REICHSTEIN (Helv. Chim. Acta, 1930, 13, 1275— 1281).—Coumarilyl chloride reacts with dry hydrogen cyanide in presence of cold ethereal pyridine forming coumarilyl cyanide, b. p. about 115°/1 mm., m. p. 100-101° (corr.), which on prolonged hydrolysis with hydrochloric acid at the ordinary temperature gives a mixture of coumarylglyoxylic acid (cf. Stoermer and Calov, A., 1900, i, 650) and its amide, m. p. 187-188° (corr.); the amide is readily hydrolysed to the acid by alkali hydroxide. When the acid is heated with aniline for a short time, 2-aldehydocoumarone, b. p. 130—131°/13 mm., m. p. 9—9.5° [semicarbazone, m. p. 245—246° (corr.; decomp.); cyanohydrin, m. p. 66.5-68°; phenylhydrazone, m. p. 136-138° (corr.)], is produced. The aldehyde is also obtained when the above cyanide is reduced with zinc dust and acetic acid and the resulting compound decomposed by potassium hydroxide. The aldehyde undergoes the Cannizzaro reaction yielding coumarylcarbinol, b. p. 105-110°/1 mm., m. p. about 26° [p-nitrobenzoate, m. p. 145-146° (corr.)]. Reduction of coumarylglyoxylic acid with hydrazine hydrate and sodium ethoxide (Wolff-Kishner method) gives coumarylacetic acid, b. p. about 145°/1 mm., m. p. 98-99° (corr.). H. BURTON.

New modes of formation of coumarone and diphenylene oxide. N. A. ORLOV and V. V. TISTSCHENKO (Ber., 1930, 63, [B], 2948-2951).-When coumarin vapour is passed through a tinned iron tube at about 860°, the gaseous product is mainly carbon monoxide with smaller amounts of hydrogen, ethylenes, and carbon dioxide. The condensate consists of coumarone with unchanged coumarin and small amounts of phenols and benzenoid hydrocarbons. A resin, closely resembling coumarone resin, is also obtained. The change occurs only under atmospheric pressure. In an autoclave at 420° or below the main products are coke and gases. Similarly, at about 880° xanthone affords diphenylene oxide and carbon monoxide mixed with a little methane and hydrogen. Dimethylpyrone affords carbon monoxide and furan derivatives apparently mixed with hydrocarbons. Under like conditions, open-chain ketones do not lose carbon monoxide smoothly. H. WREN.

Use of titanous chloride for the reduction of ethylenic linkings, flavones, and flavanones. P. KARRER, Y. YEN, and I. REICHSTEIN (Helv. Chim. Acta, 1930, 13, 1308-1319).-Unsaturated compounds are reduced by titanous chloride in aqueousalcoholic ammoniacal solution at 100° (bath) only when a carbonyl group is adjacent to the double linking. Thus, cinnamic acid, cinnamamide, and styryl methyl ketone are reduced to the corresponding saturated derivatives; cinnamylideneacetic acid affords much  $\delta$ -phenyl- $\Delta^{\beta}$ -pentenoic acid and a little  $\delta$ -phenyl- $\Delta \gamma$ -pentenoic acid. Similar reduction of flavone at 100° gives amorphous products, but at the ordinary temperature a small amount of the pinacol,  $0 < CPh=CH \\ C_6H_4 \cdot C(OH) ]_2$ , m. p. 220-220.5° (corr.), is produced. Flavanone affords a mixture of the

isomeric flavanols, m. p. 120-120.5° (corr.) (cf. Freudenberg and Orthner, A., 1922, i, 757) and 148-149° (corr.) [acetate, m. p. 97-98° (corr.)], and a small amount of the corresponding pinacol (loc. cit.). 6-Chloro- and 4'-methoxy-flavanones are reduced to 6-chloro- and 4'-methoxy-flavanols, m. p. 114-115° (corr.) and 144-145° (corr.), respectively. Treatment of 4'-methoxyflavanone with phosphorus pentachloride in benzene and decomposition of the resulting product with alcohol gives 4'-methoxyflavone, m. p. 160-161° (corr.), reduced to a small amount of the corresponding picanol (+EtOH), m. p. 147-148° (decomp.). Pentamethylcyanidin is obtained in small amount by the reduction of quercetin pentamethyl ether. H. BURTON.

Fluoran derivatives. I. Isomeric dihydroxyfluorans. M. DOMINIKIEWICZ (Rocz. Chem., 1930, 10, 667-685).-1: 8-Dihydroxyfluoran, m. p. 190°, is prepared by the fusion of phthalic anhydride with resorcinol, 1: 6-dihydroxyfluoran, m. p. 204-205°, by fusing together dihydroxybenzoylbenzoic acid and resorcinol, 2:6-dihydroxyfluoran, m. p. 179°, by substituting quinol for resorcinol in this reaction, and 4:6-dihydroxyfluoran, m. p. 180°, by using pyrocatechol in place of quinol. The following dyes, substantive for wool, are prepared: 2:7-dinitro-3: 6-dihydroxyfluoran, 3: 6-dinitro-2: 7-dihydroxyfluoran, 2: 7-dinitro-1: 6- and -1: S-dihydroxyfluoran, 3:7-dinitro-2:6- and -4:6-dihydroxyfluoran. Impure amines are obtained by the reduction of these R. TRUSZKOWSKI. dinitro-derivatives.

Thiophenols : linear dithioflavone and dithioflavanone. C. FINZI (Gazzetta, 1930, 60, 798-811; cf. A., 1926, 309, 948).-Treatment of dithioresorcinol with cinnamic or β-bromo-β-phenylpropionic acid in acetic acid solution saturated with hydrogen bromide yields  $\beta$ -thioresorcinol- $\beta$ -phenylpropionic acid, which was obtained only as a pitchy mass and gives m-phenylene-\$-disulphonyl-\$-phenylpropionic acid, C<sub>6</sub>H<sub>4</sub>(SO<sub>2</sub>·CHPh·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, m. p. 192°, on oxidation with permanganate and linear dithioflavanone (annexed formula), softening at 65-

S-CHPh CHPh-S-CH2\_CO-·CO·CH<sub>2</sub>

70°, m. p. 120-125°, when treated with phosphorus pentachloride or oxychloride in presence of alumin-

ium chloride. Ethyl phenylpropiolate and dithioresorcinol react additively, forming a mixture of ethyl esters, corresponding with : (1) m-phenylene-B-dithiolcinnamic acid, C<sub>6</sub>H<sub>4</sub>(S·CPh:CH·CO<sub>2</sub>H), m. p. 224°, which is converted into linear s-dithioflavone, (annexed

CPh-S-CH-CO-

formula), m. p. 255-256°, S-CPh when treated with phosphorus .CO.CH ' pentachloride in presence of aluminium chloride or with

concentrated sulphuric acid, and, on hydrogenation by means of sodium amalgam, gives an oily product oxidisable by permanganate to m-phenylenedisulphonyl-\$-phenylpropionic acid; (2) m-phenyl-a-dithiolcinnamic acid, C<sub>6</sub>H<sub>4</sub>[S·C(CO<sub>2</sub>H):CHPh]<sub>2</sub>, m. p. 70-73°, which loses carbon dioxide at about 190°, with formation of a pitchy compound, reducible by sodium amalgam to thioresorcinoldi-\$-phenylethyl ether,  $C_6H_4(S \cdot CH_2 \cdot CH_2Ph)_2$ ; this ether, which does not distil at 300°, even under reduced pressure, is also obtained by the interaction of thioresorcinol and β-phenylethyl chloride. T. H. POPE.

Condensation products from aryldithioglycollic acids. E. GEBAUER-FÜLNEGG and H. JARSCH (Monatsh., 1930, 56, 317-321).—Thioindigoid dyes, probably thioindigotindithioglycollic acids, are obtained when benzene-1:2-, -1:3-, -1:4-, 4-chlorobenzene-1:3-, and 2:5-dichlorobenzene-1:3-dithioglycollic acids are treated with chlorosulphonic acid at 50-60° (cf. A., 1930, 1039). These dye wool and cotton with red to violet shades; they are usually better when used in an acid bath.

H. BURTON.

Relationships between dipyrylenes and merior holo-dipyrylium salts. Action of halogens on fulvenes. F. ARNDT and L. LORENZ (Ber., 1930, 63, [B], 3121-3132).-In reply to Bergmann and von Christiani (A., 1930, 1569) evidence is adduced in favour of the view that the behaviour of xanthens and dipyrylenes towards halogen is not comparable with that of the open and carbocyclic fulvenes. The hexabromide of dixanthylene contains the total bromine as two anions BrBr<sub>2</sub>. The mode and readiness of the addition of bromine are possibly greatly influenced by the possibility of the transition of the quinonoid pyrone form into the benzenoid pyrylium form. The relationships between dipyrylenes and meri- and holo-dipyrylium salts are discussed in detail. The following observations appear new. Dithioxanthylene, m. p. 365°, is prepared by heating thioxanthione with copper powder in a current of carbon dioxide at 200°. Dithioxanthylenedisulphone, gradual decomp. 380-500°, which is prepared from dithioxanthylene and hydrogen peroxide in boiling glacial acetic acid, is unaffected by bromine. Dixanthionium perbromide, C26H16S2Br6, decomposes at 245° after darkening and softening at 220°. Tetraphenyldipyrylene is converted by perchloric acid in acetic acid into the meri-perchlorate, decomp. 287-288°, whereas with 70% perchloric acid at about 200° it yields the The meri-perchlorate of ethyl holo-perchlorate. dipyrylenetetracarboxylate, C22H24O10,HClO4, is described. Tetraphenyldithiopyrylene is transformed by chlorine in chloroform and carbon tetrachloride into black and red substances, C34H24Cl2S2, m. p. 300-310° after softening at 100°. Under similar conditions tetraphenyldipyrylene gives a black compound,  $C_{34}H_{24}O_2Cl_2$ , m. p. 305° after softening at 100°; the red compound appears to be formed transitorily. Tetraphenyldithiopyrylene and bromine yield the H. WREN. substance C34H24S,Br6.

Residual affinity and co-ordination. XXXII. Complex salts of bivalent silver. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1930, 2594—2598).— Stable compounds of bivalent silver are prepared in the following manner. When hot aqueous-alcoholic solutions of silver nitrate and of  $\alpha \alpha'$ -dipyridyl (prepared by Hein and Retter's method; A., 1928, 1262) (mercuri-iodide, sufficiently insoluble for use in the gravimetric determination of the base) are mixed,  $bis \cdot \alpha \alpha'$ -dipyridylargentous nitrate [Ag2dipy]'NO<sub>3</sub>, decomp. 155°, is obtained. This is converted by a cold, saturated solution of potassium persulphate into  $bis \cdot \alpha \alpha'$ -dipyridylargentic persulphate, [Ag2dipy]''S<sub>2</sub>O<sub>8</sub>, decomp. 137°. Trituration of this with 60% nitric acid affords a filtrate from which is obtained pentakis-

 $\alpha \alpha'$ -dipyridyldiargentic persulphate,  $[Ag_25dipy](S_2O_8)_2$ , decomp. 159°, and a residue of tris- $\alpha \alpha'$ -dipyridylargentic nitrate,  $[Ag_3dipy]''(NO_3)_2$ , decomp. 171°, and perchlorate, detonates when heated, are obtained by double decomposition. The nitrate is converted by further action of nitric acid into the complex argentoargentic nitrate,  $[Ag_22dipy](NO_3),AgNO_3,HNO_3$ , decomp. 161°, some of the univalent silver of which is removed by repeated extraction with cold alcohol. Cold 40% sulphuric acid converts bis- $\alpha \alpha'$ -dipyridylargentic persulphate into the corresponding hydrogen sulphate, decomp. 157°. All these complex salts are crystalline and highly coloured and their solutions are strong oxidising agents. Their composition indicates that bivalent silver has co-ordination numbers of 4 and 6. J. W. BAKER.

Equilibrium and "intermediate stage." F. ARNDT (Ber., 1930, 63, [B], 2963—2966).—In connexion with his views on the constitution of 1-alkyl-4pyridones and similar compounds the author defines a tautomeric equilibrium as characterised by the difference of the point of union of a hydrogen nucleus in the two formulæ. An "intermediate stage" is assumed when the two formulæ show the same relative position of all atomic nuclei and differ only by "linkings" or "charges." H. WREN.

Pyridine derivatives. VIII. Isomerism of derivatives of 2-hydroxypyridine. C. RATH (Annalen, 1930, 484, 52-64).- A study of the influence of electronegative substituents on the alkylation of 2-hydroxypyridines. 5-Nitro-2-hydroxypyridine is converted by methyl sulphate and alkali mainly into 5-nitro-1-methyl-2-pyridone, m. p. 175°, accompanied by a little 5-nitro-2-methoxypyridine, m. p. 108-109°; these are separated by distillation in steam, in which the O-ethers alone are volatile. The potassium salt of the nitrohydroxypyridine with methyl iodide gives similar results, but the silver salt gives considerably more (16%) of the O-ether, the constitution of which is proved by synthesis from 2-iodo-5-nitropyridine and sodium methoxide, and by its inertness towards phosphorus pentachloride. The N-methyl compound is converted by phosphorus pentachloride into 2-chloro-5-nitropyridine (cf. O. Fischer, A., 1898, i, 382), and by cyanogen bromide into 3-bromo-5-nitro-1-methyl-2-pyridone, m. p. 124-125°. Attempts at interconversion of the isomerides by the method of Haitinger and Lieben (A., 1885, 965) failed. 5-Amino-1-methyl-2-pyridone, m. p. 125-126° (decomp.) (dihydrochloride) and 5-amino-2-methoxypyridine, m. p. 135-136° (dihydrochloride), are obtained by reduction.

The behaviour of 5-iodo-2-hydroxypyridine (silver salt) on methylation is similar to that of the 5-nitrocompound. The following are described : 5-nitro-2ethoxy-, m. p. 91—92°; 5-nitro-2-benzyloxy-, m. p. 107—108°, and 5-iodo-2-methoxy-pyridine, b. p. 109— 110°/15 mm. [hydrochloride, m. p. 145—150° (decomp.)]; 5-nitro-1-ethyl-, m. p. 142—143°; 5-nitro-1benzyl-, m. p. 105—106°; 5-nitro-1-n-propyl-, m. p. 76—77°; 5-nitro-1-isopropyl-, m. p. 86—90°; 5-nitro-1-n-butyl-, m. p. 46—47°; 5-iodo-1-methyl-, m. p. 73—74°, b. p. 185°/12 mm.; 5-iodo-1-ethyl-, m. p. 75—76°, b. p. 180—185°/22 nm.; 5-iodo-1-n-propyl., b. p. 185—188°/15 mm. [hydrochloride, m. p. 112° (decomp.)]; 5-iodo-1-isopropyl., m. p. 110—111°; 5-iodo-1-n-butyl., b. p. about 185°/12 mm. [hydrochloride, m. p. 125° (decomp.)]; 5-iodo-1-octyl., b. p. 221—222°/12 mm. [hydrochloride, m. p. 85° (decomp.)], and 5-iodo-1-benzyl-2-pyridone, m. p. 100—101°.

H. A. PIGGOTT. B-Diketones in ring formation. II. U. BASU (J. Indian Chem. Soc., 1930, 7, 815-824; cf. A., 1930, 1443).—Alcoholic sodium ethoxide condensation of cyanoacetamide and dibenzovlmethane affords 5-20% of 3-cyano-4: 6-diphenyl-2-pyridone; prolonged interaction in presence of alcoholic diethylamine results in a much improved yield. The difference in these results may be due to the greater reversibility of the Michael reaction with sodium ethoxide (cf. Ingold and others, J.C.S., 1922, 121, 1416, 1770). The pyridone is also obtained in 75% yield from phenyl β-ethoxystyryl ketone and sodiocyanoacetamide. The inhibiting effect of aryl groups on the condensation is established by the isolation of 3-cyano-4-phenyl-6-ptolyl-2-pyridone as the main product of the reaction between benzoyl-p-toluoylmethane and cyanoacetamide; the p-tolyl group has a greater retarding action than the phenyl group. 3-Cyano-6-phenyl-4-p-tolyl-2-pyridone, m. p. 311-312°, formed also in the above condensation, is hydrolysed by 80% sulphuric acid to 6-phenyl-4-p-tolyl-2-pyridone, m. p. 237-239°. Since the former of the cyano-p-tolylpyridones is also obtained from p-tolyl β-methoxystyryl ketone, condensation must occur through the enolic form of the diketone. Dipropionylmethane and cyanoacetamide in presence of aqueous-alcoholic diethylamine give a 90% yield of 3-cyano-4 : 6-diethyl-2-pyridone, m. p. 186°, hydrolysed by hydrochloric acid at 150° to 4 : 6-diethyl-2-pyridone, m. p. 61-62°. Reaction (condensation) does not proceed so readily as with diacetylmethane; this is ascribed to the bulkier ethyl group. The isolation of only one condensation product from benzoylacetone and cyanoacetamide (loc. cit.) is in agreement with the theory that the phenyl group inhibits the reaction between the amide and the form OH CPh:CHAc. The results described are in harmony with Ingold, Perren, and Thorpe's views (J.C.S., 1922, 121, 1770) regarding the Michael reaction.

Acetylacetone and malonamide afford 60% of the theoretical amount of 4:6-dimethyl-2-pyridone-3carboxylamide after 3—4 days; with malononitrile reaction occurs more readily and 3-cyano-4:6-dimethyl-2-pyridone is produced in 77% yield. Benzoylacetone and ethyl cyanoacetate give ethyl 6-phenyl-4-methyl-2-pyridone-3-carboxylate, m. p. 216—217° (decomp.); with malononitrile, reaction is again more rapid and 3-cyano-6-phenyl-4-methyl-2-pyridone is obtained as the main product. The influence of the groups present in the addendum is further illustrated by the observation that chloroacetamide, phenylacetamide, and phenylacetonitrile do not react with acetylacetone under the usual conditions.

H. BURTON. Reactivity of conjugated systems. II. Condensation of acetylenic ketones with cyanoacetamide. C. BARAT (J. Indian Chem. Soc.,

1930, 7, 851-862) .- The Michael or Knoevenagel condensation of benzoylphenylacetylene and cyanoacetamide gives 3-cyano-4: 6-diphenyl-2-pyridone, m. p. 320° (1-methyl derivative, m. p. 175°, prepared either by methylation or condensation of the ketone with cyanoacetmethylamide), hydrolysed by 75-80% sulphuric acid to 2-hydroxy-4: 6-diphenylpyridine, m. p. 208°. This pyridine is identical with the product obtained by dehydrogenation of the tetrahydropyridine derivative prepared from phenyl styryl ketone and cyanoacetamide (A., 1930, 925). Reaction probably occurs by addition to the triple linking with subsequent cyclisation and rearrangement. p-Toluoylphenylacetylene, m. p. 72° (from p-toluoyl chloride and sodiophenylacetylene), and cyanoacetamide give 3. cyano-4-phenyl-6-p-tolyl-2-pyridone, m. p. 268° (1methyl derivative, m. p. 136-138°), hydrolysed to 2-hydroxy-4-phenyl-6-p-tolylpyridine. p-Toluoylphenylacetylene and ethyl malonate condense in presence of a trace of sodium ethoxide yielding ethyl 4-phenyl-6-p-tolyl-2-pyrone-3-carboxylate, m. p. 85° hydrolysed to 4-phenyl-6-p-tolyl-2-pyrone, m. p. 133° (decomp.). The following compounds are prepared similarly to the above: p-nitrobenzoylphenylacetyl-ene, m. p. 161-162°; 3-cyano-4-phenyl-6-p-nitroene, m. p. 161—162°; 3-cyano-4-phenyl-6-p-nitro-phenyl-2-pyridone, m. p. 332—333° (1-methyl deriv-ative, m. p. 322—324°); 2-hydroxy-4-phenyl-6-p-nitrophenylpyridine, m. p. 275—276°; ethyl 4-phenyl-6-p-nitrophenyl-2-pyrone-3-carboxylate, m. p. 148°; 4-phenyl-6-p-nitrophenyl-2-pyrone, m. p. 235°; 3-cyano-4-phenyl-6-methyl-2-pyridone, m. p. 275—276° [1-methyl derivative, m. p. 146°; the substance described by Sen (J.C.S., 1915, **107**, 1347) is probably identical with thisl: ethyl 4-menu-6-methyl 2-merone identical with this]; ethyl 4-phenyl-6-methyl-2-pyrone-3-carboxylate, m. p. 92°; 4-phenyl-6-methyl-2-pyrone, m. p. 185—186°; 3-cyano-4-phenyl-6-ethyl-2-pyridone, m. p. 267-268° (lit. 260°) (1-methyl derivative, H. BURTON. m. p. 158°).

Synthesis of contrast media for pyelography. I. Y. SUGH, I. SHIMOYA, and H. SHINDO (J. Pharm. Soc. Japan, 1930, 50, 727-733).-2-Aminopyridine when treated with potassium iodide solution gave 5-iodo-2-aminopyridine, m. p. 129°, diazotised to 5-iodopyridone, m. p. 192°; this when treated with chloroacetic acid forms 5-iodopyrid-2-one-1-acetic acid, decomp. 240° (ethyl ester, m. p. 113-114°), the sodium salt of which is employed in X-ray photography of organs. CHEMICAL ABSTRACTS.

Py-Alkylquinolines. Generalisation of the Skraup reaction to  $\alpha$ -alkylglycerols. R. DELABY and J. HIRON (Bull. Soc. chim., 1930, [iv], 1395–1400).—See this vol., 98. 2-Ethylquinoline iodoantimonate, m. p. about 180°, is described, and a modified method of preparing alizarin-blue from 3-aminoalizarin and nitrobenzene in presence of vanadic acid is given.

Quinoline compounds. II. Derivatives of 4-phenyl-2-methylquinoline. U. N. BRAHMA-CHARI and T. BHATTACHARYYA (J. Indian Chem. Soc., 1930, 7, 831—834).—Acetophenone and paraldehyde condense with *p*-nitroaniline under the conditions of the Beyer reaction to give 6-nitro-4-phenyl-2methylquinoline, m. p. 141°. This with *p*-dimethylaminobenzaldehyde forms 6-nitro-4-phenyl-2-p-dimethylaminostyrylquinoline, m. p. 64°, and is reduced by stannous chloride and hydrochloric acid to 6-amino-4-phenyl-2-methylquinoline, m. p. 188°. 8-Nitro-4phenyl-2-methylquinoline, m. p. 94°, is prepared similarly from o-nitroaniline. 8-Nitro-4-phenyl-2-p-dimethylaminostyrylquinoline and 8-amino-4-phenyl-2methylquinoline hydrochloride have m. p. 129° and decomp. above 210°, respectively. H. BURTON.

Imide and amide chlorides of non-aromatic acids. VI. New method in the quinoline series. J. VON BRAUN and A. HEYMONS [with L. SCHNITZ-SPAHN] (Ber., 1930, 63, [B], 3191-3203; cf. A., 1930, 613).—The conversion of the imide chlorides of acetarylides into amidines by loss of 1 mol. of hydrogen chloride (*loc. cit.*) is not exhibited by those derived from chloroacetarylides which, under similar conditions, smoothly lose 2 mols. of hydrogen chloride and pass into quinolines. The compounds of propionic and phenylacetic acid resemble those from chloroacetic acid, so that the process appears general for arylamides of all non-aromatic acids with the exception of acetic acid.

The action of phosphorus pentachloride (1 mol.) on chloroacetanilide (1 mol.) at the ordinary temperature gives 3-chloro-4-anilino-2-chloromethylquinoline hydrochloride, decomp. 222°, in 90-95% yield. The free base is most readily prepared by the addition of ammonia or sodium carbonate to the solution of the salt in cold pyridine; the corresponding *picrate*, m. p. 193°, is described. The base is converted by four times its weight of concentrated hydrochloric acid at 160-165° and subsequently at 175-180° mainly into 3-chloro-4-hydroxy-2-chloromethylquinoline, m. p. 303° (yield 80%), accompanied by 3:4-dichloro-2-chloromethylquinoline, m. p. 119-120° (also prepared from 3-chloro-4-hydroxy-2-chloromethylquinoline and phosphorus pentachloride in presence of phosphoryl chloride at 130-140°). With a smaller proportion of hydrochloric acid at 165°, the base is transformed into 3-chloro-4-hydroxy-2-hydroxymethylquinoline, m. p. 283°. Moderated hydrolysis of the trichloro-base by aqueous-alcoholic alkali hydroxide affords 3:4-dichloro-2-hydroxymethylquinoline, b. p. 150-154°/0.2 mm., m. p. 44°. Reduction of 3-chloro-4-anilino-2chloromethylquinoline with tin and hydrochloric acid yields 3-chloro-4-anilino-2-methylquinoline, m. p. 172° (picrate, m. p. 229°). 3-Chloro-4-hydroxy-2-chloromethylquinoline is reduced by zinc dust in boiling glacial acetic acid to 3-chloro-4-hydroxy-2-methyl-quinoline, m. p. 340°, transformed by phosphorus pentachloride into 3:4-dichloro-2-methylquinoline, m. p. 322°. Transformation of 3:4-dichloro-2chloromethylquinoline into 2-methylquinoline is effected by treatment with hydrogen iodide in glacial acetic acid at 220-240°; reduction with sodium and alcohol affords 2-methyl-1:2:3:4-tetrahydroquinoline. 3-Chloro-4-anilino-2-chloromethylquinoline is converted by cautious treatment with aqueousalcoholic potassium hydroxide into 3-chloro-4-anilino-2-hydroxymethylquinoline, m. p. 93-94°, and by aqueous-alcoholic potassium cyanide into 3-chloro-4anilino-2-cyanomethylquinoline, m. p. 156° (benzylidene derivative, m. p. 192°). With aniline 3-chloro-4anilino-2-chloromethylquinoline gives 3-chloro-4anilino-2-anilinomethylquinoline, m. p. 192° (hydrochloride; acetyl derivative, m. p. 209°). 3-Chloro-4anilino-2-dimethylaminomethylquinoline, m. p. 93° (picrate, m. p. 190—193°), is reduced by sodium and alcohol to aniline and 2-dimethylaminomethyl-1:2:3:4tetrahydroquinoline, m. p. 148—152°/15 mm. 3:4-Dichloro-2-dimethylaminomethylquinoline, m. p. 62°, and its picrate, m. p. 177°, are described. 3-Chloro-4-hydroxy-2-piperidinomethylquinoline has m. p. 233— 235°. With pyridine and isoquinoline, respectively, 3-chloro-4-anilino-2-chloromethylquinoline yields the additive products,  $C_{21}H_{17}N_3Cl_2$  and  $C_{25}H_{19}N_3Cl_2$ , m. p. 245° and 258°.

Chloroacet-p-iodoanilide, m. p. 193°, is converted by phosphorus pentachloride into 3-chloro-6-iodo-4-piodoanilino-2-chloromethylquinoline, m. p. 184° (hydrochloride, m. p. 232°; picrate, m. p. 202°), converted by diethylamine into 3-chloro-6-iodo-4-p-iodoanilino-2diethylaminomethylquinoline, m. p. 152° (picrate, m. p. 178°).

Chloroacet-*m*-chloroanilide affords 3:7-dichloro-4-m-chloroanilino-2-chloromethylquinoline, m. p. 179°, transformed by *p*-phenetidine into 3:7-dichloro-4 - m - chloroanilino-2 - p - ethoxyanilinomethylquinoline, m. p. 131°. Chloroacet-3-chloro-4-methylanilide, m. p. 102°, yields a homogeneous quinoline base,  $C_{18}H_{14}N_2Cl_4$ , m. p. 174°. The following compounds isolated previously as by-products (loc. cit.) are recognised as quinoline derivatives :  $C_{18}H_{16}N_2Cl_2$ , m. p. 160°, from o-toluidine;  $C_{18}H_{16}O_2N_2Cl_2$ , m. p. 196°, from o-anisidine;  $C_{16}H_{10}N_2Cl_4$ , m. p. 116°, from o-chloroaniline;  $C_{16}H_{10}N_2Cl_4Br_2$  (hydrochloride, m. p. 135°) from o-bromoaniline.

Propionanilide and phosphorus pentachloride afford 4-anilino-3-methyl-2-ethylquinoline, m. p. 178° (hydrochloride, m. p. 219—220°; picrate, m. p. 220—221°), converted by hydrochloric acid under different conditions into 4-chloro-3-methyl-2-ethylquinoline, m. p. 40—43°, and 4-hydroxy-3-methyl-2-ethylquinoline, m. p. 284°, transformed by phosphorus pentachloride and phosphoryl chloride into the 4-chloro-compound. Reduction of 4-anilino-3-methyl-2-ethylquinoline by sodium and alcohol gives aniline and 3-methyl-2ethyl-1:2:3:4-tetrahydroquinoline, b. p. 136—140°/ 12 mm. (hydrochloride, m. p. 193°).

Phenylacetanilide is more slowly transformed by phosphorus pentachloride into 4-anilino-3-phenyl-2benzylquinoline, m. p. 172° (picrate, m. p. 188°; hydrochloride, m. p. 209°), converted into 4-hydroxy-3phenyl-2-benzylquinoline, m. p. 308°, and reduced to aniline and 3-phenyl-2-benzyl-1:2:3:4-tetrahydroquinoline, b. p. 190-192°/0·3 mm. H. WREN.

ω-Cyano-ω-arylideneacetanilides and the conversion of their o-nitro-derivatives into quinoline derivatives. M. ISHAQ and J. N. RAY (J.C.S., 1930, 2739—2741).—Cyanoacetanilide condenses with onitrobenzaldehyde in presence of pyridine and a small amount of piperidine at 60—70° forming ω-cyano-ω-onitrobenzylideneacetanilide [o-nitro- $\alpha$ -cyanocinnamanilide], m. p. 206°, reduced by zinc dust and acetic acid to 2-anilino-3-cyanoquinoline, m. p. 208°. The nitrocompound could not be converted into a naphthinoline derivative under any of the conditions tried. The following ω-cyano-ω-arylideneacetanilides are also described : piperonylidene, m. p. 182°; m-methoxybenzylidene, m. p. 141°; 3:4-dimethoxybenzylidene, m. p. 168°; 6-nitro-3:4-methylenedioxybenzylidene, m. p. 227°, and 6-nitro-3:4-dimethoxybenzylidene, m. p. 169°. Reduction of the last two nitro-derivatives gives 2-anilino-3-cyano-6:7-methylenedioxy-, m. p. 287°, and 2-anilino-3-cyano-6:7-dimethoxy-quinolines, m. p. 237°, respectively. The following ω-cyano-ωarylideneaceto-p-toluidides are obtained similarly from cyanoaceto-p-toluidide and the appropriate aldehyde : 3:4-dimethoxybenzylidene, m. p. 198°; piperonylidene, m. p. 183°; m-methoxybenzylidene, m. p. 144°; o-nitrobenzylidene, m. p. 182°: 6-nitro-3:4-methylenedioxybenzylidene, m. p. 216°, and 6-nitro-3:4-dimethoxybenzylidene, m. p. 174°. 2-p-Toluidino-3-cyano-, m. p. 221-222°, and 2-p-toluidino-3-cyano-6:7-dimethoxyquinoline, m. p. 253°, are also prepared.

## H. BURTON.

Quinoline derivatives. XIII. Degradation of 6-methoxyquinoline-4-carboxylic acid. XIV. Derivatives of quinic and xanthoquinic acids. XV. 6-Hydroxy-4-aminoquinoline. XVI. 6substituted 4-halogenoquinolines. XVII. 6-Methoxy-4-quinolylhydrazine, 6-methoxy-4thiolquinoline, and 6-methoxyquinoline-4-sul-phonic acid. H. JOHN [with E. ANDRASOHKO] (J. pr. Chem., 1930, [ii], 128, 180-189, 190-200, 201-210, 211-217, 218-222).-XIII. Degradation of 6-methoxyquinoline-4-carboxylic acid by the Curtius method is studied (Hofmann degradation; cf. Hirsch, A., 1896, i, 626). Methyl 6-methoxyquinoline-4-carboxylate has m. p. 84°. The ethyl ester (loc. cit.) is converted by the usual methods through the hydrazide, m. p. 151° (picrate, m. p. 205°; isopropyl-idene, m. p. 135°; methylbenzylidene, m. p. 201°, and p-dimethylaminobenzylidene, m. p. 132°, derivatives), into the azide, decomp. 106°. The latter is converted by boiling alcohol into 6-methoxyquinolyl-4-urethane, m. p. 170°, and by controlled thermal decomposition into 6-methoxyquinolyl-4-carbimide, m. p. 171°, which is not attacked by boiling alcoholic potassium hydr-Boiling water converts the azide into NN'oxide. bis-(6-methoxy-4-quinolyl)carbamide, m. p. 205°, and acid hydrolysis yields 4-amino-6-methoxyquinoline, m. p. 120° (cf. loc. cit.) (sulphate; nitrate; picrate, m. p. 192°). The diacetyl derivative of the latter has m. p. 242° (picrate).

XIV.  $\beta$ -*Chloroethyl* 6-methoxyquinoline-4-carboxylate [from quinoyl ehloride hydrochloride (Karrer, A., 1918, i, 40) and  $\beta$ -chloroethyl alcohol] has m. p. 71°; from the foregoing acid chloride and the corresponding amine are obtained  $\beta$ -(6-methoxyquinoline-4-carboxylamido)ethanol, m. p. 143°, and  $\alpha\beta$ -bis-(6-methoxyquinoline-4-carboxylamido)ethane, m. p. 269° (hydrochloride; sulphate; picrate).

An improved method is described for the preparation of 6-hydroxyquinoline 4-carboxylic acid by the action of hydriodic acid (d 2.0) on the methoxycompound and numerous salts are described but not characterised [chloride (from the acid and thionyl chloride), m. p. 158° (decomp.); amide, m. p. 264°; diethylamide, m. p. 119°;  $\beta$ -chloroethyl ester, m. p. 150°].

6-Ethoxyquinoline-4-carboxylic acid (from the hydroxy-acid and ethyl iodide) has m. p. 278° (cf. the acid obtained by Karrer, *loc. cit.*, from ethyl dihydrocupreine) (*methyl* ester, m. p. 58°). Numerous salts of this acid are also described.

XV. The Curtius degradation of 6-hydroxyquinoline-4-carboxylic acid follows the same lines as that of the methoxy-acid (cf. XIII).

The methyl, n-propyl, and isopropyl esters of 6hydroxyquinoline-4-carboxylic acid have m. p. 212°, 130°, and 157°, respectively. The ethyl ester, m. p. 185·5°, is converted in the usual way through the hydrazide, m. p. 244° (hydrochloride; sulphate; nitrate; isopropylidene, m. p. above 300°, and methylbenzylidene, m. p. 276°, derivatives), into the azide, decomp. 115°. The following compounds are prepared from the azide by the usual methods : 6-hydroxyquinolyl-4-urethane, m. p. 236° (decomp.), 6-hydroxyquinolylcarbimide, m. p. 178° (hydrolysed by alcoholic potassium hydroxide to the amine described below), and NN'-bis-(6-hydroxy-4-quinolyl)carbamide, m. p. 253°. Acid hydrolysis of the urethane affords 4-amino-6-hydroxyquinoline, m. p. 264° (hydrochloride; sulphate).

XVI. 4-Amino-6-methoxyquinoline and 4-amino-6-hydroxyquinoline are converted by the usual diazoreactions into 4-halogeno-compounds (cf. Hirsch, A., 1896, i, 626), of which the following are described : 4-bromo-6-methoxyquinoline, m. p. 106° (picrate, m. p. 180°), 4-iodo-6-methoxyquinoline, m. p. 85° (picrate, m. p. 254-255°), 4-chloro-, m. p. 210°, 4-bromo-, m. p. 253°, and 4-iodo-6-hydroxyquinoline, m. p. 283°. Many salts of all these bases are described without characterisation.

XVII. 4-Chloro-6-methoxyquinoline is converted into the following derivatives: 6-methoxy-4-quinolylhydrazine, m. p. 154° (methyl-p-tolylidene derivative, m. p. 105°) (interaction of hydrazine hydrate with 4-bromo-6-methoxyquinoline gives a less satisfactory yield); 6-methoxy-4-thiolquinoline, m. p. 139° (by the method of O. Fischer; A., 1899, i, 635); and 6-methoxyquinoline-4-sulphonic acid, m. p. 292° (by the hydrogen sulphite method of Besthorn and Geisselbrecht; A., 1920, i, 562) (salts described).

R. CHILD.

Doebner's reaction. X. L. MUSAJO (Gazzetta, 1930, 60, 673—677; cf. A., 1930, 222).—The reaction between furfuraldehyde,  $\beta$ -naphthylamine, and pyruvic acid has been studied and the following secondary products have been isolated : 3-(2'-furyl)-1:2:3:4 - tetrahydro -  $\beta$  - naphthoquinoline - 1 carboxylic acid, m.p. 200°, and  $\beta$ -naphthyl-2-furfurylamine, C<sub>10</sub>H<sub>7</sub>·NH·CH<sub>2</sub>·C<sub>4</sub>H<sub>3</sub>O, b. p. 225—230°/17 mm. The nitroso-derivative, m. p. 98°, of the latter compound has been prepared. O. J. WALKER.

Formation of aromatic thiosulphonic acids from disulphides. E. W. McCLELLAND and L. A. WARREN (J.C.S., 1930, 2690-2693).-2:2'-00'-Dithiodiphenyl-4:5-dihydroglyoxaline gives with sulphur dioxide in boiling alcoholic solution 2-phenyl-4:5-dihydroglyoxaline-o-thiosulphonic acid,

 $SR \cdot C_6H_4 \cdot C < NH \cdot CH_2 (1)$  (R=SO<sub>3</sub>H), m. p. 228° (decomp.), the constitution of which follows from its conversion by potassium cyanide into 2-*phenyl*-4:5-*di*-hydroglyoxaline o-thiocyanate, m. p. 180° (I, R=CN).

The thiosulphonic acid is similarly obtained from the thiol (I, R=H), and also from the hydrobromide and perbromide of the tricyclic compound (cf. A., 1930, 95). The thiol is regarded as the intermediate in all these cases, and, in consequence of the non-occurrence of the reaction with a representative series of aryl disulphides, the reaction is ascribed to the betaine structure of the former. 2-Phenyl-4:5-dihydroglyoxal-ine-m-thiosulphonic acid, m. p. 246° (decomp.), -p-thiosulphonic acid, m. p. 248° (decomp.), and p-thiocyanate, m. p. above 265°, are prepared from the corresponding dithiodiphenyldihydroglyoxalines.

H. A. PIGGOTT. Synthesis of 1-2-thiolhistidine. J. N. ASHLEY and C. R. HARINGTON (J.C.S., 1930, 2586-2590) .--*l*-Histidine methyl ester dihydrochloride in aqueous solution is converted by benzoyl chloride and powdered sodium carbonate at 0° into methyl ayd-tribenzamido- $\Delta y$ -pentenoate, hydrolysed by boiling 10% methylalcoholic hydrogen chloride to methyl a8-dibenzamidoy-ketovalerate (cf. Windaus, Dorries, and Jensen, A., 1922, i, 60). This is converted by further hydrolysis with 20% hydrochloric acid into the dihydrochloride of  $\alpha\delta$ -diamino- $\gamma$ -ketovaleric acid, a concentrated aqueous solution of which with 1 mol. of sodium thiocyanate at 100° and subsequent treatment of the reaction mixture with sodium acetate, affords 1-2-thiolhistidine, darkens about 290°, not melting at 310°,  $[\alpha]_{5461}$  -9.5° in N-hydrochloric acid [dihydrochloride, m. p. 197—199° (decomp.); monopicrate, m. p. 156° (not analytically pure)]. The constitution and optical purity of the amino-acid were proved by its oxidation with ferric sulphato to *l*-histidine,  $[\alpha]_{5461} - 41.4^{\circ}$ , identical with a genuine specimen and giving identical derivatives.

J. W. BAKER. Dioximes. LXXII. E. DURIO and M. BISSI (Gazzetta, 1930, 60, 899-903) .- Conditions are specified for obtaining an improved yield of dioxytetraphenylpyrazine, O:N CPh:CPh N:0,2AcOH, m. p. 322° (acetic acid free) (decomp.), which Auwers and Meyer (A., 1889, 403, 713) obtained in small amount, together with diphenylglyoxime peroxide, by oxidising a-benzildioxime (diphenylglyoxime) with potassium ferricyanide in basic solution. Two distinct reactions here occur: (1) a simple dehydrogenation, giving the peroxide, and (2) elimination, as nitrous acid, of two hydrogen atoms and two oximino-groups from two molecules of a-benzildioxime, the residues of which then unite to form dioxytetraphenylpyrazine. The latter, which is not formed by oxidation of  $\beta$ - or  $\gamma$ -benzildioxime under similar conditions, is deoxygenated, with formation of tetraphenylpyrazine, when treated with either nascent hydrogen or phosphorus pentachloride. Neither p-tolyldioxime nor anisyldioxime, although similar in many properties to a-benzildioxime, yields any trace of dioxypyrazine when oxidised by potassium ferricyanide. T. H. POPE.

Conjugated double linkings. XV. Constitution of indolenine-yellow. R. KUHN, A. WINTER-STEIN, and G. BALSER (Ber., 1930, 63, [B], 3176-3184).—The constitution assigned hitherto to indolenine-yellow is not in harmony with the known effect of replacing the •CH:CH• group by •CH:N•. The mode of formulation is based on the analogy of O:N·OH to O:CH·OH, but the comparison is not valid in this case, since the condensation of 1:3:3-trimethyl-2-methyleneindoline salts with nitrous acid in presence of acetic anhydride differs from that with formic esters in that 1 mol. of hydrogen cyanide is lost in addition to 1 mol. of water. To indolenine-yellow the constitution  $C_6H_4 < \frac{CMe_2}{NMe} > C \cdot CH:C < \frac{CMe_2}{NMe} > C_6H_4$  is

therefore ascribed; it thus becomes a lower vinylene homologue of indolenine-red,

$$C_6H_4 < CMc_2 > C \cdot CH:CH \cdot CH:C < CMc_2 > C_6H_4.$$

Attempts to prepare indolenine-yellow by the condensation of 1:2:3:3-tetramethylindoleninium salts with 1:3:3-trimethylindolinone do not give the desired product. When, however, 1:3:3-trimethyl-2-methyleneindoline in glacial acetic acid is treated with sodium nitrite and then with perchloric acid 2 - formoximino - 1 : 3 : 3 - trimethylindoleninium perchlorate, C<sub>6</sub>H<sub>4</sub> CMe<sub>2</sub> C·CH:N·OH, m. p. 215° (decomp.), is almost quantitatively precipitated; it decomposes when heated in acetic anhydride into hydrocyanic acid and 1:3:3-trimethylindolinone. When warmed with 1:3:3-trimethyl-2-methyleneindoline in acctic anhydride at 80-90° it gives indolenine - yellow. 2 - Formoximino-1:3:3:5:7pentamethylindoleninium perchlorate, m. p. 210° (decomp.), and 1:3:3-trimethyl-2-methyleneindoline give 5:7-dimethylindolenine-yellow, isolated as the perchlorate, m. p.  $250\cdot5^{\circ}$  (decomp.). This salt is also obtained from 2-formoximino-1:3:3-trimethylindoleninium perchlorate and 1:3:3:5:7-penta-methyl-2-methyleneindoline. The identity of the salts is explained on the basis of König's hypothesis that the anion in a dye of this type cannot be assigned to one or other nitrogen atom, but is attached to both, thus giving a system of "flowing heteropolar linkings." H. WREN.

Oxidation. IV. Action of ferric chloride and hydrogen peroxide on S-alkylthiosemicarbazones. Formation of triazoles. S. C. DE and T. K. CHAKRAVORTY (J. Indian Chem. Soc., 1930, 7, 875-878).-Oxidation of an aqueous-alcoholic solution of benzaldehyde-S-methyl- and -ethyl-thiosemicarbazone with hydrogen peroxide affords 3-methylthiol-, m. p. 164°, and 3-ethylthiol-5-phenyl-1:2:4-triazoles, m. p. 166°, respectively. 4-Phenylthiosemicarbazide and methyl iodide are allowed to react in boiling alcohol, the mixture is treated with benzaldehyde, whereby the hydriodide, m. p. 153°, of benzaldehyde-4-phenyl-S-methylthiosemicarbazone, m. p. 66-67° (hydrochloride), separates. The semicarbazone is oxidised as above to 3-methylthiol-4: 5-diphenyl-1:2:4-triazole, m. p. 165-166°. Similarly, benzaldehyde-4-phenyl-S-ethylthiosemicarbazone, m. p. 78° [hydriodide, m. p. 118°; hydrochloride, m. p. 178° (de-comp.)], gives 3-ethylthiol-4:5-diphenyl-1:2:4-triazole, m. p. 148°; benzaldehyde-4-o-tolyl-S-methylthiosemicarbazone, m. p. 62° [hydriodide, m. p. 189° (decomp.); hydrochloride, m. p. 194° (decomp.)], yields 3-methylthiol-5-phenyl-4-0-tolyl-1:2:4-triazole, m. p. 130°; benzaldehyde-4-o-tolyl-S-ethylthiosemicarbazone (hydriodide, m. p. 123°; hydrochloride, m. p. 167°) affords 3-ethylthiol-5-phenyl-4-o-tolyl-1:2:4-triazole, m. p. 107°; benzaldehyde-4-p-tolyl-S-methylthiosemicarbazone, m. p. 71° [hydriodide, m. p. 180° (decomp.); hydrochloride, m. p. 130° (decomp.)], gives 3-methylthiol-5-phenyl-4-p-tolyl-1:2:4-triazole, m. p. 176°; benzaldehyde-4-p-tolyl-1:2:4-triazole, m. p. 176°; benzaldehyde-4-p-tolyl-S-ethylthiosemicarbazone (hydrochloride, m. p. 158°; hydriodide, m. p. 165°) yields 3-ethylthiol-5-phenyl-4-p-tolyl-1:2:4-triazole, m. p. 148°. Ferric chloride may be used as the oxidising agent, but the products obtained are less pure. H. BURTON.

 $\gamma$ -Triazines : synthesis of thiolaminotriazines. A. OSTROGOVICH and V. GALEA (Atti R. Accad. Lincei, 1930, [vi], 11, 1108—1116).—By the method previously described (A., 1912, i, 320; this vol., 101) the following compounds have been prepared. 2-Amino-6-thiol-4phenyl-1:3:5-triazine, m. p. 281—282° (decomp.), forms silver and copper (+0.5H<sub>2</sub>O) salts, a picrate, m. p. 193—194° (decomp.), and a 5- or 6-methyl derivative, m. p. 170—171°. 2-Amino-6-thiol-4-o-tolyl-1:3:5triazine, m. p. 243—244° (decomp.), forms a silver salt and a picrate, m. p. 224—225° (decomp.). 2-Amino-6-thiol-4-m-tolyl-1:3:5-triazine, m. p. 272— 273° (decomp.), forms a silver salt and a picrate, m. p. 210—211° (decomp.). 2-Amino-6-thiol-4-p-tolyl-1:3:5-triazine, m. p. 279—280° (decomp.), forms a silver salt and a picrate, m. p. 191—192° (decomp.). 2-Amino-6-thiol-4-p-anisyl-1:3:5-triazine, m. p. 282—283°, forms a silver salt and a picrate, m. p. 198—199° (decomp.) T. H. POPE.

compounds. III. Alkylation of Triazole nitro-1:2:3-benztriazoles. O. L. BRADY and C. V. REYNOLDS (J.C.S., 1930, 2667-2673).-In agreement with Zincke and Helmert (A., 1896, i, 300), thermal decomposition of the methiodide obtained by the action of methyl iodide on 6-nitro-1:2:3-benztriazole affords only 6-nitro-3-methyl-1:2:3-benztriazole, which is converted by methyl sulphate into 6-nitro-1: 3-dimethyl-1: 2: 3-benztriazolinium methosulphate, [NO2·C6H3<NMe>N]+MeSO4, m. p. 110° (decomp.) [chloride, m. p. 136° (decomp.)]. Thermal decomposition of either the methosulphate or the chloride affords only 6-nitro-3-methyl-1:2:3-benztriazole, identical with a specimen synthesised by the action of nitrous acid on 4-nitro-2-aminomethylaniline. Alkylation of 6-nitro-1:2:3-benztriazole with methyl sulphate and 2N-sodium hydroxide, however, affords the 3-methyl derivative together with a larger yield of 6-nitro-1-methyl-1:2:3-benztriazole, m. p. 187°, converted by methyl sulphate at 100° into 6-nitro-1: 3-dimethyl-1: 2: 3-benztriazolinium methosulphate (above), and reduced by sodium hyposulphite to the 6-amino-compound, m. p. 201°, which affords 1-methyl-1:2:3-benztriazole by elimination of the amino-group in the usual manner. Similarly, methylation of 7-nitro-5-methyl-1:2:3-benztriazole with methyl sulphate and 2N-sodium hydroxide yields a mixture of 7-nitro-1: 5-dimethyl- (Pinnow, A., 1901, i, 485) and a larger amount of 7-nitro-3: 5dimethyl-, m. p. 196°, -1:2:3-benztriazole. The latter

is reduced to the corresponding 7-amino-compound, m. p. 190°, which by deamination affords 3:5-dimethyl-1:2:3-benztriazole. A mechanism for the formation of these derivatives, based on the assumption that the benztriazoles consist of an equilibrium mixture of two tautomeric forms, is suggested. In each case the methyl derivative in which the methyl group is attached to the nitrogen atom in the m-position to the nitro-group is converted, by heating with methyl sulphate alone, into the isomeride in which the methyl group is attached to the nitrogen in the o- or p-position to the nitro-group, the latter isomeride being the sole product of the action of methyl sulphate alone on the benztriazole. Thus 7-nitro-5-methyl-1:2:3-benz-triazole is converted by methyl sulphate and subsequent thermal decomposition of the chloride obtained from the methosulphate so formed into 7-nitro-1: 5dimethyl-1:2:3-benztriazole, this product also being obtained by similar treatment of 7-nitro-3:5dimethyl-1:2:3-benztriazole. J. W. BAKER.

2:5-Diphenyl-1:2:3-triazole-4-carboxylic acid. M. GALLOTTI [with G. BARRO and L. SALTO] (Gazzetta, 1930, 60, 866—872; cf. A., 1925, i, 306).—Phenyl oximinoethyl ketone phenylhydrazone, NHPh·N:CPh·CMe:N·OH, m. p. 210°, forms an acetyl derivative, m. p. 137°, which, when boiled with aqueous sodium carbonate, gives 2:5-diphenyl-4methyl-1:2:3-triazole. The latter, which was not purified, is oxidised by alkaline permanganate to 2:5diphenyl-1:2:3-triazole-4-carboxylic acid, m. p. 208— 209°. o-Tolyl oximinoethyl ketone, m. p. 114—115°, obtained by treating the parent ketone with isoamyl nitrite, gives a phenylhydrazone, m. p. 175—177°, which forms an acetyl compound, m. p. 140°, and this yields 2-phenyl-5-o-tolyl-4-methyl-1:2:3-triazole when boiled with aqueous sodium carbonate.

T. H. POPE.

1-Hydroxy- and 1-amino-derivatives of theobromine. C. A. ROJAHN and H. FEGELER (Arch. Pharm., 1930, 268, 567-572).-An attempt has been made to obtain derivatives of theobromine which are soluble in water and possess a narcotic action. Theobromine, glycol chlorohydrin, and 10% aqueous sodium hydroxide at 125° yield 1-β-hydroxyethyl-theobromine, m. p. 193° (acetate, m. p. 139°; benzoate, m. p. 151°; phenylurethane, m. p. 125°), which with phosphorus pentachloride in boiling chloroform gives  $1-\beta$ -chloroethyltheobromine, m. p. 152°. This with diethylamine at 100° yields 1-diethylaminoethyltheobromine, isolated as the picrate, m. p. 155-156°, with aniline, 1-B-anilinoethyltheobromine, m. p. 171°; and with p-phenetidine, 1-p-phenetylaminoethyltheobromine, m. p. 156°. Attempts to condense theobromine and ethyl β-bromoethyl ether yielded only hydroxyethyltheobromine. 1 - B - Hydroxypropyl theobromine, m. p. 129° (acetate, m. p. 112°; benzoate, m. p. 162°; phenylurethane, m. p. 175-176°), formed in small yield from sodium theobromine and β-chloron-propyl alcohol in xylene at 110-120°, yields with phosphorus pentachloride 1-β-chloropropyltheobromine, m. p. 144°, from which 1-β-anilinopropyltheobromine picrate, m. p. 179-181°, and 1-β-dimethylaminopropyltheobromine picrate, m. p. 250° (decomp.), are obtained. H. E. F. NOTTON.

Porphyrin syntheses. XXXV. Hæmin, hæmatin, and protoporphyrin. H. FISCHER, A. TREIBS, and K. ZEILE (Z. physiol. Chem., 1930, 193, 138-166; cf. this vol., 101) .-- Synthetic hæmatoporphyrin was converted into tetramethylhæmatoporphyrin. The m. p. and mixed m. p. of the latter confirmed the identity of the synthetic hæmatoporphyrin with that obtained by analysis. The imides (a-methoxyethylcitraconimide) obtained on oxidation of the two specimens) were identical. Bromo- and iodo-hæmin were prepared from blood and also from protoporphyrin. Although the crystalline form varied according to the method of crystallisation there was little doubt of the identity of the respective products. Hæmin and protoporphyrin each crystallise in various forms which indicate varying degrees of purity rather than constitutional J. H. BIRKINSHAW. divergence.

Porphyrin synthesis. XXXVI. Conversion of mesoporphyrin IX into a porphyrinmonopropionic acid, and some porphyrin syntheses. H. FISCHER and A. ROTHAAS (Annalen, 1930, 484, 85-112).-The product obtained by reduction of mesochlorin with zinc dust and acetic acid is converted by oxidation and esterification into a methyl ester, m. p. 206-207°, not identical with the dimethyl ester of mesoporphyrin IX. Mesoporphyrin IX, when similarly treated, gives a mixture of three new porphyrins and a little ætioporphyrin (determined spectroscopically). The main product (isolated as methyl ester), m. p. indefinite (copper salt, m. p. 175°), is indicated by analysis to be derived by reduction of one of the propionic acid groups to propyl. It is not identical with either of the porphyrins derived by loss of a carboxyl group, nor with either of the expected propyl derivatives, the synthesis of which is described. Its conversion into an indifferent rhodin, m. p. 259-260°, confirms the constitution arrived at by analysis. As by-products are obtained an isomeric mesoporphyrin (as methyl ester), m. p. 197°, not identical with the known mesoporphyrins of similar m. p., or with those described below, and the methyl ester of a porphintripropionic acid, m. p. 257° (copper salt, m. p. 277°; iron salt), the constitution of the last being assumed from the formation of an acid rhodin, m. p. 205°. The hypothesis is advanced that these products are formed by decomposition followed by recombination, and is supported by the isolation of identical products from mesoporphyrin XI by similar treatment

The following are described : 5-bromo-4: 3'-dimethyl - 3 - ethyl - 4' - propyl-5' - bromomethyl pyrromethene hydrobromide (methene IV), decomp. 195° (from 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylic acid and 2:4-dimethyl-3-propylpyrrole, followed by 3:5:3'-trimethyl-4'-ethyl-4-propulbromination); pyrromethene hydrobromide (methene VII), m. p. 211° (from 3: 5-dimethyl-4-propylpyrrole-2-aldehyde and 3:5:4':5'-tetramethylpyrrometheneopsopyrrole); 4:3'-dipropionic acid hydrobromide (methene IX), m. p. 232° [dimethyl ester, m. p. 180° (decomp.)], hydrochloride, m. p. 173° (dimethyl ester, m. p. 169-170°) (from cryptopyrrolealdehydecarboxylic acid and hæmopyrrolecarboxylic acid : converted by bromin-

ation into the 5:5'-dibromomethyl hydrobromide, m. p. 191°, and a small quantity of an isomeride, decomp. 150°). Mesoporphyrin XI [iron salt; copper salt, m. p. above 299°; dimethyl ester, m. p. 174.5° (iron salt, m. p. 263°; copper salt, m. p. 189°)] is obtained by fusion of 4:3'-dimethyl-3:4'-diethyl-5:5'-dibromomethylpyrromethene and brominated 3:3'-dimethylpyrromethene-4: 4'-dipropionate hydrobromides with succinic acid at 185-190°. 1:3:5:8-Tetramethyl - 2: 4 - diethyl - 6 - propylporphin-7 - propionic acid (methyl ester, m. p. 237°) is obtained, accompanied by mesoporphyrin V, by fusion of methenes III (cf. A., 1928, 902) and IV with methylsuccinic acid at 135-140°. Similar treatment of a mixture of methenes V (loc. cit.) and VII leads to 1:3:5:8-tetramethyl-2:4-diethyl-7-propylporphin-6-propionic acid (methyl ester, m. p. 215°) and meso-porphyrin II. Mesoporphyrin VI [hydrochloride; iron salt; copper salt, m. p. 314°; dimethyl ester, m. p. 199° (iron salt; copper salt, m. p. 210°)] may be obtained by fusion of a mixture of 5:5'-dibromo-4:4'dimethyl-3: 3'-diethylpyrromethene hydrobromide (A., 1926, 621) and methene IX with succinic acid at 180-190°, or by heating it with hydrogen bromide in acetic acid at 170-180°. Mesoporphyrin VIII [iron salt; dimethyl ester, m. p. 184-186° (iron salt, m. p. 223°; copper salt, m. p. 210°)] is the product of fusion of methene IX, 5:5'-dibromo-3:3'-dimethyl-4:4'diethylpyrromethene hydrobromide, and succinic acid at 195°. Oxidation of mesorhodin with chromium trioxide in sulphuric acid gives methylethylmaleimide and hæmatic acid. H. A. PIGGOTT.

Ring synthesis of porphyrins [with substituted and unsaturated side-chains]. IV. A bromovinylpyrrole and its transformations. H. FISCHER and O. Süs (Annalen, 1930, 484, 113-130).-Ethyl 2: 4-dimethyl-3-\beta-carboxyvinylpyrrole-5-carboxylate and bromine in carbon disulphide give an impure dibromide, which when heated with aqueous alcohol at 100° passes into ethyl 2: 4-dimethyl-3-β-bromovinylpyrrole-5-carboxylate (I), m. p. 158° (decomp.) (dibromide). Reduction of I with a solution (d 1.45) of hydrogen iodide in acetic acid at 100° causes elimination of the vinyl group (cf. A., 1926, 178) with the production of 2:4-dimethylpyrrole, whilst catalytic reduction (platinum-black) in ether affords ethyl cryptopyrrolecarboxylate, m. p. 94°. Treatment of I with silver cyanide, molecular silver, silver oxide, or copper powder in methyl alcohol at 90-95° gives ethyl 2: 4-dimethyl-3-aβ-dimethoxyethylpyrrole-5-carboxylate, m. p. 112°; when the reaction is carried out in presence of alcohol, ethyl 2: 4-dimethyl-3-β-ethoxyvinylpyrrole-5-carboxylate, m. p. 87°, results. Treatment of I with sulphurvl chloride (1 mol.) in ether gives a chloro-derivative, m. p. 168°; the dichloroderivative obtained by the action of 2 mols, of the chloride is hydrolysed by aqueous alcohol to ethyl 2-aldehydo-4-methyl-3-3-bromovinylpyrrole-5-carboxylate, m. p. 140° azine, m. p. 230° (decomp.); phenyl-hydrazone, m. [p. 142° (decomp.)]. This aldehyde condenses with cryptopyrrole in acetic and hydrobromic acids, forming 5-carbethoxy-4:3':5'-trimethyl-4'-ethyl-3-3-bromovinylpyrromethene hydrobromide, not melted at 300° after darkening at 170° [the 5-carboxy-methene hydrobromide is obtained similarly from 2-aldehydo-4-methyl-3- $\beta$ -bromovinylpyrrole-5-carboxylic acid, m. p. 238° (decomp.)]. Treatment of I with 3 mols. of sulphuryl chloride in ether and decomposition of the resulting trichloro-compound with alcohol gives ethyl 4-methyl-3- $\beta$ -bromovinylpyrrole-2:5-dicarboxylate, m. p. 115° (the 2-methyl 5-ethyl ester, m. p. 131°, is obtained similarly, using methyl alcohol). Catalytic reduction of the free dicarboxylic acid, chars from 230° without melting, furnishes 4-methyl-3-ethylpyrrole-2:5-dicarboxylic acid, which when heated at 240° yields opsopyrrole.

Ethyl 2: 4-dimethyl-3-\beta-carbethoxyvinylpyrrole-5carboxylate, m. p. 134°, prepared by esterification of the 3-\beta-carboxy-derivative or from ethyl 3-aldehydo-2:4-dimethylpyrrole-5-carboxylate and ethyl hydrogen malonate in presence of aniline at 100° (cf. A., 1926, 1261), is reduced catalytically (platinum-black) in ether to ethyl 2:4-dimethyl-3-3-carbethoxyethylpyrrole-5-carboxylate, m. p. 73°. When the dibromide, m. p. 121° (decomp.), of the above earbethoxyvinyl derivative is treated with alcoholic potassium hydroxide, a mixture of an unidentified bromine-containing substance, m. p. 196° (decomp.), and ethyl 2:4-dimethyl-3-\beta-carbethoxy- \beta-ethoxyvinylpyrrole-5-carboxylate, m. p. 163°, is produced; with methyl-alcoholic potassium hydroxide, ethyl 2:4-dimethyl-3-β-carbethoxy-ab-dimethoxyvinylpyrrole-5-carboxylate, m. p. 178°, results. Oxidation of ethyl 2 : 4-dimethyl-3-βcarboxyvinylpyrrole-5-carboxylate with chromic oxide in acetic acid gives ethyl 3-carboxy-2: 4-dimethylpyrrole-5-carboxylate. H. BURTON.

Amino-1-methylbenzoxazoles and their conversion into the arsinic acids of o-aminophenol. M. A. PHILLIPS (J.C.S., 1930, 2685-2690).--o-Acetamidophenol gives only a 15% yield of 1-methylbenzoxazole (hydrochloride) when treated with 5N. hydrochloric acid or 2N-sodium hydroxide at 90°, simple hydrolysis to o-aminophenol being the main The nitro-1-methylbenzoxazoles are best reaction. prepared by distillation of the corresponding nitro-acetor -diacet-amidophenols at 10-20 mm., and thus are obtained : 3-, m. p. 125°, 4-, m. p. 154° (hydro-chloride), and 6-, b. p. 240-250°/18 mm., m. p. 112°, -nitro-1-methylbenzoxazole. Dilute mineral acids or alkali hydroxides reconvert them into the nitroaminophenols, whilst reduction with iron powder and boiling 10% acetic acid affords the corresponding aminoderivatives and thus are obtained: 3-, m. p. 67° (acetyl derivative, m. p. 218°); 4-, b. p. 160-170°/20 mm., m. p. 77—78° (dihydrochloride; acetyl derivative, m. p. 205°); and 6-, m. p. 106° (acetyl derivative, m. p. 145-146°), -amino-1-methylbenzoxazoles, whilst acetylation of the 5-amino-compound (Newbery and Phillips, A., 1928, 311) gives the 5-acetamido-deriv-ative, m. p. 120° (dihydrate, m. p. 83°). After reduction of the mixture of 4- and 5-nitro-compounds obtained by nitration of 1-methylbenzoxazole (Newbery and Phillips, loc. cit.) only the pure 5-amino-derivative separates (64% yield). Reduction of 5-nitro-2-acetamidophenol with boiling dilute acetic acid and iron powder affords the corresponding 5-amino-compound (hydrochloride), but fails with 2nitro-4-acetamidophenol, whilst reduction of 3-nitro4-acetamidophenol with activated aluminium and 90% alcohol gives a 30% yield of the 3-amino-compound, isolated as its hydrochloride. Ethyl chloroformate and sodium hydroxide convert 5-nitro-2aminophenol into 5-nitro-2-carbethoxylaminophenol, m. p. 170°, reduced by alkaline sodium hyposulphite to the 5-amino-derivative, m. p. 129° (acetyl derivative, m. p. 233°). Application of the Bart reaction (action of copper arsenite on the diazotised amino-compound) to either the aminobenzoxazoles or the corresponding acetamidophenols affords the o-aminophenolarsinic acids, of which 4-carbethoxylamino-3-hydroxyphenylarsinic acid is new. J. W. BAKER.

Oxidation of leucomethylene-blue. A. REID (Biochem. Z., 1930, 228, 487-490; cf. A., 1930, 1381). -During the catalytic oxidation of leucomethyleneblue by copper, hydrogen peroxide is produced. It follows that the appearance of hydrogen peroxide during the oxidation of an organic substance gives no indication as to whether the process is a direct autoxidation or an oxidation in which a heavy metal is involved as oxygen carrier. The oxidation of leucomethylene-blue which takes place in the presence of proteins and is a surface phenomenon not appreciably influenced by the presence either of heavy metals or of substances such as carbon monoxide or hydrogen cyanide (which form complex compounds with heavy metals) also results in the production of W. MCCARTNEY. hydrogen peroxide.

Sparteine. P. KARRER, B. SHIBITA, A. WETT-STEIN, and L. JACUBOWICZ (Helv. Chim. Acta, 1930, 13, 1292-1308).-Sparteine methiodide when converted into the methohydroxide and distilled yields demethylsparteine,  $C_{15}H_{25}N_2Me$ , b. p. 170–172°/ 11 mm. (this and the compounds derived from it are probably mixtures of isomerides), reduced by hydrogen in presence of platinum and hydrochloric acid to dihydromethylsparteine, b. p. 176-181°/9 mm. This reacts with methyl iodide in benzene at 100° forming a methiodide hydriodide convertible into dihydrodedimethylsparteine, b. p. 174-182°/8.5 mm., and thence into tetrahydrodimethylsparteine. Four-fold repetition of the above process affords a pentadecane, b. p.  $242^{\circ}/729$  mm.,  $d_{4}^{187}$  0.7740,  $n_{D}^{20}$  1.43304, which might be δ-methyl-ζ-propyl-n-undecane, ζ-propyl-n-dodecane, or  $\zeta$ -methyl- $\eta$ -ethyl-n-dodecane, assuming that one of the formulæ previously proposed for sparteine (A., 1929, 200) is correct. These hydrocarbons have been synthesised for comparison with the above pentadecane.

Ethyl n-amylmalonate is converted by the usual methods into methyl-n-amylmalonic acid, m. p. 104° (ethyl ester, b. p. 130—132°/12 mm.), and thence into α-methylheptoic acid, b. p. 121—122°/13 mm. Zinc diethyl and α-methylheptoyl chloride give ethyl α-methylhexyl ketone, b. p. 191—193°/728 mm., which with magnesium n-amyl bromide affords ethyl-namyl-α-methylhexylcarbinol, b. p. 140—141°/10 mm. Dehydration of this with oxalic acid furnishes an olefine, C<sub>15</sub>H<sub>30</sub>, b. p. 236—237°,  $d_4^{2+6}$  0.7889,  $n_5^{2+6}$ 1.44195, reduced by hydrogen in presence of platinum and acetic acid to ζ-methyl-η-ethyl-n-dodecane, b. p. 240—242°/729 mm.,  $d_4^{3+8}$  0.7769,  $n_7^{3+1}$  1.43545. Oxidation of propyl-n-hexylcarbinol with chromic oxide in acetic acid yields propyl n-hexyl ketone, b. p. 201-203°/726 mm., 87-89°/11 mm. (semicarbazone, m. p.  $51-52^{\circ}$ ), which with an excess of magnesium *n*-amyl bromide affords mainly an olefine, C<sub>15</sub>H<sub>30</sub>, b. p. 239-241°,  $d_4^{182}$  0.7825,  $n_D^{182}$  1.44336. Catalytic reduction of this gives ζ-propyl-n-dodecane, b. p. 241-243°/730 mm., d<sub>4</sub><sup>15.6</sup> 0.7729, n<sub>D</sub><sup>20</sup> 1.43277. β-Bromopentane and ethyl sodiomalonate furnish the ethyl ester, b. p. 120-121°/11 mm., of β-methylpentane-αα-dicarboxylic acid, m. p. 92-93°, which when heated passes into β-methylhexoic acid, b. p. 207-209°/728 mm. The chloride of this reacts with zinc propyl iodide in toluene, forming propyl B-methylamyl ketone, b. p. 192-193°/715 mm. The carbinol from this and magnesium *n*-amyl bromide is dehydrated by potassium hydrogen sulphate at 200° to an olefine, C15H30, b. p. 236°/725 mm., d19 5 0.7805, np 1.44215, reduced catalytically to S-methyl-ζ-propyl-n-undecane, b. p.  $235-236^{\circ}/727 \text{ mm.}, d_1^{186} 0.7733, n_0^{20} 1.43262.$ 

H. BURTON.

Alkaloid from Anona reticulata, Linn. A. C. SANTOS (Philippine J. Sci., 1930, 43, 561).—Alcohol extraction of the trunk bark affords, after removal of phenolic bases, about 0.03-0.04% of an alkaloid,  $C_{17}H_{16}O_3N$  (one methylenedioxy-group), m. p. 122-123°,  $[\alpha]_{12}^{\infty 3}$ -83.01° in chloroform (hydrochloride; chloroplatinate). The name anonaine is suggested to distinguish the alkaloid from others occurring in Anona species (cf. Callan and Tutin, A., 1912, ii, 81; Trimurti, J. Ind. Inst. Sci., 1924, 7, 232).

R. CHILD. Alkaloids of Berberis Thumbergii, D.C. var. Maximowiczii, Franch. I. H. KONDO and M. TOMITA (Arch. Pharm., 1930, 268, 549-559).-The acidified aqueous solution of the alcoholic extract of the root contains the following tertiary bases, which are precipitated by ammonia: (a) oxyacanthine (Späth, A., 1929, 1319; von Bruchhausen and Scholtze, A., 1930, 98) (methyl ether hydrochloride, m. p. 261°); (b) a substance, m. p. 207-209°, but identical in all other respects with oxyacanthine; (c) berbamine (Santos, Diss., Westfäl. Univ., Münster, 1929) (methyl ether hydrochloride, m. p. 264°), which has an absorption spectrum almost identical with that of oxyacanthine, and (d) oxyberberine, now found for the first time in nature. After removal of berberine as hydrochloride, the following quaternary bases were precipitated as iodides and separated after reduction to their tetrahydro-derivatives : shobakunine (iodide, m. p. 204-206°), isolated as tetrahydroshobakunine, C<sub>16</sub>H<sub>11</sub>O(NMe)(OMe)<sub>3</sub>, m. p. 140° (hydrochloride, m. p. 242°; methiodide, m. p. 253°), jatrorrhizine, and a H. E. F. NOTTON. trace of columbamine.

Resolution of tetrahydropalmatine and tetrahydroberberrubine into their optically active components. E. SPÄTH and W. LEITHE (Ber., 1930, 63, [B], 3007-3012).—When treated with the equivalent amount of d-tartaric acid in alcohol, dltetrahydropalmatine yields d-tetrahydropalmatine hydrogen d-tartrate, from which d-tetrahydropalmatine, m. p. 141-142°,  $[\alpha]_{10}^{20} + 291°$  in alcohol, identical with the natural base, is readily obtained. The mixture of residual bases when treated with l-tartaric acid yields the l-base hydrogen l-tartrate, from which l-tetrahydropalmatine, m. p. 141—142°,  $[\alpha]_{D}^{\infty}$  —294° in alcohol, is derived.

dl-Tetrahydroberberrubine, m. p. 187—188° (ethyl ether, m. p. 128°), is resolved into components by means of ammonium d- $\alpha$ -bromocamphor- $\pi$ -sulphonate in alcohol and dilute acetic acid; the salt of the d-base separates more rapidly than that of the l-base. d-*Tetrahydroberberrubine* has m. p. 195—196°,  $[\alpha]_{15}^{15}$ +303° in chloroform, +298° in ethyl alcohol, whereas the l-base has m. p. 195—196°,  $[\alpha]_{15}^{15}$  —304° in chloroform. The mixture of equal amounts of the d- and l-base has m. p. 186°. These results are not in harmony with the observations of Kitasato (A., 1927, 1094).

H. WREN.

Quinoline derivatives. XVIII. Ouitenine. H. JOHN [with E. ANDRASCHKO] (J. pr. Chem., 1930, [ii], 128, 223-228).-The following derivatives of quitenine (Skraup, A., 1889, 626) are described: quitenine chloride (from quitenine and thionyl chloride), m. p. 206°; quitenine methyl ester, m. p. 217° (by esterification with methyl alcohol and sulphuric acid) (Goodson and others, A., 1930, 1310, give m. p. 170°); quitenine ethyl ester, m. p. 198° (Bucher, A., 1894, i, 152, gives m. p. 198°; Goodson, loc. cit., gives m. p. 201°); and quiteninehydrazide (from the last-named and hydrazine hydrate), m. p. 236° (benzylidene, m. p. 179°, and methylbenzylidene, m. p. 223°, derivatives). Treatment of the hydrazide with cold aqueous sodium nitrite gives the azide (not isolable), which is transformed by water into NN'-bisquitenylcarbamide, m. p. 154°. R. CHILD.

LVII. Strychnos alkaloids. Oxidation of tetrahydrostrychnine and certain derivatives, H. LEUCHS [with, in part, F. KRÖHNKE] (Ber., 1930, 63, [B], 3184–3189).—Oxidation of tetrahydrostrychnine with chromic acid and dilute sulphuric acid at 20° affords a mixture of a substance,  $C_{17}H_{20}O_4N_2$ , m. p. 243–245° (decomp.) after softening at 230° (perchlorate, dihydrate and anhydrous,  $[\alpha]_{3}^{13}$  +73.8° d for the anhydrous salt), and an amino-acid,  $C_{21}H_{22}O_4N_2,4H_2O$ , not molten below 300° (hydro-chloride,  $[\alpha]_{15}^{15} -24 \cdot 0^{\circ}/d$ ; hydrobromide). In the amino-acid the benzene nucleus of the base appears to persist unchanged. ON-Diacetyltetrahydrostrychnine, when similarly oxidised, loses the O-acetyl group and yields an *amino-acid*,  $C_{23}H_{26}O_4N_2$ , decomp. 305° after softening at 180–200° and foaming at 220° (perchlorate,  $[\alpha]_{D}^{20} - 118.5^{\circ}/d$  in water). The aminoacid is obtained in better yield from the N-monoacetyl derivative. The following observations are incidental: strychnidine hydroperchlorate,  $[\alpha]_{15}^{17} - 10 \cdot 1^{\circ}/d$  in water, and hydrochloride,  $[\alpha]_{15}^{17} - 13 \cdot 5^{\circ}/d$  in  $0 \cdot 1N$ -hydrochloric acid; tetrahydrostrychnine hydroperchlorate,  $[\alpha]_{15}^{19}$  $-74.9^{\circ}/d$ , and hydrochloride,  $[\alpha]_{15}^{15}$   $-86.6^{\circ}/d$ ; N-mono-acetyltetrahydrostrychnine, m. p. 157-159°, or m. p. 197—199° after desiccation  $(hydroperchlorate, [\alpha]_{b}^{1}+104^{\circ}/d; hydrochloride, [\alpha]_{b}^{1}+122\cdot3^{\circ}/d); diacetyl$ tetrahydrostrychnine, as mixture of anhydrous and hydrated compounds (hydroperchlorate); dibromotetrahydrostrychnine,  $C_{21}\dot{H}_{24}O_2\dot{N}_2Br_2$ , m. p. 248—250° (decomp.) after softening at 238° (hydrobromide; H. WREN. hydrochloride,  $[\alpha]_{D}^{15} - 23 \cdot 2^{\circ}/d$ .

Constitution of Strychnos, yohimbe, and quebracho alkaloids. E. SPATH and H. BRET-
SCHNEIDER (Ber., 1930, 63, [B], 2997-3006).--Strychnine in alkaline solution is treated on the waterbath with potassium permanganate until the latter substance is only slowly consumed. The acids thus produced are separated by their differing acidity and from one fraction N-oxalylanthranilic acid, decomp. 202-203° (methyl ester, m. p. 152°), is obtained; thermal decomposition of the normal potassium salt affords anthranilic acid. Examination of the product obtained by Warnat (A., 1926, 1263) by the oxidation of yohimboaic acid proves its identity with N-oxalylanthranilic acid; Warnat's acid and its methyl ether have the compositions  $C_9H_7O_5N$  and  $C_{11}H_{11}O_5N$ , instead of C8H7O4N and C10H11O4N as recorded. The products of the decomposition of vohimbine and the specific rotation of the base and of the acid derived therefrom coincide almost completely with Hahn's data (A., 1930, 1194) for quebrachin. Oxidation of the acid derived from quebrachin hydrochloride affords N-oxalylanthranilic acid. Great similarity is therefore observed at any rate in one portion of the molecular structure of strychnine and of the vohimbe and quebracho alkaloids with the ring system of yohimbol. In them the ring system I must be present in a quinoline or an indole ring. Brucine is more readily oxidised than strychnine, but affords



N-oxalyl-4: 5-dimethoxyanthranalic acid; the alkaloid therefore contains the complex II.

Methyl hydrogen N-oxalyl-4 : 5-dimethoxyanthranilic acid, m. p.  $230-232^{\circ}$  (decomp.) after softening at 229°, is prepared by heating methyl 6-aminoveratrate with anhydrous oxalic acid in a vacuum at  $110-140^{\circ}$ ; the dimethyl ester has m. p.  $206-207^{\circ}$ .

H. WREN.

**Oxonitine.** E. SPÄTH and F. GALINOVSKY (Ber., 1930, 63, [B], 2994—2997).—Oxonitine, m. p. 277—278° (vac. decomp.),  $[\alpha]_{15}^{15}$ —48° in chloroform, has the formula  $C_{32}H_{43}O_{12}N$  and contains the four methoxyl groups present in aconitine. The composition is greatly confirmed by determination of the benzoyl groups in oxonitine and aconitine. This is effected by hydrolysis of the compounds followed by acidification and extraction of the liberated benzoic acid by ether. The acid is sublimed at 130—150°/10 mm. and weighed.

Reply is made to Akabori and Saito (A., 1930, 1445). H. WREN.

M. p. of pure yohimbine. K. WARNAT (Ber., 1930, 63, [B], 2959—2961).—Contrary to Hahn and Schuch (A., 1930, 1194), pure yohimbine has m. p. 234—235°; the preparation of Hahn and Schuch was probably contaminated with  $\alpha$ -yohimbine, from which it is not readily separated by fractional crystallisation. H. WREN.

Identity of  $\alpha$ -yohimbine with isoyohimbine. G. HAHN and W. SCHUCH (Ber., 1930, 63, [B], 2961— 2962; cf. Warnat, preceding abstract).—The  $\alpha$ -yohimbin of Lillig and Kreitmair (Merck's Jahresber., 1928, 20) and Hahn and Schuch (A., 1930, 1194) is not identical with the isoyohimbine of Hahn and Schuch (loc. cit.). H. WREN.

Alkaloids of Sinomenium and Cocculus. XXIX. Dauricine. H. KONDO and Z. NARITA. XXX. Alkaloids of Cocculus saramentosus, Diels. H. KONDO and M. TOMITA (J. Pharm. Soc. Japan, 1930, 50, 589-593, 633-644).-XXIX. Treatment of dauricine with methyl-alcoholic alkali and ethyl bromide affords ethyldauricine ethobromide, decomp. 136-139° (platinum salt, decomp. 215-218°), which, with 20% potassium hydroxide solution, gives a-ethyldauricinethylmethine (methiodide, decomp. 162-165°). The methiodide, when treated with potassium hydroxide, afforded a substance oxidisable to an acid. m. p. 276-279°, not identical with 4-methoxy-3: 4'diphenyl ether 1: l'-dicarboxylic acid, m. p. 312°. The corresponding ethoxy-acid has m. p. 276-279°. The formula

OMe·C:CH·C·CH<sub>2</sub>·CH<sub>2</sub>·NMe

OH·C:CH·C CH·CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OMe is proposed for dauricine.

XXX. Menisarine, m. p. 203° [gold salt, dccomp.; platinum salt, decomp.  $304^{\circ}$ ; hydrochloride, decomp. 279°; hydrobromide,  $C_{37}H_{38(36)}O_6N_{2,2}HBr,2H_2O$ , decomp. 285°; methiodide, decomp. 269—270°; acetyl derivatives:  $OAc \cdot C_{37}H_{37(35)}O_5N_2$ , m. p. 141°;  $(OAc)_3C_{37}H_{35(33)}O_3(:NAc_3)_2(OAc)_2$ , m. p. 105°], when reduced by zine in acid solution gave a compound  $C_{37}H_{40(42)}O_6N_2$ , m. p. 162°, and when treated with methyl sulphate followed by potassium iodide afforded the compound  $C_{34}H_{28(26)}O_2N_2(OMe)_4$ ,2MeI m. p. 252—263°. The structure of menisarine is discussed. CHEMICAL ABSTRACTS.

Identification of alkaloids by precipitation. I. Natural classification of alkaloids based on precipitation. C. C. FULTON (J. Assoc. Off. Agric. Chem., 1930, 13, 491-497).-The usual reagents are compared with phosphomolybdic acid as a standard precipitant and are classified according as their sensitivities with a particular alkaloid are equal to, or less than, that of phosphomolybdic acid. The alkaloids may be arranged similarly, according to their sensitivity towards precipitating agents, but to avoid inconsistencies they are classified in groups. The nine groups embrace amines, proteins, and basic dyes, which are precipitable by the reagents, and the remaining alkaloid classes are designated as the caffeine, aniline-pyridine, atropine, cotarnine, quinine, and narcotine classes. The classification corresponds with the data of precipitation from 2% solutions and with the solubility in water and the basic strength of the free alkaloids. The concentrations of the solutions never exceed 1: 1000, and a few mg. of the alkaloid suffice for the classification and tentative identification. H. J. DOWDEN.

Microchemical detection of alkaloids in plants. XIV. Cytisine. G. KLEIN and E. FARKASS (Oesterr. Bot. Z., 1930, 79, 107—124; Chem. Zentr., 1930, ii, 1257—1258).—The most sensitive and characteristic reaction for cytisine is that of Bertheaumé employing potassium tri-iodide which gives rosettes of dark brown prisms. The distribution of cytisine in Laburnum anagyroides and its presence in 15 Papilionaccæ is recorded. Cytisine does not appear to be identical with ulexine. Laburnum contains thiocarbamide. A. A. ELDRIDGE.

Aromatic arsenic compounds containing sulphur groups attached to the nucleus. II. Thiocyano- and disulphido-groups. H. J. BAR-BER (J.C.S., 1930, 2725-2729).-Diazotisation of 4aminophenylarsinic acid and subsequent treatment with a solution of cuprous thiocyanate containing potassium thiocyanate gives a 30% yield of 4-thio-cyanophenylarsinic acid, converted by boiling 2Nsodium hydroxide into an amorphous substance which when oxidised in sodium hydrogen carbonate suspension with iodine in potassium iodide gives diphenyl disulphide-4:4'-diarsinic acid (King and others, A., 1926, 851). 2-Thiocyanophenylarsinic acid is similarly prepared and converted into diphenyl disulphide-2: 2-diarsinic acid, which is also obtained, contaminated somewhat with the disulphoxide from 2-sulphinophenylarsenious oxide (A., 1930, 1456), by mild reduction with boiling alcoholic sulphur dioxide containing a little hydrogen iodide, or with very dilute sulphuric-hydriodic acid solution at 95°, followed by oxidation of the arsinoxide to the arsinic acid. It is suggested that the thiol group formed by hydrolysis of either the thiocyano- or disulphido-group reacts with the arsinic acid group as follows :  $R \cdot AsO_3H_2 + 4R'SH = RAs(SR')_2 + R' \cdot S \cdot S \cdot R' + 3H_2O$ , thus giving a complex intramolecular thioarsinite of the type  $[-S \cdot C_6 H_4 \cdot As(S \cdot C_6 H_4 \cdot As <)_2]_n$ , which regenerates the disulphide arsinic acid on oxidation. It is considered very improbable that the thiol group would remain intact under the conditions used by Krishna and Krishna (A., 1929, 1320) for the supposed preparation of 4-thiolphenylarsinic acid. 3-Nitro-4-aminophenylarsinic acid is similarly converted by diazotisation and potassium cuprothiocyanate into 3-nitro-4-thiocyanophenylarsinic acid, which loses its sulphur group when hydrolysed with 2N-sodium hydroxide, yielding only tarry material. Reduction of 2-sulphinophenylarsenious oxide in hot glacial acetic acid with hypophosphorous acid (d 1.14) and potassium iodide, with sodium hyposulphite, or with zine and hydrochloric acid gives a *substance*, m. p.  $177-178^{\circ}$ , to which the annexed structure is assigned; it is also obtained by similar reduc-



tion of the 2:2'-disulphide- or 2thiocyanophenyl-arsinic acid. It is stable to boiling alkali, is slowly

oxidised by iodine in sodium hydrogen carbonate suspension to the disulphide-arsinic acid, and rapidly to 2-sulphophenylarsinic acid by concentrated nitric acid. J. W. BAKER.

Aromatic boron compounds and arylmercuric salts derived therefrom. W. KÖNIG and W. SCHARRNBECK (J. pr. Chem., 1930, [ii], 128, 153-170). -A series of arylboric acids has been prepared by the interaction of isobutyl borate and the appropriate Grignard reagent (cf. Khotinsky and Melamed, A., 1909, i, 864) for investigation of their trypanocidal activity; certain of the acids have considerable activity in vitro, but are unsuitable for chemotherapeutic application owing to the ease of hydrolytic fission of the boric acid residue from the aromatic nucleus. The following new acids are described and revised m. p. recorded : p-bromophenyl-, m. p. 266° (oxide, m. p. 280°), o-chlorophenyl-, m. p. 149°, o-

anisyl-, m. p. 105° (Michaelis and others, A., 1894, i, 190, give 165°), m-anisyl-, m. p. 147° (oxide, m. p. 159°), o-tolyl-, m. p. 168° (loc. cit., 161°), m-tolyl-, m. p. 157° (Khotinsky, loc. cit., 137-140°), and α-naphthyl-boric acid, two modifications, m. p. 248° and 266°, respectively (Michaelis, loc. cit., 259°). The borobenzoic acids, CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·B(OH)<sub>2</sub>, are obtained by oxidation of the corresponding tolylboric acids (Michaelis and Richter, A., 1901, i, 355) : o-borobenzoic acid, m. p. 152°, and m-borobenzoic acid, m. p. 240° (basic lead salt,  $C_{14}H_{12}O_{10}B_2Pb_3$ ; normal barium salt; silver salt of "pyro"-acid,  $C_{14}H_8O_7Ag_4B_2$ ). Diaryl-boric acids,  $Ar_2B$ ·OH, are formed as by-products in the preparation of the arylboric acids, or, better, by the use of 2 mols. of the Grignard reagent; diphenylborie acid, b. p. 150-155°/20 mm., m. p. 57.5° (Michaelis, loc. cit., gives b. p. 215-235°/17 mm.), di-p-anisyl-, m. p. 107°, di-p-bromophenyl-, m. p. 113°, and di-β-naphthyl-boric acid, b. p. 135-138°/14 mm., m. p. 172°.

Mercuric salts readily displace the boric acid residue with formation of corresponding arylmercuric salts, of which the following are new: p-bromophenylmercuric chloride, m. p. 235°, and acetate, m. p. 188°; o-chlorophenylmercuric chloride, m. p. 133°; m-anisylmercuric chloride, m. p. 158°, and acetate, m. p. 120°; o-anisylmercuric acetate, m. p. 101°; o-, m. p. 131°, and m-chloromercuribenzoic acid, m. p. 258°, and m-acetoxymercuribenzoic acid, m. p. above 310°. R. CHILD.

Formation of a heterocyclic ring closed through mercury atoms. II. L. VECCHIOTTI and M. PANCIERA (Gazzetta, 1930, 60, 904-909; cf. A., 1929, 203).-By heating o-dibromobenzene at 120° with 2% sodium amalgam in petroleum solution a substance,  $C_6H_4Hg$ , which does not melt even at 300°, was obtained. From its chemical behaviour

it probably has the structure  $C_6H_4 < Hg > C_6H_4$ . O. J. WALKER.

Bis-p-phenetyl telluride and its derivatives. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1930, 2599-2601).-By the action of magnesium p-ethoxyphenyl bromide on tellurium dibromide in ether is obtained bis-p-phenetyl telluride, R2Te (R= p-EtO·C<sub>6</sub>H<sub>4</sub>·), m. p. 64°, converted by chlorine in carbon tetrachloride into the corresponding telluridichloride, R2TeCl2, identical with the specimen previously obtained by Morgan and Drew (A., 1926, 83). The original constitution assigned to the dichloride is thus confirmed, despite the contrary evidence of parachor measurements (Burstall and Sugden, A., 1930, 399), which suggested that it was a nuclear-substituted telluride. The telluridichloride is converted by boiling water into the corresponding tellurioxychloride, (R2TeCl)2O, decomp. 193°, and by boiling 2N-aqueous alkali into the telluroxide, R2TeO. Bis-p-phenetyl telluri-dibromide, m. p. 127°, and -diiodide, m. p. 144°, are obtained similarly. Concentrated nitric acid converts these three tellurihalides into o-halogenated-p-nitrophenetoles, the yield being greatest with the di-iodide. p-Anisyl-p-phenetyl telluridichloride, m. p. 165-166°, prepared by heating p-phenetyl telluritrichloride with 4 mols. of anisole

at 100°, is reduced by zinc dust and glacial acetic acid to p-anisyl p-phenetyl telluride, m. p. 45°.

J. W. BAKER. Clupein. II. K. FELIX and A. LANG (Z. physiol. Chem., 1930, 193, 1-14; cf. A., 1929, 1322).-Trypsin-kinase was allowed to act on clupein hydrochloride B at  $p_{\rm H}$  8.4 until no further action occurred. The enzyme was then destroyed and the solution hydrolysed with intestinal erepsin at  $p_{\rm H}$  7.8. The trysin-kinase hydrolysis liberated 4 mols. of arginine, 6 amino-groups, and 6 acid equivalents; the erepsin set free 4 arginine mols., 4 amino-groups, and 5 acid equivalents. Four of the amino-groups and four acid equivalents in the first hydrolysis belong to the arginine. The two remaining amino- and acid groups may belong to the unhydrolysed portion, or to monoamino-acids. The clupein molecule appears to be built symmetrically from two similar halves, one of these being hydrolysed by trypsin-kinase.

J. H. BIRKINSHAW.

Sphingomyelin. W. MERZ (Z. physiol. Chem., 1930, 193, 59—87).—Cerebroside-free sphingomyelin preparations with P: N ratio of 2:1 were obtained from human brain. Sphingomyelin on catalytic hydrogenation furnishes hydrosphingomyelin,  $[\alpha]_{i}^{su}$ +12.85°; the latter on acetylation forms monoacetylhydrosphingomyelin, various fractions of which were hydrolysed. Stearic, lignoceric, and nervonic acids were obtained, showing that there are three sphingomyelins present in the product from brain, differing in their fatty acid constituents.

J. H. BIRKINSHAW.

 $d-\alpha$ -Aminonorvaleric acid (norvaline) as a constituent of proteins. E. ABDERHALDEN and F. REICH (Z. physiol. Chem., 1930, **193**, 198—200). d-Norvaline was obtained from the products of acid hydrolysis of caseinogen. J. H. BIRKINSHAW.

"Acetyl bases " from proteins. N. TROENSE-GAARD, F. WREDE, and H. G. MYGIND (Z. physiol. Chem., 1930, 193, 49—55).—Two crystalline acetyl bases were obtained from the syrupy mixture formed by the acetolysis of proteins (cf. A., 1926, 634); base A,  $C_{10}H_{14}O_2N_2$ , isolated as the chloroaurate, m. p. 193° (darkens at 175°), and base B,  $C_9H_{11}ON_3$  (chloroaurate, m. p. 184° (decomp.); chloroplatinate, blackens at 260°; m-nitrobenzoyl derivative, m. p. 185°). The bases were obtained from serum-globulin, serum-albumin, globin, fibrin, and caseinogen. Gliadin yielded only base B, silk-fibroin neither base. J. H. BIRKINSHAW.

Fission products of hydrogenated proteins. I. N. TROENSEGAARD and H. G. MYGIND (Z. physiol. Chem., 1930, 193, 171–180).—In addition to the bases described above, there were isolated piperidine, isoamylamine, and two bases yielding crystalline derivatives from the acetolysis of proteins and reduction of the acetyl products : base,  $C_{11}H_{22}N_2$ : picrate (A<sub>2</sub>B), decomp. 231°; chloroaurate, m. p. 197° (decomp.); reineckate, m. p. 185°; base,  $C_{14}H_{22}N_2$ : styphnate (A<sub>2</sub>B), m. p. 234° (decomp.); chloroaurate, m. p. 197° (decomp.); chloroplatinate, m. p. 257° (decomp.); picrate, m. p. 242° (decomp.). All m. p. are uncorr. Both new bases were obtained from gliadin and caseinogen, and  $C_{14}H_{22}N_2$  from globin in addition. J. H. BIRKINSHAW.

Constitution of soluble proteins. (Reversibly dissociable component systems.) S. P. L. SÖREN-SEN (Compt. rend. Trav. Lab. Carlsberg, 1930, 18, No. 5, 1-124, and Kolloid-Z., 1930, 53, 306-318; cf. this vol., 38) .-- The conception of proteins as reversibly dissociable component systems is discussed with reference to experimental data on the fractionation and solubility of egg-albumin, horse-serumalbumin, horse-serum-globulin, casein, and wheat gliadin (published by the author and his colleagues during the past 13 years) and to modern views (Meyer, Staudinger) on the structure of high-molecular substances. Svedberg's work on the determination of mol. wt. of proteins is discussed. The necessity of discriminating between reversible dissociation and true protein scission is emphasised. H. BURTON.

Glutelins. VI. Optical rotations of glutelins from wheat, rye, barley, maize, and rice. F. A. CSONKA, M. J. HORN, and D. B. JONES (J. Biol. Chem., 1930, 89, 267–273).—The following values for  $[\alpha]_{2}^{pv}$ in 0.5*M*-sodium hydroxide solution were obtained : wheat  $\alpha$ -glutelin  $-85 \cdot 1^{\circ}$ , wheat  $\beta$ -glutelin  $-76 \cdot 6^{\circ}$ , rye glutelin  $-81 \cdot 2^{\circ}$ , barley  $\alpha$ -glutelin  $-111 \cdot 1^{\circ}$ , maize  $\alpha$ -glutelin  $-72 \cdot 6^{\circ}$ , rice glutelin  $-65 \cdot 1^{\circ}$ . The curves representing the course of racemisation of gliadin and of the glutelins of wheat in 0.5M-sodium hydroxide solution at 38° are hyperbolic.

C. R. HARINGTON.

Structure of the polypeptide associates obtained from gelatin and gelatin-peptone by means of acetic anhydride. VII, VIII. A. FODOR and C. EPSTEIN (Biochem. Z., 1930, 228, 310-314, 315-326).—VII. Results obtained from the examination of other fractions confirm in the main the conclusions formerly reached (A., 1930, 1197). The procedure of Frankel and Kuk (*ibid.*, 1198) has been adopted.

VIII. The glycerol-soluble product obtained when gelatin is heated with glycerol (cf. A., 1928, 1387) has been treated with acetic anhydride and the products formed have been separated by fractional precipitation. Consideration of the mol. wt. of the purified materials and of their other properties leads to the conclusion that the gelatin molecule consists of associations of comparatively simple polypeptides. Peptides formed from more than six amino-acids are probably not present in the molecule. W. MCCARTNEY.

Fine structure of gelatin micelle. O. GERNGROSS, K. KERRMANN, and W. ABITZ (Biochem. Z., 1930, 228, 409—425).—From the examination of Röntgen diagrams of unstretched, stretched, and swollen gelatin and collagen, conclusions which satisfactorily explain the properties of the substances are reached regarding the ways in which the constituent aminoacids of the proteins are combined and grouped. The so-called crystalline and amorphous constituents of the substances probably differ only in the way in which they are arranged and not in their forms. The structure of collagen is very similar to that of gelatin. W. MCCARTNEY.

Determination of amino-acids formed by hydrolysis of proteins. III. Application of the processes of esterification and acetylation to the hydrolysis products of proteins. E. CHERBULIEZ, P. PLATTNER, and S. ARIEL (Helv. Chim. Acta, 1930, 13, 1390-1402) .- The protein is hydrolysed by hydrochloric (or sulphuric) acid, the hydrolysate neutralised with sodium (or barium) hydroxide, and cystine and tyrosine are allowed to crystallise. The filtrate is made alkaline, evaporated in a vacuum to remove ammonia, the residue acidified, the residual amino-acids are esterified by Fischer's method, and the esters acetylated by the method previously described (A., 1929, 685). The acetylated esters are extracted with chloroform and freed from resinous material by adding the concentrated extract to much ether; the resins are thereby precipitated, and this material is subjected to the esterification-acetylation process and again separated into esters and resin. The residue from the ethereal extract is then fractionally distilled and the various esters are hydrolysed by 20% hydrochloric acid. When an appreciable residue remains after distillation, it is subjected to the above process and redistilled. The esters of acetylated diamino-acids do not distil; in some cases the diamino-acids are removed from the hydrolysate first. The above method, with slight modifications, is illustrated by analyses of serum-albumin, casein, and silk fibroin. The results indicate that it is the best method of analysis. H. BURTON.

Micro-sublimation. A. CHALMETA (Anal. Fís. Quím., 1930, 28, 1407—1419).—An account is given of the application of micro-sublimation methods to the identification of small quantities of material, and especially of caffeine and theobromine in pharmacentical and other products. The sensitivity of the method is dependent on the content in the mixture under examination, but quantities of  $7 \times 10^{-6}$  g. may be detected with certainty. Precipitation reactions suitable for the identification of sublimates of caffeine and theobromine which are too small for their recognition under the microscope are described. In certain cases glucosides may be identified by examination of the sublimates obtained after hydrolysis. H. F. GILLEE.

Volumetric determination of methoxyl and ethoxyl groups. F. VIEBÖCK and C. BRECHER (Ber., 1930, 63, [B], 3207-3210).—The method described previously (this vol., 107) is adapted to microchemical analysis. H. WREN.

Determination of alanine. A. I. KENDALL and T. E. FRIEDEMANN (J. Infect. Dis., 1930, 47, 171— 175).—Lactic acid resulting from interaction of alanine and nitric acid is determined after interfering

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substances have been removed with copper sulphate and calcium hydroxide. CHEMICAL ABSTRACTS.

New reactions of creatine and creatinine. J. A. SÁNCHEZ (Semana Méd., 1930, II, 616-617).--(1) The solution (1 c.c.) of creatinine (1 in  $10^4$ ) is treated with 1 drop of silver nitrate solution and I drop of sodium hydroxide solution and is heated at  $100^\circ$ ; the unreduced silver oxide is dissolved in a drop of acetic acid, and a drop of ammonia solution is added, a comparison of the volume of the silver being employed to determine the creatinine. (2) Creatinine (0.02-0.03 g.) is boiled with water (2 c.c.) and mercuric oxide (0.05 g.); resorcinol (0.05 g.) is dissolved in the decanted liquid, 2 c.c. of sulphuric acid then being added without mixing. A blue colour, dependent on the formation of oxalic acid, is formed at the interface. (3) Creatinine forms cinnamon-red crystals with Dragendorff's reagent.

CHEMICAL ABSTRACTS.

Determination of quinine, cinchonine, and cinchonidine with the quinhydrone electrode, and the choice of end-points in alkaloid titrations. E. B. R. PRIDEAUX and F. T. WINFIELD (Analyst, 1930, 55, 561-565).—Since the changes in  $p_{it}$  during neutralisation of the alkaloid bases have been determined either colorimetrically or by the hydrogen electrode, the dissociation constants may be calculated and the values of  $p_{\rm H}$  at the end-point (the titration exponent  $p_{\rm T}$ ) deduced. The  $p_{\rm T}$  of the chosen indicator should be as near as possible to that of the base hydrochlorides etc. For strong monoacid bases  $(k=1\times10^{-3}$  to  $10^{-4})$ , e.g., piperidine, coniine, berberine, hydrastine, any ordinary indicator changing at  $p_{\rm H}$  7.0—5.0 may be used. For weaker monoacid bases ( $k=1\times10^{-5}$  to 10<sup>-6</sup>) methyl-red is best (excepting atropine, cocaine, tropacocine). Di-acid alkaloids having  $k_1$  about  $1 \times 10^{-6}$  and  $k_2$   $1 \times 10^{-8}$ or less have their titration exponents calculated differently and show important differences to the monoacid bases. Bromocresol-purple is a suitable indicator, or if an alcoholic solution is necessary bromophenol-blue gives good results for brucine or strychnine. Nicotine and quinine belong to this class. The quinhydrone electrode offers many advantages and the titration is best carried out by dissolving the base in a known excess of standard acid and titrating back. Details are given for titration of quinine (0.05, 0.01, and 0.005M solutions), cinchonine (0.002), and cinchonidine (0.100 and 0.002-M solutions). Dilute conchonine and cinchonidine (0.002M solutions) should be titrated with ethylred as well as methyl-red. D. G. HEWER.

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Determination of oxygen and carbon monoxide in blood. J. SENDROY, jun., and S. H. LIU (J. Biol. Chem., 1930, 89, 133-152).—The gases are completely extracted from blood in the apparatus of Van Slyke and Neill (A., 1924, ii, 872) and after absorption of carbon dioxide with sodium hydroxide are transferred to a special absorption pipette containing alkaline pyrogallol to remove the oxygen; the residual mixture of carbon monoxide and nitrogen is returned to the apparatus (in which the blood has in the meantime been replaced by a mixture of glycerol and sodium chloride solution) and the carbon monoxide is determined by absorption with cuprous chloride. The method gives results in good agreement with those obtained by the more complex technique of Van Slyke and Robscheit-Robbins (A., 1927, 475). C. R. HARINGTON.

bases described above, there were two

Origin of chlorophyll and its relation to blood-pigments. II. K. NOACK and W. KIESS-LING (Z. physiol. Chem., 1930, 193, 97—137; cf. A., 1929, 727).—On reduction with iron and formic acid, methylphæophorbide a yields methylprotophæophorbide, m. p. 264—265°. Reduction of phæophytin by the same method at 0—5° gives an impure protophæophytin similar to that prepared from pumpkin seeds. The crude product forms protophytochlorin trimethyl ester, m. p. 234—235°, on esterification with methyl-alcoholic hydrogen chloride. The same substance is obtained direct from phæophytin by reduction, hydrolysis, and esterification, also from methyl protophæophorbide. The hydrolysis of the trimethyl ester yields pure protophæophorbide.

Phylloerythrin, prepared from ox-bile, on hydrolysis gives phylloerythrincarboxylic acid. The latter with diazomethane yields *phylloerythrin trimethyl ester*, m. p. 230-232°, and with methyl-alcoholic hydrogen chloride the monomethyl ester. Hydrolysis with methyl-alcoholic potassium hydroxide furnishes a *dicarboxylic acid monoester*, which swells at 250-270°. Esterification of the latter gives a *trimethyl* ester, m. p. 210-212°. A *dicarboxylic acid diester* was also obtained. Certain phylloerythrin-like substances were prepared from the protophæophytin series. A reduction product of methylphæophorbide *a* yields a *monomethyl* ester, m. p. 296-298°. A *monomethyl* ester, m. p. 272-274°, was obtained in one case from the preparation of protophæophorbide.

J. H. BIRKINSHAW. Maintenance and production of hæmoglobin on synthetic diets. Determination of copper. D. L. DRABKIN and C. S. WAGGONER (J. Biol. Chem., 1930, 89, 51—75; cf. A., 1929, 1476).—Rats suffering from nutritional anæmia on a milk diet recovered when transferred to a synthetic diet containing iron but lower in copper content than the milk diet. Nevertheless addition of iron to the latter diet did not prevent the development of anæmia. Previous administration of copper failed to increase the resistance of rats to nutritional anænia. It is therefore doubted whether copper has any connexion with this type of anæmia.

In using the method of Biazzo (B., 1926, 383) for the determination of copper it is important to remove iron before the stage of development of colour; this is best achieved by addition of sodium pyrophosphate solution. In the potassium ethyl xanthate method (Scott, "Standard Methods of Chemical Analysis," New York, 1917) control of the  $p_{\rm u}$ , which should be maintained near 3.8, is essential.

C. R. HARINGTON.

Crystalline methæmoglobin from horse-blood. M. LEVY (J. Biol. Chem., 1930, 89, 173—183).—The paste of oxyhæmoglobin crystals prepared from horse-blood by the method of Ferry and Green (A., 1929, 338) is diluted with water and either reduced by evacuation and agitation or brought into solution by means of potassium hydroxide, and then oxidised with potassium ferricyanide in 10% excess, when the methæmoglobin crystallises. Alternatively, the oxyhæmoglobin paste is diluted, treated with 10% of alcohol, and kept at 37— $38^{\circ}$  for 70—80 hrs. Figures are given for the solubilities of the preparations thus S obtained in phosphate buffers of varying  $p_{\rm H}$  and ionic strength. Minimum solubility occurs at  $p_{\rm H}$  6.8. Solutions of methæmoglobin are stable for several weeks at 2—4°, and thermodynamical arguments show that the formation of oxyhæmoglobin in such solutions in presence of oxygen is possible only to a minute extent. C. R. HARINGTON.

Constitution of proteins of serum and of organs. III. A. BLANKENSTEIN and A. FISCHER (Biochem. Z., 1930, 228, 437—442; cf. A., 1930, 1305).—When the proteins in various samples of human, ox-, and horse-serum are separated by fractional precipitation with ammonium sulphate solution it is necessary that this be exactly neutral if comparable results are to be obtained in the analysis of the fractions. The proteins obtained thus from kidneys, liver, and lungs are chemically different from each other and from those derived from serum or musculature. W. MCCARTNEY.

**Protein-carbohydrate groupings in plasma of** animals. H. BIERRY (Compt. rend., 1930, 191, 1381—1382).—Plasma-proteins are autoclaved with dilute potassium hydroxide solution (N/3 or N/6) at 120° for  $\frac{1}{2}$  hr. and the polysaccharide is precipitated with 8 vols. of spirit. Acid hydrolysis of this material gives *d*-mannose and *d*-galactose.

P. G. MARSHALL.

Determination of carbon and nitrogen in the total crystalloid substances in blood-serum. A. BOIVIN (Compt. rend. Soc. Biol., 1930, 103, 153—155; Chem. Zentr., 1930, ii, 260).—The values obtained with the filtrate from precipitation with sodium tungstate (Folin and Wu) do not differ from those obtained with the ultra-filtrate of the tenfold diluted serum by more than 5%. Increase or decrease of the concentration of sulphuric acid (0.67N) leads to incorrect results. A. A. ELDRIDGE.

Blood-creatinine. O. H. GAEBLER (J. Biol. Chem., 1930, 89, 451-466).—The previous work (A., 1928, 437) on the isolation of creatinine from protein-free blood-filtrates has been repeated, using, however, magnesium oxide instead of lead hydroxide for the decomposition of the precipitate with Lloyd's reagent. Preliminary treatment of the blood-filtrates with kaolin renders the isolation of creatinine impossible whilst leaving the chromogenic value of these filtrates for Jaffe's reaction unaffected. It therefore appears that blood contains a substance other than creatine or creatinine which yields the latter when the above-mentioned isolation procedure is employed.

C. R. HARINGTON.

Folin's method for determining blood-aminoacids. P. M. RE and D. POTICK (Compt. rend. Soc. Biol., 1930, 103, 1283—1285; Chem. Zentr., 1930, ii, 592).—Folin's method gives accurate results only when the amino-acid does not exceed 5 mg. per 100 c.c. Trichloroacetic acid is preferred to tungstic or phosphotungstic acid as protein precipitant for blood. A. A. ELDRIDGE.

Colorimetric determination of blood-nitrogen. A. CASSUTO (Presse méd., 1930, 38, 1155—1157).— Blood-filtrate (after use of trichloroacetic acid) is digested with sulphuric acid and copper sulphate; nesslerisation follows. CHEMICAL ABSTRACTS. Deproteinising blood-serum. G. TURNER (J. Lab. Clin. Med., 1930, 15, 720-723).—A method for the electrolytic precipitation of protein from antitoxic sera is described. CHEMICAL ABSTRACTS.

Analysis of the osmotic pressures of serumproteins, and mol. wt. of albumin and globulins. G. S. ADAIR and M. E. ROBINSON (Biochem. J., 1930, 24, 1864-1889).-Serum-albumin can be recrystallised four times without change in the mol. wt. (cf. Svedberg and Sjögren, A., 1929, 203). Adair's methods for the determination of mol. wt. of proteins in non-ideal solutions have been developed with the special purpose of determining the mol. wt. of serumproteins in the physiological range of hydrogen-ion and salt concentrations. The mean value of the mol. wt. of horse-serum albumin in 27 experiments was  $72,000\pm3000$ . One preparation gave a value of 67,000. Sorensen's provisional estimate of 45,000 when corrected for deviation from the ideal solution laws is 74,000. Preliminary determinations indicate that the scrum-albumins of the ox and sheep have mol. wt. about 70,000. The mean value of the mol. wt. of the unfractionated globulin of the horse is 175,000 (maximum and minimum 182,000 and 154,000 in 17 experiments). The unfractionated globulins of the ox and the sheep gave similar results. Euglobulin prepared by a rapid method resembles total globulin, and the mol. wt. obtained by the authors is, therefore, higher than the value obtained by Svedberg, namely, 103,800. The osmotic pressure of the total serumprotein before fractionation has been studied from the point of view of Dalton's law of partial pressures and it appears that serum-protein is not a compound of albumins and globulins. The state of aggregation of the proteins in the untreated serum appears to be the same as their state of aggregation in the purified proteins prepared by the methods used in this work. The protein solutions which have been examined are beyond the range of application of Donnan's formulæ for osmotic pressure. Methods for determining  $p_i$ , the pressure due to the excess of diffusible ions inside the membrane, in non-ideal solutions are described and calculations of  $p_i$  and of  $p_p$ , the partial pressure of the protein ions, have been made. A method is suggested for ascertaining the valency of the protein ions in non-ideal solutions. S. S. ZILVA.

Comparison of colorimetric and electrometric methods for determination of the  $p_{\rm H}$  of serum or plasma. R. J. FOSBINDER and J. W. SCHOONOVER (Biochem. J., 1930, 24, 1805–1810).—The colorimetric method of Hastings and Sendroy (A., 1924, ii, 869) may be used with accuracy for the determination of the  $p_{\rm H}$  of blood or plasma at 38°. Determinations carried out at 38° on 28 samples of diluted plasma from cancerous and normal subjects reveal no discrepancy between the colorimetric and glass electrode methods. The  $p_{\rm H}$  of normal plasma or blood lies between 7.35 and 7.38. S. S. ZILVA.

Determination of alcohol in blood, T. HIRA-MATSU (Sei-i-kwai Med. J., 1929, 48, No. 12, 21—51).— The method depends on the proportionality between the intensity of the black colour produced by interaction between osmic acid and alcohol with the concentration of the alcohol. For 0.02% 30 hrs.' development is required. The alcohol should be removed from the blood by distillation. Alcohols other than ethyl give the reaction, but ketonic substances do not interfere. CHEMICAL ABSTRACTS.

A volatile organic chlorine compound in blood. N. MORRIS and S. MORRIS (Biochem. J., 1930, 24, 1716-1722).-After preliminary drying of serum the amount of chlorine recovered is less than when no drying is employed. This is due to the loss of chlorine in the form of a volatile organic chlorine compound. The corpuscles of the blood contain a much greater amount of this volatile compound. The maximum of volatilisation takes places when the drying has proceeded for at least 400 hrs. The amount of chlorine lost by distillation can be accounted for in the distillate. When compounds such as urea, histamine, glycine, and primary and secondary amines are added to the blood in progressively increasing amounts, the curve showing the effect of concentration of the added substance on volatile chlorine resembles the coagulator concentration curves. The addition of ammonium sulphate yields a similar curve, although the maximum and minimum values are lower than those found with urea. When a chloride or a very dilute acid is added the results obtained are the inverse of those obtained with NH2 or NH1 groups, producing an increase in the amount of volatile chlorine. There is a gradual decrease in the volatile organic chlorine to a value which remains steady at about 5 milliequiv. below the original, when mixtures of blood and coagulator are kept before drying. Thereafter prolonged keeping does not appreciably alter the amount of volatile S. S. ZILVA. chlorine.

Blood-cholesterol balance. L. BUGNARD and C. SOULA (Compt. rend., 1930, 191, 1382—1384).— The cholesterol content of venous plasma is higher than that of arterial plasma by 0.13 g. per litre. Lowering the  $p_{\rm H}$  of blood increases the cholesterol content of plasma and vice versa, although with separated plasma such variations do not occur. The partition between plasma and corpuscles is controlled by the reaction of the medium. P. G. MARSHALL.

Blood-calcium and oxalate precipitation. Partition of calcium between corpuscles and serum or plasma. C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1930, 12, 1269-1297).-The methods of blood-calcium determination are investigated. Precipitation by ammonium oxalate is shown to be incomplete; the method finally adopted is a modified combination of those of Kramer and Tisdall (A., 1921, ii, 595, 655) and of Hirth (A., 1923, ii, 698). The blood is deproteinised by trichloroacetic acid, the filtrate digested with nitroperchloric acid, taken to dryness, and the calcium in the residue determined. The total plasma- and serum-calcium are equal, whilst the erythrocytes contain a small but varying amount of calcium. F. O. HOWITT.

Fission of tributyrin in the blood and serum of various animals. W. TAKAHASHI (Pflüger's Archiv, 1930, 225, 42–48; Chem. Zentr., 1930, ii, 1243).—The order of diminishing ability of blood to cause fission of tributyrin is : rabbit, cat, horse, man, dog, ox. In cat's and horse's blood the serum contains the active agent. A. A. ELDRIDGE.

Physiological blood coagulant. O. BEYER (Chem.-Ztg., 1930, 54, 1007).—A solution containing the substance which causes formation of thrombin with subsequent stasis and coagulation of the blood is obtained by extracting ox-liver with alcohol, precipitating the extract with ether, and dissolving the wax-like precipitate in water. The solution can be sterilised in steam at  $95^{\circ}$  for  $\frac{1}{2}$  hr. without decrease in activity. F. O. HowITT.

Blood coagulation. H. J. FUCHS (Klin. Woch., 1930, 9, 243-245; Chem. Zentr., 1930, i, 3804-3805). -Blood coagulation is regarded as consisting of two simultaneous processes: (1) The blood-corpuscles contain prothrombin-cytozyme, which forms thrombin with the plasma-calcium ions. In hæmophilia or after injection of peptone the excess of antiprothrombin is so great that the formation of thrombin is arrested and the conversion of fibrinogen into fibrin is retarded. (2) Prothrombin is present in plasma only as antiprothrombin, a carbohydrate-like substance which passes from the liver into the blood, and is thereby inactivated for plasma coagulation. If sufficient free prothrombin is not present, but enough cytozyme is available, thrombin is formed in presence of calcium ions. Cytozyme phosphatides, but not prothrombin or antiprothrombin, possess species A. A. ELDRIDGE. specificity.

Mechanism of passage of clot-arresting substances (antiprothrombin) into the blood after injection of Witte's peptone. M. VON FALKEN-HAUSEN (Z. gcs. exp. Med., 1930, 70, 535—542; Chem. Zentr., 1930, i, 3805).—Intravascular injection of Witte's peptone into the goose, as into the dog, leads to uncoagulability of the blood. If the liver is removed, acceleration of blood coagulation is observed. Hence the antiprothrombin arises chiefly from the liver. The action of the peptone is attributed to that of a phosphatide. A. A. ELDRIDGE.

Specific agglutination and precipitation. I. Mechanism of the reactions. H. EAGLE (J. Immunol., 1930, 18, 393-417).—Agglutinating and precipitating antibodies are a specifically altered fraction of the serum-globulin. The antigen-antibody complex, regardless of its type, contains this antibodyglobulin. The factors determining specific flocculation are discussed. The hydrophilic antigen is covered with a film of immune globulin, denatured by its combination with antigen. In the absence of electrolytes the charge due to the ionisation of this protein is sufficient to prevent aggregation; minute concentrations of electrolyte, however, depress this surface charge below the critical value necessary for stability. The optimum hydrogen-ion concentration for flocculation is intermediate between that of the original cell and that of the antibody-globulin.

CHEMICAL ABSTRACTS.

Antigenic properties of yeast-invertase. K. MATSUOKA (Z. physiol. Chem., 1930, 193, 167—170).— Intravenous injection of invertase from beer-yeast autolysate into rabbits yielded a serum which inhibited the inverting capacity of the enzyme (cf. Knaffl-Lenz, A., 1922, i, 694). Addition of pig's serum as activator to the invertase preparation increased the production of the inhibitor. Injection of sucrose did not produce a serum capable of inverting this sugar unless pig's serum was added as activator. J. H. BIRKINSHAW.

Highly unsaturated fatty acids of the brains of the ox, pig, and sheep. J. B. BROWN and W. C. AULT (J. Biol. Chem., 1930, 89, 167-171).-The brain-tissue was hydrolysed with sodium hydroxide; the soaps were extracted with butyl alcohol, and the fatty acids liberated by treatment of the extract with hydrochloric acid. The acids were brominated in ethereal solution and the insoluble bromides converted into the methyl esters of the corresponding unsaturated acids. The high iodine values (340-350) of this material from the brains of the ox and sheep confirm the previous suggestion of the occurrence of tetracosapentenoic acid (A., 1929, 1329). Pig's brain yielded a preparation with iodine value corresponding with that of methyl arachidonate, the presence of which was, however, excluded by the fact that the bromide did not melt below 250°; the presence of an isomeride of arachidonic acid is suggested.

C. R. HARINGTON.

Cephalin from human brain. H. RUDY and I. H. PACE (Z. physiol. Chem., 1930, 193, 251-268).— In the characterisation of cephalin the titration value, which corresponds with the amino-nitrogen value, is employed. It may also be used to determine the cephalin content of lecithin-cephalin mixtures. Unhydrolysed cephalin gives, in water, aminonitrogen values about 10% too high. In human brain, besides the cephalins of low carbon content, there are cephalins present of high carbon content, there are cephalins present of high carbon content, gorresponding fairly well with the theoretical value. Barium salts of cephalin were obtained and used in separating cephalin from mixtures of cephalin and lecithin. J. H. BIRKINSHAW.

Placental enzymes. WEHEFRITZ and E. GIER-HAKE (Arch. Gynäkol., 1928, 135, 212—222; Chem. Zentr., 1930, ii, 252).—The placenta, of whatever age, contains arginase in quantity unrelated to the age. Preformed urea or urease could not be detected in the placenta. A. A. ELDRIDGE.

Glycogen of rabbit's liver. M. SAHYUN and C. L. ALSBERG (J. Biol. Chem., 1930, 89, 33-39).-Fresh rabbit's liver was extracted by grinding with two successive portions of 3% aqueous trichloroacetic acid; the extracts, after clearing on the centrifuge, were treated with 2 vols. of 95% alcohol. The precipitated glycogen was dissolved in 3% trichloroacetic acid, again precipitated with alcohol, and then repeatedly dissolved in water and precipitated with alcohol, if necessary with addition of a little ammonium acetate. After dehydration with alcohol and ether followed by drying over calcium chloride, the glycogen had 0.2% of ash (including traces of calcium and iron) and 0.032% of phosphorus; when hydrolysed it yielded more than 95% of the theoretical amount of reducing sugar. When heated to 105° the glycogen C. R. HARINGTON. became less soluble.

Change in the colloidal condition of the muscleproteins in mortification and in fatigue. H. J. BRITISH CHEMICAL ABSTRACTS .- A.

DEUTICKE (Pflüger's Archiv, 1930, 224, 1-43; Chem. Zentr., 1930, i, 3808).—On long preservation, minced muscle loses the property of forming hexosediphosphoric acid from phosphoric acid and carbo-hydrate in presence of fluoride. Physico-chemical changes in the muscle-protein take place, the solubility in various salt solutions diminishing. The same changes were observed in isolated and in minced frog's muscle during rigor. The protein of fatigued isolated frog's muscle also is less soluble. Both changes were observed in living muscle after severe A. A. ELDRIDGE. insulin convulsions.

Effect of various buffer mixtures on the solubility of protein of active, fatigued, dying, and rigid muscle. J. HENSAY (Pflüger's Archiv, 1930, 224, 44-61; Chem. Zentr., 1930, i, 3088; cf. preceding abstract).—Under otherwise similar conditions the solubility of muscle-proteins in potassium salt solutions is greater than that in sodium salt solutions, and in phosphate mixtures greater than in acetate mixtures. The solubility in buffer mixtures is least at  $p_{\rm H}$  5. With increase in the salt content of the extractive medium the absolute quantity of protein dissolved increases. The "ageing" of muscle-protein was shown by increase in solubility (at  $p_{\rm fl}$  4 in an acetate mixture); with a phosphate mixture the solubility always diminished for given  $p_{\rm H}$  and concentration values. Similar solubility changes were exhibited by fatigued muscle; in rigor the solubility in phosphate diminished and in strongly acid acetate either diminished or was unchanged.

A. A. ELDRIDGE. A. A. ELDRIDGE. Muscle-globulin (myosin). II. Properties. J. T. EDSALL. III. Anisotropy and vortex angle. IV. Streaming anisotropy. A. L. von MURALT and J. T. EDSALL (J. Biol. Chem., 1930, 89, 289-313, 315-350, 351-386).-II. Fresh muscle is mineed and extracted at a low tormersture with dilute minced and extracted at a low temperature with dilute potassium chloride solution buffered with phosphate at  $p_{\rm H}$  7.0—8.5; the globulin is precipitated from the extract by dilution with water. After purification by repeated re-dissolution in dilute salt solution and precipitation by dilution or by salting out it forms a viscous fluid which cannot be crystallised. The acidand base-binding capacity of the protein is at a minimum over the range  $p_{\rm II}$  6.2—6.6. At  $p_{\rm II}$  5—6 the globulin is insoluble in all concentrations of salt; at reactions more acid than  $p_{\rm ff}$  5 0 or more alkaline than  $p_{\rm In}$  10.0 no salt is required for its dissolution. In potassium phosphate solution at  $p_{\rm H}$  7.4 the protein is almost insoluble at ionic strengths up to 0.25; as the ionic strength increases to 0.4 the solubility shows a sudden large increase, followed by a decrease, until at ionic strength 3.5 solubility has again become very low. Myosin is also precipitated at 0° and  $p_{\rm H}$  7.0 by 4.4-4.6M-sodium chloride and by one third saturation with neutralised ammonium sulphate. Associated with its high degree of hydration it exhibits a high degree of viscosity. In the almost complete absence of salt at the isoelectric point myosin forms gels the rigidity of which is much increased by addition of small amounts of alkali.

III. Solutions of myosin exhibit streaming anisotropy. The concentric cylinder apparatus and

technique employed for the investigation of this phenomenon are described. The vortex angle of all preparations ranged from 65° to 78°, the precise value being determined by concentration and by the angular velocity of the rotating cylinder; it was independent of the age of the solutions, which differed in this respect from the vanadium pentoxide sols examined by Freundlich and others (A., 1925, ii, 199, 200; 1926, 241). Rise of temperature decreased the vortex angle, this effect being correlated with coincident changes in the viscosity of the solution. Gels of myosin showed abnormal behaviour, there being observed two vortex crosses, one at an angle of 63° for the part of the solution in opposition to the fixed cylinder, and one at 45° in the part near the rotating cylinder, the intermediate part of the solution appear-ing as an isotropic ring. This phenomenon is ascribed to the thixotropic character of the gel, which becomes liquefied in the region near the fixed cylinder where the shearing stresses are greatest; the vortex angle of  $45^{\circ}$  in the rigid part of the gel is due to elastic deformation. The constancy of the vortex angle  $(77.5-78.5^{\circ})$  for solutions of moderate or high concentration at 2-4°) is taken to indicate that the anisotropic myosin is present in solution in particles of uniform and constant shape. The mechanism of the formation of the vortex cross is discussed.

IV. The streaming double refraction of myosin solutions has been quantitatively measured with the aid of a Senarmont compensator, and it is found that double refraction and angular velocity are related, at constant temperature and  $p_{II}$ , in a manner which is characteristic for a given concentration of protein and is independent of the age of the solution. Denaturation of the protein by any means abolishes the phenomenon of streaming anisotropy altogether. The latter is therefore a characteristic property of myosin, and the fact that different preparations fail to exhibit entirely identical relationships is due to the incomplete removal of contaminating isotropic proteins. The results are discussed in their relation to the anisotropy of muscle fibres.

C. R. HARINGTON.

Biose of chitin. M. BERGMANN, L. ZERVAS, and E. SILBERKWEIT (Naturwiss., 1931, 19, 20).— Hydrolysis by acetylation of the chitin of crab results in the separation of the octa-acetyl derivative, m. p.  $289^{\circ}$ ,  $[\alpha] + 50^{\circ}$  in acetic acid, iodine value 31.3, of a disaccharide, chitobiose. F. O. HOWITT.

Zinc content of rat's liver at various ages. G. BERTRAND and (MME.) Y. BRANDT-BEAUZEMONT (Compt. rend., 1930, 191, 1410-1411).-The zinc content of the livers of white rats has been deter-mined at the ages of 1, 15, and 30 days, and at 7 months, the mean values being, respectively, 114.31, 51.31, 36.84, and 32.42 mg. of zinc per 100 g. of dried liver. Thus in agreement with previous results relating to the whole rat (A., 1930, 953) the quantity of zinc present decreases progressively with increase in J. W. BAKER. age.

Microchemical detection of urease in tissue. P. B. SEN (Indian J. Med. Res., 1930, 18, 79-82).-Use is made of the interaction of urease with urea to form

ammonium carbonate, which then affords insoluble heavy-metal carbonates. CHEMICAL ABSTRACTS.

Rapid method for tissue diagnosis. C. F. GESCHICKTER, E. P. WALKER, A. M. HJORT, and C. H. MOULTON (Stain Tech., 1931, 6, 3–12).—The following procedure is suitable for either fresh or formalin-fixed frozen sections. The sections are collected from the microtome in a solution containing potassium dihydrogen phosphate (6.75 g.), N-sodium hydroxide (30 c.c.), distilled water (570 c.c.), glycerol (200 c.c.), 95% alcohol (200 c.c.). They are then stained for 20—30 sec. in a bath containing thionine eosinate (0.75 g.), barium eosinate (0.25 g.), azure-A (0.25 g.), dissolved in 100 c.c. of a mixture of ethylene glycol (4 parts) and 95% alcohol (1 part) with 0.2% of glacial acetic acid. The excess of stain is then removed in two successive changes of 20% glycerol in 95% alcohol. The sections are then dehydrated for 10—15 sec. in diethylene glycol monobutyl ether and finally cleared in *n*-butyl phthalate for 20 sec., when they are ready for mounting. H. W. DUDLEY.

Glycogen. III. Glycogen in pigeon's lenses. S. HARADA (Sei-i-kwai Med. J., 1929, 48, No. 12, 1— 20).—The lenses of pigeons, but not of dogs or rabbits, contain glycogen; in polyneuritic pigeons the amount is often subnormal.

CHEMICAL ABSTRACTS.

Phosphatides. II. Highly unsaturated fatty acids in the phosphatide from different organs. E. KLENK and O. VON SCHOENEBECK (Z. physiol. Chem., 1931, 194, 191—192; cf. this vol., 112).—The unsaturated acids are separated from the total fatty acids of the phosphatide from ox-liver by Tsujimoto's method (A., 1921, i, 78), converted into their methyl esters, and fractionated. Hydrolysis of the highboiling fraction (iodine value 249) after reduction, gives erucic acid, also obtained similarly from brainlecithin. Bromination of the unsaturated acids from the liver-phosphatide affords, in addition to ethersoluble products, some insoluble arachidonic acid octabromide. H. BURTON.

Mucin of articular liquids. C. ACHARD and M. PIETTRE (Compt. rend., 1930, 191, 1412-1414).--After separation of fibrinous clots by centrifuging, precipitation of articular liquid with an equal volume of acetone causes separation of a synovial mucin (larger volumes of acetone are necessary to cause flocculation of the proteins), purified by repeated precipitation from its aqueous solution with acetone and washing with dry ether. The sulphur content of the powder, dried in a vacuum over sulphuric acid, is 0.70%, that is, only half that normally present in serum-proteins. Also the viscosity of a 0.8% aqueous solution ( $\eta^{20}$  5.389) is much greater than that of a solution of serum-proteins of the same concentration  $(\eta^{20} \ 1.090).$ J. W. BAKER.

Determination of protein in cerebrospinal fluid and other body-fluids. I. BERGER (Klin. Woch., 1930, 9, 888—889; Chem. Zentr., 1930, ii, 592—593).—The turbidity caused by the addition of sulphosalicylic acid is compared (apparatus described) with that produced in a standard solution of protein. A. A. ELDRIDGE. Extra-hepatic production of bile-pigments in surviving organs. V. Z. ERNST and E. HALLAY (Biochem. Z., 1930, 228, 354—365; A., 1925, i, 732).—No relation could be found between the amount of bile-pigment in the parenchyma of the surviving spleen of the dog and the number of red blood-corpuscles which are decomposed there during perfusion. W. MCCARTNEY.

Polarimetric determination of bile acids in body-fluids and organs. F. ROSENTHAL (Arch. exp. Path. Pharm., 1930, 157, 165—177).—The method given by Hoppe-Seyler ("Handb. Chem. Analyse," 1893, p. 451) has been modified. Thus for liver tissue etc. optically active sterols are removed by ether after saponification by potassium hydroxide, and the acidified aqueous layer is concentrated and treated with magnesium sulphate. The bile acids are extracted from the precipitate with alcohol, the extract is evaporated to dryness, treated with potassium hydroxide and hydrogen peroxide, made up to a known volume in 65% alcohol, and the rotation determined. F. O. Howrtt.

Determination of bile salts in bile ; gasometric determination, formol titration, and biliary sulphur determination. L. CUNY (J. Pharm. Chim., 1930, [viii], 12, 485–498, and Bull. Soc. Chim; biol., 1930, 12, 1298–1318; cf. A., 1929, 592). -The gasometric determination of bile salts, depending on the determination of amino-nitrogen before and after alkaline hydrolysis, is affected by the interval necessary between the two dcterminations, and a modified process is described in which free aminoacids, urea, and ammoniacal nitrogen are oxidised with sodium hypobromite previous to hydrolysis of the bile salts, which are unaffected by the hypobromite. As a control method the bile, after treatment with alcohol and subsequent filtration, is treated with sodium hypobromite and hydrolysed, and, after elimination of cholalic acid and carbonates, neutral formaldehyde is added and the liquid titrated with baryta solution. A modification of the benzidine method for the volumetric determination of sulphur in body-fluids is adapted to the determination of biliary sulphur. E. H. SHARPLES.

Human milk : (a) carbohydrates ; (b) analysis. M. POLONOVSKI and A. LESPAGNOL (Bull. Soc. Chim. biol., 1930, 12, 1170—1194, 1195—1211).—(a) The disagreement in lactose content of human milk as determined by rotation and reducing power is explained by the presence of other carbohydrates. The residue from alcohol precipitation and ether extraction of fat on fractional crystallisation from methyl alcohol yields "gynolactose," m. p. about 205°,  $[\alpha], -12°$ . In addition, a third carbohydrate occurs which has a low dextrorotatory power and yields galactose on acid hydrolysis. Some physical properties of these new sugars are described.

(b) The carbohydrates are determined by precipitation with silicotungstic acid, oxidation of the filtrate with dichromate, and iodometric titration of excess of dichromate, lipins by extraction of the silicotungstic acid precipitate by ether, and caseinogen by the volumetric method of Baudouin and Lewin (A., 1927, 476). F. O. HowITT. Does the antirachitic vitamin exist in human milk? A. MACOHI and P. SCALPATI (Arch. Ist. Biochem. Ital., 1930, 2, 625—638).—Human milk contains varying amounts of the antirachitic vitamin. T. H. POPE.

Lactenin. F. S. JONES and H. S. SIMMS (Science, 1930, 72, 456-457).—The properties and possible uses of the substance in milk named lactenin, which inhibits the growth of certain bacteria, are summarised. L. S. THEOBALD.

Phrynolysin. L. Gózony and F. HOFFENREICH (Zentr. Bakt. Par., 1930, 115, 377-383; Chem. Zentr., 1930, i, 3068) .- Phrynolysin, the cutaneous gland fluid of Bombinator igneus, possesses agglutinating and hæmolytic properties, the latter being difficult to conserve, as it is much weakened by alcohol, chloroform, or ether. The toxin acts differently at different times and on different animals. An acid reaction inhibits toxicity, but an alkaline reaction promotes it; with phosphate buffer mixture it is first noticeable at  $p_{\rm H}$  7.4. Phrynolysin contains lipase as well as a diastatic enzyme, but a proteolytic enzyme could not be detected. It agglutinates leucocytes, liver cells, and semen. Attempts to prepare the pure toxin failed. It contains albumin, however, and the ninhydrin reaction is strongly positive. Bile acid could not be detected.

L. S. THEOBALD.

Clinical test for urinary acetone and acetoacetic acid. J. A. BEHRE (J. Lab. Clin. Med., 1928, 13, 770-772).—The pink colour produced when salicylaldehyde is heated with acetone is employed to detect acetone and acetoacetic acid in urine; 1 mg. of acetone, or the equivalent amount of acetoacetic acid, in 100 c.c. can be detected. Addition of a drop of dilute aqueous potassium dichromate before the urine is heated partly overcomes the inhibiting effect of formaldehyde. CHEMICAL ABSTRACTS.

Determination of urinary sugar by Bertrand's method. F. JÜSTEN (Arch. Pharm., 1930, 268, 559-565).—A modification of Bertrand's method is described in which the standard solutions of the D. A. B. VI are used. The dextrose content may then be obtained from Allihn's tables, but it is given with sufficient accuracy, when the urine is diluted to contain 0.1-0.75% of dextrose, by the expression 3.30n mg., where n c.c. of 0.1N-permanganate are required to reoxidise the ferric sulphate reduced by the cuprous oxide formed. A further check is given by the iodometric determination of the excess of Fehling's solution (cf. A., 1929, 1099).

H. E. F. NOTTON. Determination of sulphide-sulphur in fæces. J. S. LORANT and F. REIMANN (Biochem. Z., 1930, 228, 300—309).—Air, freed from oxygen and sulphur dioxide, is drawn through an acidified suspension of fresh fæces in sodium borate solution, hydrogen sulphide being collected in zinc acetate solution. The sulphide being collected in zinc acetate solution. The sulphide content of this solution is then determined by the method of Lorant (A., 1930, 181). Hydrogen sulphide produced during digestion but ordinarily lost from the fæces can be fixed, possibly completely, in the fæces by administration of reduced iron or ferrous chloride. W. MCCARTNEY.

Trypsin preparations suitable for the prevention of adhesions. R. P. WALTON (J. Pharm. Exp. Ther., 1930, 40, 403—411).—Relatively stable active preparations of trypsin are obtained by extracting a dried trypsin powder with 75% glycerol in water and filtering the extract through a Chamberland filter under pressure, rejecting the first portion of the filtrate. The glycerol extracts are effective in proventing peritoneal adhesions when introduced into the peritoneal eavity (cf., Ochsner and Mason, Proc. Soc. Exp. Biol. Med., 1928, 25, 524). W. O. KERMAGK.

Tryptophan and histidine lack in pernicious anæmia. Hæmatogenic amino-acid therapy. G. FONTÈS and L. THIVOLLE (Compt. rend., 1930, 191, 1395—1397).—Liver extracts arc effective in the cure of pernicious anæmia only in so far as they contain tryptophan and histidine. Daily subcutaneous injection of 100 mg. of tryptophan and 200 mg. of histidine rapidly gives rise to a normal blood count, increase in hæmoglobin content, and increase in weight, all of which are maintained for at least 6 months without further treatment. P. G. MARSHALL.

Glutathione in pathological blood. K. VARELA, E. APOLO, and A. VILAR (Klin. Woch., 1930, 9, 1029—1030; Chem. Zentr., 1930, ii, 937).—The normal glutathione content of human blood is 47 mg. per 100 c.c.; in pathological conditions variations between the limits 28 and 66 mg. were observed. Low values are always observed in anemia, and usually in diabetes. A. A. ELDRIDGE.

Carcinogenic substances and their fluorescence spectra. E. L. KENNAWAY and I. HIEGER (Brit. Med. J., 1930, i, 1044-1046).—An attempt has been made to correlate fluorescence and carcinogenesis. The carcinogenic material formed by the action of aluminium chloride on tetrahydronaphthalene shows a bluish-violet fluorescence and gives a spectrum consisting of three bands at 4000, 4180, 4400 Å. The 1:2:7:8- and the 1:2:5:6-dibenzanthracenes give spectra of a similar type and produce cancerous tumours in mice. Other carcinogenic materials such as gasworks tar and its products, tars from yeast, muscle, and hair also show bands at the wave-lengths quoted above, but, on the other hand, certain materials such as crude oleic acid and benzyl oleate show the same spectrum but have not produced cancer. Further, non-fluorescent commercial tetralin has produced cancer in mice. The results suggest, however, the possibility of using fluorescence for a preliminary examination of materials suspected of carcinogenic L. S. THEOBALD. properties.

Formation of phospholipins during autolysis of normal and neoplastic tissue. A. H. ROFTO and L. M. CORREA (Bull. Soc. Chim. biol., 1930, 12, 1247—1254).—The phospholipin contents of the spleen and liver, both normal and in varying stages of tumour growth, were followed by the technique of Artom (A., 1926, 201). Liver tissue contains almost twice as much phospholipin as does tumour tissue, in both cases the amount being reduced by autolysis at 38° in presence of sodium fluoride. With tumour growth the phospholipin contents of fresh and autolysed tissue diminish and then remain constant, whilst the non-phosphorus lipins have a higher value and run a somewhat parallel course.

F. O. HOWITT. Metabolism of tumours. O. WARBURG (Biochem. Z., 1930, 228, 257—258).—In tumour tissues the injury to respiration is transmitted in cell division. P. W. CLUTTEBBUCK.

Correlation between arginine and vitamin-Bcontent of diets and effect of thyroxine on tumour growth. G. GILROY (Biochem. J., 1930, 24, 1659-1665; cf. A., 1930, 948, 1309, 1468).-Tumour growth is inhibited in implanted male mice kept on a diet deficient in arginine to an extent similar to that induced by a diet deficient in vitamin-B. When thyroxine is also injected there is a steady loss of weight and a high mortality in the animals. The addition of gelatin to the above diet and to a diet deficient in vitamin-B causes only a temporary recovery, whilst wheat germ induces a permanent increase in weight in unimplanted mice. Injection of arginine increases the loss of weight. Injections of thyroxine had a slight but definite inhibitory effect on tumour growth in spite of an increase in weight; the less marked effect in this second experiment is due to the larger quantity of food consumed by mice receiving thyroxine as compared with untreated controls.

S. S. ZILVA.

Vitamins and tumour growth. IV. Vitamin-B consumption by growing rat-tumour. W. NAKAHARA and E. SOMEKAWA (Proc. Imp. Acad. Tokyo, 1930, 6, 345—347; cf. A., 1929, 718).—The vitamin-B content of the liver of rats fed on a diet deficient in vitamin-B is not reduced by inoculation of the animal with rapidly growing Fujinawa ratsarcoma. It is concluded that vitamin-B consumption by the tumour is negligibly small.

A. COHEN.

Colloidal osmotic pressure of the blood in diabetes mellitus. I. M. RABINOVITCH (Arch. Int. Med., 1930, 46, 752—767).—The colloidal osmotic pressure was frequently higher than the value expected from the protein content. This phenomenon was associated with hypercholesterolamia, to which it is considered to be due. High blood-pressures were shown by diabetics with hypercholesterolamia and cedema. It is suggested that the hypertension is necessary to overcome the increased colloidal osmotic pressure of the blood for urinary secretion.

# G. F. MARRIAN.

Lipæmia. Effect of insulin on blood-fat and on alimentary lipæmia in normal and diabetic man. N. I. NISSEN (Acta med. Scand., 1930, 73, 99—124; Chem. Zentr., 1930, ii, 259).—The neutral fat-cholesterol values in normal fasting persons varied during 6 hrs. from 0.081 to 0.088 mg. per 100 c.c.; after oral administration of dextrose (100 g.) 0.058—0.071; in obesity 0.082—0.094. After intravenous injection of dextrose, or in diabetes, similar values were observed. Values after subcutaneous injection of dextrose were: normal, 0.067—0.77, diabetic 0.082—0.100. The blood-fat after administration of 60 g. of fat reached 0.100 mg. per 100 c.c. (normal), 0.146 mg. (obese). Administration of insulin in either case did not affect the lipæmie curves. A. A. ELDRIDGE. Relation of the plasma-sugar to the corpusclesugar in normal and diabetic individuals. H. J. JOHN (J. Lab. Clin. Med., 1930, 15, 713— 719).—The red corpuscles of diabetic individuals are less capable of absorbing and retaining sugar than those of normal individuals; normally the corpuscular sugar is slightly lower than the plasma-sugar.

#### CHEMICAL ABSTRACTS.

Favus. R. BINAGHI and G. FALCONI (Annali Chim. Appl., 1930, 20, 547—558).—The pungent perfume of the flowers and fresh seeds of *Vicia faba*, or ingestion of the raw or cooked seeds, is regarded as the cause of favus, which occurs more especially in Sardinia, where beans are eaten in large quantities. A glucosidic compound, vicin, which is not cyanogenetic, a phytosterol (viciosterol), and a sugar not yet identified have been isolated from the beans.

T. H. POPE.

Goitre survey in albino rats. R. McCARRISON (Brit. Med. J., 1930, i, 989—992).—Vitamin-deficiency is the direct or indirect cause of goitre. Iodine has an effect only when administered to deficiently fed rats, and in these cases goitre formation is favoured. L. S. THEOBALD.

Nutrition and the action of the thyroid gland. I. Influence of caseinogen on the metabolism of hyperthyroidism. II. Significance of vitamins on the course of experimental thyroidism [with M. KNUCHEL and W. SPICHTIN]. III. Influence of nutritive mixtures on the metabolic disturbances of hyperthyroidism. I. ABELIN (Biochem. Z., 1930, 228, 165-188, 189-210, 211-232).--I. Various glandular organs, especially the liver, form a means of protection against the flooding of the organism with thyroid hormone. When thyroid is first administered, the liver retains large amounts and converts it into products which are excreted in the bile. With further administration, the liver gradually loses the power of storing glycogen, of metabolising fat, and of forming creatine and creatinine. The excess of hormone is also used by muscle, heart, respiratory organs, and intestine, and these also lose their glycogenstoring power. Accompanying changes of metabolism occur also in the nervous system, especially the central nervous system. The livers of rats fed with caseinogen and excess of thyroid do not lose their glycogen-storing power as quickly as when thyroid alone is administered, caseinogen having a protective action on the liver.

II. The disturbances due to administration of thyroid are also alleviated by feeding vitamin-rich products (cod-liver oil, egg-yolk, yeast, tomato, carrots, spinach), the presence of vitamins-A and -B being especially important; administration of bone marrow is especially beneficial.

III. Tables summarise the results of metabolism experiments with rats, showing experimental hyperthyroidism, on a number of diets containing caseinogen, fats, vitamins, etc., and confirm the conclusions of the previous papers. P. W. CLUTTERBUCK.

Inflammation. III. Fixation of a metal in inflamed areas. IV. Fixation of foreign protein at site of inflammation. V. MENKIN (J. Exp. Med., 1930, 51, 879-887; 52, 201-213).-The fixation of iron, injected as colloidal iron or ferric chloride, in inflamed tissue is described; foreign protein, when injected, likewise accumulates in inflamed tissue. CHEMICAL ABSTRACTS.

Non-sugar reducing substances of human blood in pathological conditions. F. K. HERBERT and M. C. BOURNE (Biochem. J., 1930, 24, 1787-1793).-The concentration of the non-diffusible reducing substance, which is most probably glutathione, in whole blood varies with the hæmatocrit reading for the corpuscle volume. The results in one case of myelogenous leucæmia suggest that the concentration of non-diffusible reducing substance in leucocytes and ervthrocytes is of the same order. The concentration of the non-diffusible reducing substance in corpuscles varies, but in the majority of cases the variation from the normal average is within experimental error. In two cases of marked secondary polycythæmia the non-diffusible substance is above the normal average. S. S. ZILVA.

Lipoid nephrosis. H. MOORE and W. R. O'FARRELL (Brit. Med. J., 1930, ii, 242-243, 243-244).-The condition, which included reversal of the blood-albumin : globulin ratio with marked diminution of total protein, was ameliorated, with rise in serumprotein, by treatment which included administration of thyroxine, hydrochloric acid, and iron.

CHEMICAL ABSTRACTS. Boltz test in urine analysis. A. T. BRICE (Arch. Int. Med., 1930, 46, 778-781).—The Boltz test with acetic anhydride and sulphuric acid (Amer. J. Psychiat., 1923-1924, 3, 111) was used to examine urines from different types of medical and surgical cases. Negative reactions were given by urines from normal males on an average diet. A high percentage of positive reactions was given by urines from cases of degenerative diseases of the kidneys, acute infections, and appendicitis. Many of the positive reactions were obtained with protein-free urines. The reaction is believed to be due to the presence of an amino-acid. It may prove to be of value for the early diagnosis of kidney disease.

### G. F. MARRIAN.

Nature of the sugar inpentosuria. A correction. I. GREENWALD (J. Biol. Chem., 1930, 89, 501) .- The sugar isolated from the urine (A., 1930, 1311) should be described as l-xyloketose. C. R. HARINGTON.

Rickets. IV. Concentration of inorganic phosphorus in the blood in rickets. G. A. CHAIN (Zhur. exp. Biol. Med., 1929, 13, 56-59).-The blood-phosphorus [inorganic] increases when the blood is kept; the increase takes place more slowly in serum. The blood-phosphorus in rachitic children is 2.9 mg. per 100 c.c. (normally 5.1 mg.). In rats with experimental rickets the blood-phosphorus falls from 11.4 to 4.4 mg. per 100 c.c., but the fall can be prevented by the administration of fish oils.

### CHEMICAL ABSTRACTS.

Calcium content of striated muscle of rachitic animals. V. G. HAURY (J. Biol. Chem., 1930, 89, 467-469).-Striated muscle of normal rats contains on the average 74.0 mg. of calcium per 100 g., that of rachitic rats 41.6 mg. per 100 g. C. R. HARINGTON.

Serum-chlorides and chloride excretion in experimental scurvy. L. RANDOIN and A. MICHAUX (Compt rend., 1930, 191, 1378-1380) .--Chloride retention is found in guinea-pigs kept on a vitamin-C-deficient diet, a further proof of the development of nephritis on such a diet.

#### P. G. MARSHALL.

Hypertrophy and atrophy of muscular organs. IV. Right ventricle in tricuspid insufficiency. J. JACOBI and H. WASSERMEYER. V. Heart-muscle in experimental beri-beri. H. WASSER-MEYER (Arch. exp. Path. Pharm., 1930, 157, 234-243, 244-250).-IV. Extirpation of the tricuspid valve in the rabbit heart results in a primary increase in the ammonia content of the right ventricle muscle, and, 25-31 days after the operation, in a secondary phase with further increase of ammonia and reduction of glycogen contents which in the normal right ventricle are 0.00133+0.00014% of ammonia and 0.43+0.03% of glycogen.

V. In the normal pigeon's heart, the ammonia content (2-4 mg. per 100 g.), the post-mortem ammonia formation, and that on incubation at 38° in 2% sodium hydrogen carbonate solution show no difference from those of pigeons suffering from beri-beri. In the latter, however, the glycogen and the lipoidal phosphoric acid contents are higher than the normal  $(0.30 \pm$ F. O. HOWITT. 0.08% for glycogen).

Content of fibrinogen, albumin, and globulin in the plasma of tubercular guinea-pigs. C. VIDAL (Compt. rend. Soc. Biol., 1930, 103, 347-349; Chem. Zentr., 1930, i, 3069) .- In the first stages of infection the ratio albumin : globulin in the bloodplasma is less than normal; the lowering increases during the first three months after infection, but the ratio increases again during the final stages. The total protein content and the fibrinogen content are diminished at first, but are increased in the last stages. L. S. THEOBALD.

Copper and tuberculosis. P. SEABRA (Arch. Pharm., 1930, 268, 565-567).-The mean copper content, determined after incineration, by the method of Dick and Spacu (A., 1927, 746), of the lungs of three persons dying of tuberculosis was 0.1 mg., and that of three persons dying of other diseases, 0.9 mg. after making allowance for the copper content of the retained blood. The decrease in copper content appears to run parallel with the increasing extent of H. E. F. NOTTON. the lesions.

Metabolism of the albino rat during prolonged fasting at two different environmental temperatures. K. HORST, L. B. MENDEL, and F. G. BENEDICT (J. Nutrition, 1930, 3, 177-200).-The total metabolism of rats fasting at 26° was at a lower level than that of the group fasting at 16°, but the decrease in the total metabolism as the fast pro-gressed was greater. The basal metabolism of adult female rats fasting at 26° and about 24 hrs. after food was 600-700 g.-cal. per m.2 of body surface per CHEMICAL ABSTRACTS. 24 hrs.

Metabolism of nerves on stimulation. O. MEYERHOF and W. SCHULZE (Biochem. Z., 1930, 228. 1-5).-The criticisms of Winterstein (Pfluger's Archiv, 1930, 224, 749) of the work of Gerard, Meyerhof, et al. (A., 1928, 198, 910) on the metabolism of nerves in which the increased utilisation of oxygen and output of carbon dioxide of nerves during stimulation is shown to correspond closely with that required by the heat changes, are controverted. The close agreement relates to stimulation of the whole nerve and not to a local stimulation and to stimulation of peripheral nerves under the conditions laid down.

#### P. W. CLUTTERBUCK.

Effect of glycine on the oxygen demand of surviving organs. A. BORNSTEIN and H. F. ROESE (Pflüger's Archiv, 1929, 223, 498-508; Chem. Zentr., 1930, i, 3078).

Proliferation of rat and mouse epithelium and the thiol group. S. P. REMANN (Protoplasma, 1930, 10, 82-83).—Comparison of the effects of cresol and of thiocresol on rat and mouse skin shows that the thiol group has a stimulative effect on cell division.

Nuclein synthesis in the development of eggs. J. NEEDHAM and D. NEEDHAM (Compt. rend. Soc. Biol., 1930, 104, 671-674; Chem. Zentr., 1930, ii, 938).----There is practically no change in the extractable nucleoprotein-phosphorus during the development of A. A. ELDRIDGE. eggs of marine animals.

Colorimetric determination of the tyrosine and tryptophan content of various crude protein concentrates. W. D. MCFARLANE and H. L. FULMER (Biochem. J., 1930, 24, 1601-1610).-The tyrosine and tryptophan content of the proteins of butter-milk powder is much higher than that of the other crude protein materials examined. There is no appreciable difference in the tyrosine content of fish meal, cod-liver meal, meat meal, and tankage. In general the tryptophan content of fish meal is higher than that of meat meal, although conflicting results were obtained according to the methods used. The alkali digest of the crude protein materials contains a substance or substances (not indole), precipitable by mercuric sulphate and giving a blue colour with the phenol reagent, which, unlike tryptophan, is soluble in toluene. The results obtained after extraction of the alkali hydrolysates with toluene appear to represent the true tyrosine and tryptophan content of these protein concentrates.

#### S. S. ZILVA.

Embryonic mortality in the chick. I. Effect of diet on the nitrogen, amino-nitrogen, tyrosine, tryptophan, cystine, and iron content of the proteins and on the total copper of the hen's egg. W. D. McFarlane, H. L. FULMER, and T. H. JUKES (Biochem. J., 1930, 24, 1611-1631).-The source of protein in the diet of the hen has a marked influence on the mortality of the embryos during incubation. There is, however, no significant difference in the total nitrogen, total amino-nitrogen, tyrosine, tryptophan, and cystine content of the proteins of eggs of poor hatchability. The diet of the hen has no influence on these values nor on the total ash and iron content of the egg-yolk proteins. The copper content of the hen's egg varies considerably. S. S. ZILVA.

Arginine metabolism. I. Relation of arginine content of diet to increments in tissuearginine during growth. C. W. SCULL and W. C.

Rose (J. Biol. Chem., 1930, 89, 109-123).-The increase in the total arginine content of the growing rat on diets low in this amino-acid greatly exceeds the arginine ingested with the food, from which it is concluded that, for the rat at least, arginine is not an essential constituent of the diet. C. R. HARINGTON.

Proteopexic function of the liver. R. MARTENS (Bull. Soc. Chim. biol., 1930, 12, 1212-1246).-Variations in amino- and polypeptide-nitrogen of the blood entering or leaving the liver as determined by the amino-nitrogen in the filtrate from a trichloroacetic acid precipitation before and after acid hydrolysis were followed in normal and diseased animals and also after ingestion of gelatin, amino-acids, and meat. The normal liver is able to synthesise polypeptides (cf. Abderhalden and London, A., 1908, ii, 51), whilst the diseased liver has an efferent blood-stream with a content of amino-nitrogen much higher and of polypeptide-nitrogen only slightly higher than the normal. F. O. HOWITT.

Excretion of creatine-like substances as a function of the magnitude of the endogenous expenditure of nitrogen. E. F. TERROINE, R. BONNET, P. DANMANVILLE, and (MLLE.) G. MOUROT (Compt. rend., 1930, 191, 1473-1475).-The total nitrogen, creatine, and creatinine content of the excreta of rats and guinea-pigs has been determined under conditions of inanition produced by feeding on a protein-free diet, preceded in some cases by administration of benzoic acid, phloridzin, or phosphorus as a toxic substance. Under such conditions when the endogenous nitrogen metabolism is reduced to a minimum the amount of creatinine remains constant, whilst the creatine follows the total nitrogen content, increasing when the latter is increased either by J. W. BAKER. dieting or a specific reagent.

Nitrogenous metabolism of the sucking calf on a milk diet. (Determination of total nitrogen, carbamide, uric acid, creatinine, creatine, hippuric acid, and ammonia.) S. J. ERLER and K. J. PAVLOVSKY (Biochem. Z., 1930, 228, 89-100) .--The urine of a sucking calf on a milk diet is alkaline, contains creatine, uric acid, considerable amounts of hippuric acid, is deficient in ammonia, has a creatinine coefficient of 20.33 and a percentage of carbamide-nitrogen smaller than in the adult animal. The curves for the daily excretion of all the above nitrogenous substances show small wave-like variations.

P. W. CLUTTERBUCK. Production of ammonia in, and ammonia content of, frog muscle. VII. J. K. PARNAS, W. LEWINSKI, J. JAWORSKA, and B. UMSCHWEIF (Biochem. Z., 1930, 228, 366-400; cf. A., 1929, 598). Embdon and bis construction -Embden and his co-workers employ methods leading to results and conclusions which differ greatly from those of the authors. Since the methods of the former workers are unsatisfactory and the errors in their results great and variable their conclusions cannot be accepted. W. MCCARTNEY.

Ammonia production in the frog heart. I. P. OSTERN (Biochem. Z., 1930, 228, 401-406).-Ammonia, in amounts probably proportional to the work done, is produced by the beating frog heart. Traumatic production of ammonia occurs in the

A. G. POLLARD.

heart muscle but proceeds more slowly than in skeletal muscle. W. MCCARTNEY.

Ammonia formation in the kidney. G. EMBDEN and H. SCHUMACHER (Pflüger's Archiv, 1929, 223, 487—495; Chem. Zentr., 1930, i, 3077—3078).—The ammonia formed during 3.5 hrs.' treatment with 2% sodium hydrogen carbonate solution at 37° from pulverised kidney which had been frozen in liquid air has been determined; 100 g. of kidney formed 12—16 mg. of ammonia. After destruction of the deaminising enzyme, about 60% of the ammonia formed is liberated by the addition of an enzyme which eliminates ammonia only from muscle-adenylic acid. Caffeine diuresis diminishes the content of substances yielding ammonia. L. S. THEOBALD.

Biological values of proteins. I. Measurement of the nitrogenous exchange of rats for determining biological value of proteins. H. CHICK and M. H. ROSCOE. II. Biological value of purified caseinogen and influence of vitamin- $B_2$  on biological values determined by the balance-sheet method. M. A. B. FIXSEN (Biochem. J., 1930, 24, 1780—1782, 1794—1804).—I. The method consists in the determination of the average daily nitrogenous balance-sheet on a diet containing a definite proportion of the protein under investigation. The provision of vitamins-B was ensured by the administration of purified concentrates from yeast which contained very small quantities of nitrogen.

II. The biological value of purified caseinogen as determined by means of 12 metabolism experiments on adult male rats is 45, a figure considerably lower than that found by previous workers. In experiments in which the intake of calories from fat and carbohydrate combined fell below a certain value, the use of ingested protein for fuel is at once indicated by the underestimation of the biological value. The absence of either vitamin- $B_1$  or  $-B_2$  from the diet caused a decline in appetite within 48 hrs. So great was this decline in absence of vitamin- $B_1$  that the intake of calories was too low to allow trustworthy figures to be obtained for the calculation of biological values. The absence of vitamin- $B_{0}$  from the diet does not appear to prevent the economical use of ingested nitrogen, provided the calorie intake from fat and carbohydrate is adequate. There was no evidence either of variations in biological value at different levels of intake or of the existence of different biological values for growth and maintenance. S. S. ZILVA.

Influence of high- and low-protein diet on the basal metabolism and the chemistry of blood and urine in normal women. C. C. WANG and others (J. Nutrition, 1930, 3, 79–98).—A highprotein diet for 5 weeks was followed by reduction (with constant caloric value) during 3 weeks to a low-protein diet for 4 weeks and then, a month later, by a normal diet for 2 weeks. There was no marked difference in basal metabolic rate. During the high-protein period the blood-non-protein-nitrogen, -urea-nitrogen, and -creatine, but not the -uric acid, -creatinine, or -calcium, were increased. During the low-protein period the blood-sugar was slightly and -lactic acid markedly increased. The total urinary nitrogen, urea-nitrogen, ammonia-nitrogen, uric acid, and creatine varied directly with the protein intake, whilst the creatinine and lactic acid remained constant. CHEMICAL ABSTRACTS.

Comparative values of different food proteins for reproduction and lactation in the rat. II. Milk, egg, and meats. M. M. CLAYTON and M. J. CUMMINGS (J. Nutrition, 1930, 3, 23–38).—Egg is superior to milk for both reproduction and lactation. The difference in results on egg and milk rations containing Osborne and Mendel's salt mixture is due partly to a difference in ash content. Muscle-protein is of lower value than that of milk, egg, or the glandular meats. The vitamin-E content of dried products decreases in the order : egg, milk, beef round, liver, kidney. More vitamin-E is needed for lactation than for reproduction. Vitamin- $B_1$  is of special significance in lactation. CHEMICAL ABSTRACTS.

Nutritional potency of fresh, cooked, dry, and alcohol-extracted liver. J. S. McHARGUE, W. R. Roy, and F. E. HULL (J. Nutrition, 1930, 3, 49-60).— Raw liver, but not liver dried at 100°, was an adequate growth supplement to a synthetic diet in rats.

CHEMICAL ABSTRACTS. Nutritive value of cereal breakfast foods. IV. Response of the human stomach. H. D. BLOUGH, J. S. CARMAN, and E. M. AUSTIN (J. Nutrition, 1930, 3, 1—16). CHEMICAL ABSTRACTS.

Nutritive value of cereal breakfast foods. V. Biological value of some cereal proteins as determined on rats. H. A. MATTILL and M. M. CLAYTON (J. Nutrition, 1930, 3, 17-22).—Average biological values were: milk 89, "precooked oats" 82, wheat preparations 73, 72.

#### CHEMICAL ABSTRACTS.

Effect of cooking on the digestibility of meat. W. M. CLIFFORD (Biochem. J., 1930, 24, 1728—1733). —Raw meat is digested *in vitro* much more slowly than cooked meat. Over-cooked meat is very slowly digested as compared with under-cooked meat. The maximum rate of digestion is obtained with undercooked roast meat. Rewarming under-cooked meat does not diminish its digestive rate. Reheating, with consequent over-cooking, diminishes the rate of digestion. The rate of digestion of meat (raw or cooked) is the same whether trypsin alone be used or pepsin followed by trypsin. S. S. ZILVA.

Nutritive equilibrium and synthetic milk. L. RANDOIN and R. LECOQ (Compt. rend. Soc. Biol., 1929, **102**, 371—373; Chem. Zentr., 1930, ii, 261).— With mixtures similar in composition to dried milk nutritive equilibrium is reached with pigeons only within narrow limits; in particular there is an optimum as regards vitamin-B. A. A. ELDRIDGE.

Deficiencies of synthetic diets in chick nutrition. A. G. HOGAN and C. L. SHREWSBURY (J. Nutrition, 1930, 3, 39–48).—Dried yeast (40%) must be included in simplified rations.

CHEMICAL ABSTRACTS. Influence of salted yeast on the growth of young rats. L. ROSENOV and M. ROSENOV (Biochem. Z., 1930, 228, 163-164).—Salting forms a good method of preserving fodder yeast. Addition of salted yeast to bread as fodder gives an acceleration of the growth of rats by 36-60% in 24 days.

P. W. CLUTTERBUCK. Effect of yeast administration on the chemical condition of muscle and liver in chronic training and in isolated muscular effort. C. PI-SUNER BAYO and G. LISS (Z. physiol. Chem., 1930, 193, 193—197).—Addition of yeast to dogs' diet normally produces no increase in liver-glycogen. In dogs performing regular exercise (chronic experiment), the liver showed a very high fat content after administration of yeast. Yeast seems also to increase the lactic acid. In the acute experiment, yeast administration prior to the exercise causes a very large increase in liver-glycogen.

J. H. BIRKINSHAW. Influence of food-stuffs on the acid-base balance of cattle urine. F. J. WARTH and N. K. AYYAR (Biochem. J., 1930, 24, 1595—1600).—The urines from green fodders and cereal straws contain excess of alkali and large amounts of carbon dioxide. Those from over-ripe hays contain little carbon dioxide and are neutral or acid. The urine from wheat straw is acid. Progressive ripening of a fodder tends to increase the acidity of the urine; climatic conditions may modify the effect of ripening. The urines examined contain only traces of phosphoric acid. The buffering is effected by organic acids of which hippuric acid forms nearly two thirds. S. S. ZILVA.

Soft pork. IV. Influence of diet low in fat on composition of body-fat of pigs. N. R. ELLIS and J. H. ZELLER (J. Biol. Chem., 1930, 89, 185—197). —Pigs reared on a diet of low fat content stored fat at a normal rate. The degree of saturation of the fat increased with the size of the animal, this phenomenon being principally due to a continuous diminution in the proportion of linoleic acid. C. R. HARINGTON.

Behaviour of  $\delta$ -keto-*n*-hexoic acid in the perfused liver. W. L. DULLÈRE and H. S. RAPER (Biochem. J., 1930, 24, 1672—1677).—The sodium salt of  $\delta$ -ketohexoic acid on perfusion through the liver yields a considerable amount of acetone substances which indicates that it undergoes  $\beta$ -oxidation and not further  $\gamma$ - or  $\delta$ -oxidation in the animal body. Succinic acid is normally found in the liver in small amount and is not influenced by the perfusion of blood.

#### S. S. ZILVA.

Carbohydrate content of foods. I. Plant foods. II. Food value of vegetable carbohydrates. R. A. McCANCE and R. D. LAWRENCE (Med. Res. Council Spec. Rep., 1929, No. 135, 73 pp.). —Data concerning the carbohydrate content of various fruits, nuts, and vegetables are recorded. The food value of vegetable carbohydrates other than starch and sugars is discussed.

#### CHEMICAL ABSTRACTS.

Effects of high-sugar diets on the growth and structure of the rat. C. M. JACKSON (J. Nutrition, 1930, 3, 61-75).—Little difference was observed between starch-fed and sugar-fed rats.

CHEMICAL ABSTRACTS. Effect of oats on carbohydrate metabolism. I. A. PARTOS (Z. ges. exp. Med., 1930, 71, 538-542; Chem. Zentr., 1930, ii, 939).—Oat husk, fed to fasting

rabbits, caused a fall in blood-sugar, whilst ingestion of grain resulted in hyperglycamia.

A. A. ELDRIDGE. Carbohydrate metabolism of washed muscle. A. UTEVSKI (Biochem. Z., 1930, 228, 135-145).-The formation of acetaldehyde from pyruvic, fumaric, and malic acids in presence of normal and washed muscle, and washed muscle to which boiled muscle extract had been added, is investigated. The formation of aldehyde is scarcely detectable in autolysing washed muscle or after addition of glycogen, dextrose, lævulose, and glycerol. Traces of aldehyde are obtained with addition of ethyl alcohol and lactates but with pyruvates almost the normal amount is obtained. Washing of muscle causes the loss of oxidative but not of carboxylase power, and addition of boiled muscle extract leads to a return of oxidative power. The conversion of fumaric into malic acid proceeds as readily with washed as with unwashed muscle. The further attack on the malic acid is greatly decreased with washed muscle, but becomes normal on addition of boiled muscle extract. P. W. CLUTTERBUCK.

Methods of sugar degradation in the animal organism. E. BUMM and K. FEHRENBACH (Z. physiol. Chem., 1930, 193, 238-250).—Red muscle alone hydrolyses glycogen, dextrose only in presence of hexokinase. Addition of co-enzyme-T does not promote dextrose hydrolysis. White muscle hydrolyses both carbohydrates; addition of co-enzyme-Taccelerates the action on dextrose, but does not affect hydrolysis of the polysaccharide. Inversely, cozymase stimulates the hydrolysis of glycogen only by white muscle. The total glycolysis in presence of all four components dextrose, glycogen, co-enzyme-T, and co-zymase is the sum of the glycolysis due to the two reactions.

Kidney hydrolyses dextrose rapidly and glycogen slowly, but hexosephosphoric acid, the intermediate product of glycogen hydrolysis, is very rapidly attacked. Glycolysis of dextrose by kidney is stimulated by yeast co-zymase and also by coenzyme-*T*, but the course of the reaction appears to be different in the two cases. J. H. BIRKINSHAW.

Metabolism of monohexoses intravenously infused at a constant rate. Dextrose, lævulose, and galactose in blood. W. PIESKOW and M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1930, 103, 415—416; Chem. Zentr., 1930, i, 3076).—The infusion of these sugars in the dog at the rate of 2 g. per kg. per hr. during 3 hrs. has been followed. The dextrose in the blood is unchanged by the addition of lævulose or galactose. The form of the curves correlating the blood-sugar with the amount of sugar added and the effect of insulin thereon is described.

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Assimilation of intravenously injected monohexoses. Phosphorus and water metabolisms. E. OWSIANY and M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1930, 416-418; Chem. Zentr., 1930, i, 3076-3077; cf. preceding abstract).—Dextrose and lævulose are assimilated to the same extent (90-100%), but galactose to about 30%. During the sugar infusion the blood-phosphorus falls to 2 mg. per 100 c.c. and in the urine to less than 1 mg. per hr. Insulin increases both diminutions and lengthens the time of the lowered phosphorus content, but does not hinder the return of the latter to the normal.

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Production of lactic acid after intravenous injection of monohexoses. M. LANIEWSKI and M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1930, 103, 419-420; Chem. Zentr., 1930, i, 3077; cf. preceding abstract).-Infusion of dextrose at first increases the lactic acid of the blood and urine, the value falling only when infusion has ended. Lævulose produces an even stronger effect, and in both cases the effect of insulin is still more pronounced. The action L. S. THEOBALD. of galactose is slower.

Specific dynamic effect and the oxidation of dextrose, lævulose, and galactose. M. WIER-ZUCHOWSKI (Compt. rend. Soc. Biol., 1930, 103, 420-422; Chem. Zentr., 1930, i, 3077).-In the previous investigations (cf. preceding abstracts) 0.5 g. of sugar per kg. per hr. was oxidised; 34% of dextrose, 41% of lævulose, and 56% of galactose were assimilated. Insulin increased oxidation in those cases, e.g., lævulose, in which assimilation was unaffected. The relationship between lactic acid formation and the specific dynamic effect is discussed.

L. S. THEOBALD.

Influence of oxygen on lactic acid formation in muscle. A. HAHN, E. FISCHBACH, and H. NIEMER (Z. Biol., 1930, 91, 53-62).-The lactic acid content of freshly-pulped muscle shaken with oxygen is constant. Under the same conditions, the carbohydrate content is also constant, or shows a slight decrease. In a vacuum lactic acid increases, but becomes stationary when the carbohydrate content has fallen to a value equivalent to 18-21 mg. of dextrose per 10 g. of muscle. These results are regarded as incapable of explanation by Meyerhof's view that identical phenomena are observed in pulped muscle and in the recovery of intact muscle. A. COHEN.

Metabolism of acetaldehyde. I. Assimilation limits in normal dogs. R. MANCKE (Arch. exp. Path. Pharm., 1930, 157, 372-380).-During 30 and 98 hrs., respectively, 55 and 85 g. of acetaldehyde were absorbed without toxic effects being observed. F. O. HOWITT.

Intermediary iron metabolism. E. STARKEN-STEIN (Z. ges. exp. Med., 1929, 68, 425-440; Chem. Zentr., 1930, ii, 262).-A complex ferric-protein compound is formed from simple inorganic ferrous compounds and circulates in the blood as an intermediary metabolic product; it differs from ferric chlorideprotein precipitates. Complex formation is assisted by carboxyl groups (monocarboxylic acids and aminoacids) and hydroxyl groups (polyalcohols, glycerol, and sugar). On injection of iron tartrate, malate, or citrate, but not on that of gluconate, an iron-sodium complex is formed; injected ferric sodium lactate or gluconate remains in the organism as a complex. Simple amino-acids of the protein molecule do not produce the ferric-protein complex, in which the iron is anionic. Only anionic iron is physiologically active. Simple inorganic ferrous compounds are biologically important as sources of the necessary iron.

A. A. ELDRIDGE.

Effect of crude fibre on retention of calcium and phosphorus. M. A. BLOOM (J. Biol. Chem., 1930, 89, 221-233).-The retention of calcium and phosphorus by young rats on a basal diet containing 0.9%of spinach ash and only a small amount of fibre was reduced by the substitution of 5% of dried spinach (raw or cooked) for the spinach ash and was not significantly affected by the addition of crude fibre (filter-paper) in amounts up to 8% of the diet. C. R. HARINGTON.

Possible significance of hexosephosphoric esters in ossification. Calcification in vitro. VIII. R. ROBISON and K. M. SOAMES. IX. R. ROBISON, M. MACLEOD, and A. H. ROSENHEIM (Biochem. J., 1930, 24, 1922-1926, 1927-1941).-VIII. Whilst calcification in vitro may occur in solutions of inorganic salts supersaturated with respect to the bone salt, calcification will take place with lower concentrations of calcium and inorganic phosphates, if phosphoric ester is also present, even in very small amount.

IX. In inorganic solutions with salt concentrations approximating to those in plasma, calcification was obtained with concentrations of calcium varying from 2.5 to 50 mg. per 100 c.c. and of inorganic phosphate varying from 1 to 20 mg. per 100 c.c. Calcification was observed at somewhat lower levels of the product  $[Ca] \times [P]$  when the concentration of calcium was high and that of phosphate low than under the reverse conditions. With concentrations of calcium around 10 mg. per 100 c.c. some degree of calcification was usually obtained in 16 hrs. when the concentration of inorganic phosphate was such that the product  $[Ca] \times [P]$  was equal to 30. Variations were, however, observed in the minimum level required with bones from different rats. This variability in response was apparent also in the extent of the deposit obtained at higher  $[Ca] \times [P]$  levels. Definitely higher  $[Ca] \times [P]$ levels were necessary for calcification when the concentration of sodium hydrogen carbonate was reduced from 0.2% to 0.03%, and still higher levels were required when the salt was entirely omitted. This suggests that the compound normally deposited in calcifying cartilage is a complex carbonato-phosphate (carbonato-apatite) rather than a mixture of basic phosphate and carbonate. It is confirmed that sodium chloride in concentrations as low as 0.034M (0.2%) has an inhibitory effect on calcification in inorganic solutions. Potassium chloride in concentrations up to 0.01M (twice the concentration in plasma) had no appreciable inhibitory effect. Magnesium in concentration 0.0008M (slightly lower than that in plasma) affected adversely calcification and with higher concentrations the inhibitory effect was pronounced. The inorganic solutions in which calcification occurred were all supersaturated with respect to the calcium salt deposited. In presence of phosphoric ester, however, calcification occurred at [Ca]×[P] levels much lower than 30, whilst at higher levels the effect of the ester was seen in the greatly increased extent and density of the deposit. The increased calcification which occurred in presence of phosphoric ester tended to mask the favourable effect of sodium hydrogen carbonate and the inhibitory effects of sodium chloride and magnesium. There was

no evidence that any of the inorganic radicals directly influenced the enzyme mechanism. Between  $p_{\rm H}$  7.2 and 7.8 no marked optimum was found for calcification in presence or absence of ester. Calcification was obtained at  $p_{II}$  6.5 with very high [Ca]×[P] levels (60-80) in inorganic solutions, and at the low level 24 in presence of phosphoric ester. Formaldehyde completely inhibited calcification in inorganic solutions and almost completely inactivated the phosphatase mechanism. The presence of chloroform or potassium cyanide strongly inhibited calcification in inorganic solutions, but had no appreciably effect in solutions containing phosphoric ester. Bone slices after being soaked for 24 hrs. in chloroform, acetone, or alcohol, or desiccated in a vacuum over sulphuric acid failed to calcify on subsequent immersion in inorganic solutions of high  $[Ca] \times [P]$  levels. In solutions containing phosphoric ester, however, extensive calcification occurred and the deposits were normal in appearance. In normal calcification of the skeleton there are two mechanisms, the first the bone phosphatase which produces the necessary degree of supersaturation in the matrix, and the second which assists in the deposition of the bone salt from this supersaturated solution. S. S. ZILVA.

Development and phosphatase activity in vivo and in vitro of the mandibular skeletal tissue of embryonic fowl. H. B. FELL and R. ROBISON (Biochem. J., 1930, 24, 1905—1921).— The embryonic mandibular skeleton of the fowl consists of a rod of cartilage (Meckel's cartilage) surrounded by a sheath of membrane bone. The distal part of this cartilage does not ossify and synthesises no phosphatase. The membrane bone surrounding Meckel's cartilage develops high phosphatase activity. Explants of Meckel's cartilage from 6-day embryos neither ossified nor synthesised phosphatase in vitro. Explants of the mandibular mesoderm (pre-membrane bone) during growth in vitro developed ossification centres and synthesised phosphatase. S. S. ZILVA.

Measurements of the acid taste and their bearing on the nature of the nerve receptor. N. W. TAYLOR, F. R. FARTHING, and R. BERMAN (Protoplasma, 1930, 10, 84–97).—Determinations of the "threshold concentration " for sourness of numerous organic acids by Taylor's method (A., 1929, 347) are described and the relative concentration gradients of the non-ionised acids calculated. The addition of polar groupings, OH, >C:C<, >C:O,  $CO_2H$ ,  $NH_2$ , to organic acids renders the penetration of the acid to the nerve receptor 20—500 times as difficult. Lengthening the carbon chain by addition of  $CH_2$ groups makes penetration easier. It is concluded that the organic acids are absorbed by a tissue which resembles fat rather than protein. A. G. POLLARD.

Nature of the nerve receptor for the acid taste as indicated by the absorption of organic acids by fats and proteins. N. W. TAYLOR (Protoplasma, 1930, 10, 98—105).—Distribution coefficients of a number of organic acids between olive oil and water were determined. The relative effects of the groups  $\cdot$ OH, :CO,  $\cdot$ SO<sub>3</sub>H,  $\cdot$ NH<sub>2</sub>, and :C:C: on the coefficients are of the same nature and order of magnitude as their effects on the concentration gradients of the undissociated acids between water and the nerve receptor (cf. preceding abstract). Specific effects of the amino- and phenyl groups are recorded. Changes in the  $p_{\rm ir}$  of gelatin to which increasing proportions of the acids were added are represented by a series of curves the relative positions of which are determined by their dissociation constants. The various polar groups affect the position of the curves only in so far as they affect dissociation constants and the results are not paralleled by the taste experiments. The nerve-ending which the acid penetrates and stimulates to give the sensation of sourness is concluded to have the characteristics of fat and not of protein. A. G. POLLARD.

Alkali deficit and dextrose tolerance in the dog. H. J. DEUEL, jun., and M. GULICK (J. Biol. Chem., 1930, 89, 93—95).—Dextrose tolerance in dogs is not impaired by the acidosis which results from administration of ammonium chloride. C. R. HARINGTON.

Toxicity of ethylene chlorohydrin. J. D. PRATT (Nature, 1930, 126, 995).—Attention is directed to fatalities which have occurred from inhaling the vapour of ethylene chlorohydrin, which appears to act as a metabolic poison. L. S. THEOBALD.

Carbohydrate metabolism following guanidine deglycogenation. F. BISCHOFF and M. L. LONG (J. Nutrition, 1930, 3, 201-216).-Insulin increases the utilisation of dextrose at normal or hyperglycamic levels by guanidine-deglycogenated rabbits with or without storing glycogen. Adrenaline decreases the utilisation of injected dextrose in animals in which the liver has been depleted of glycogen and has been deprived (by means of guanidine derivatives) of the power of storing glycogen; hence normal adrenaline hyperglycæmia is not entirely due to an increased output of dextrose by the liver. Adrenaline increases the blood-lactic acid and insulin does not affect it in rabbits suffering from guanidine-deglyco-CHEMICAL ABSTRACTS. genation.

Chemical constitution and pharmacological properties of methylglyoxaline derivatives. J. V. SUPNIEWSKI (Compt. rend. Soc. Biol., 1928, 98, 1229-1230; Chem. Zentr., 1930, i, 3809).-Glyoxaline, 4-hydroxymethylglyoxaline and glyoxaline-4-aldehyde cause increased blood-pressure in cats, and contract the isolated guinea-pig uterus. 4-Methylglyoxaline or 5-methyl-4-hydroxymethylglyoxaline when injected intravenously into cats causes a diminution in blood-pressure, and with rabbits produces increased peristaltic contractions. 4-Chloromethylglyoxaline reduces the blood-pressure; 4aminomethylglyoxaline causes first a rise and then a fall in blood-pressure, uterine contraction in guinea-pigs, and intestinal contraction in rabbits. 2-Thio-4methylglyoxaline [?] causes with cats a fall in bloodpressure, and increase of respiratory movement. 4-Diethylaminomethylglyoxaline causes a fall in blood-pressure in cats, and uterine contraction in guinea-pigs. 4-Piperidylmethylglyoxaline causes in cats a marked fall in blood-pressure, contracts the isolated guinea-pig uterus, and is diuretic. Glyoxaline-4-carboxylic acid, -4:5-dicarboxylic acid, and 2-thio-4-methylglyoxaline [?] have no particular pharmacological properties. A. A. ELDRIDGE.

Antipyretic action of 3-aminohydrocarbostyril, its isomerides and derivatives. K. WATANABE (J. Biochem., Japan, 1930, 12, 71-81).-1-, 3-, and 7-Aminohydrocarbostyril are strongly antipyretic, but the 1- and 3-derivatives are toxic; diacetyl-3-aminohydrocarbostyril is antipyretic and less toxic. m-Aminophenylalanine, but not p-compound, exhibits some antipyretic action.

CHEMICAL ABSTRACTS. Isotonic soap solution for injection. PICON (J. Pharm. Chim., 1930, [viii], 12, 481—484).—A stable, neutral soap solution, miscible with water and salt solution, is prepared by dissolving 100 g. of ricinoleic acid in 700 c.c. of warm 10% alcoholic sodium hydroxide solution followed by removal of the alcohol. A 1% solution (wt./vol.) of the soap thus obtained in 0.7% sodium chloride solution forms an isotonic solution which is not changed by sterilisation, produces only feeble hæmolysis, does not coagulate the blood, and has given satisfactory results when injected into human beings. E. H. SHARPLES.

Toxicity of rotenone, isorotenone, and dihydrorotenone to goldfish. W. A. GERSDORFF (J. Amer. Chem. Soc., 1930, 52, 5051-5056).—The minimum toxic concentrations of rotenone, isorotenone, and dihydrorotenone are determined by the method previously described (A., 1930, 1316) to be 0.0125, 0.055, and 0.005 mg. per litre, respectively. H. BURTON.

Heart tonics. IV. Digitalis standardisation; a new assay method. W. NYIRI and L. DUBOIS (J. Pharm. Exp. Ther., 1930, 40, 373-401).—The factors affecting the pharmacological assay of digitalis preparations have been investigated and a method in which the rabbit is used as test animal is recommended. W. O. KERMACK.

Phloridzin diabetes. II. Relationship between state of nutrition and dextrose tolerance. H. J. DEUEL, jun. (J. Biol. Chem., 1930, 89, 77—91).— Although in the fasting condition the phloridzinised dog exhibits a dextrose tolerance curve similar to that of a diabetic animal, if the sugar tolerance be observed 14 hrs. after a heavy dose of carbohydrate the responses of phloridzinised and normal animals are closely similar. This affords additional evidence (cf. A., 1927, 987) that the action of phloridzin is exclusively renal and does not affect the normal processes of oxidation of carbohydrate. C. R. HARINGTON.

Action of "trional" on normal blood constituents. F. G. GERMUTH (Amer. J. Pharm., 1930, 102, 653—658).—Subcutaneous or intravenous injection daily for 10 days of an aqueous-alcoholic solution of trional causes a decrease in the body-weight of rabbits with an increase in the uric acid, sulphate, sugar, and creatinine content, and a decrease in the iron, calcium, magnesium, chlorine, total phosphorus, acid-soluble phosphorus, protein-combined phosphorus, and total solid content, and in the d and n of the blood. H. E. F. NOTTON.

Pharmacology of local anæsthetics. III. Comparison of  $\gamma$ -2-methylpiperidinopropyl benzoate hydrochloride with cocaine and procaine on experimental animals. C. L. Rose, H. W. COLES, and H. E. THOMPSON (J. Lab. Clin. Med., 1930, 15, 731-735).— $\gamma$ -2-Methylpiperidinopropyl benzoate hydrochloride is intermediate in toxicity between cocaine and procaine.

#### CHEMICAL ABSTRACTS.

Disturbance of carbohydrate economy in ether narcosis. H. Fuss (Klin. Woch., 1930, 9, 410; Chem. Zentr., 1930, ii, 265).—In normal dogs the blood-lactic acid was markedly raised unless oxygen was freely administered. With phloridzinised or fasting dogs only a slight rise was observed; hence in normal animals the excess of lactic acid appears to originate from the reserve carbohydrate. The hyperglycæmia is not, however, repressed by administration of oxygen; hyperglycæmia and excessive urinary excretion of sugar were not observed with dogs poor in glycogen. Ether-narcotised dogs showed no increase of blood-acetone and -acetoacetic acid, whilst the  $\beta$ -hydroxybutyric acid was only slightly and irregularly increased. Acetone and acetoacetic acid were not found in the urine. In glycogen-impoverished dogs the blood-ketone substances increased 24 hrs. after narcosis. The alkali reserve always diminished during ether narcosis; ketonic substances are not the cause of the acidosis. In ether-oxygen narcosis there was a slight fall in the alkali reserve.

#### A. A. ELDRIDGE.

[Pharmacological] action of nitrogen oxidescarbon monoxide mixtures. W. WIRTH (Arch. exp. Path. Pharm., 1930, **157**, 264—285).—A mixture of the two gases in definite proportions and air causes death in cats, whereas an equal concentration of either constituent results only in slight illness.

# F. O. HOWITT.

Action of arsenite on tissue respiration. A. SZENT-GYÖRGYI (Biochem. J., 1930, 24, 1723-1727).—Arsenite strongly inhibits the respiration of minced liver tissue, but has no effect on oxygen activation and little effect on hydrogen activation. In yeast arsenite in higher concentrations inhibits respiration, but has no effect on alcoholic fermentation. S. S. ZILVA.

Relation between trypanocidal and spirochæticidal activities of neosalvarsan. T. F. PROBEY and G. W. McCov (U.S. Pub. Health Repts., 1930, 45, 1716—1728).—Two brands of neosalvarsan of widely different trypanocidal activity are approximately equally effective (a) in clearing the chance of spirochætes, (b) in healing the lesion without clinical relapse, and (c) in influencing the Kahn reaction in experimental rabbit syphilis over periods of 67—SS days. A. COHEN.

Circulation of bismuth in the organism. C. LEVADITI, Y. MANIN, and A. HOWARD (Compt. rend. Soc. Biol., 1929, 102, 813—816; Chem. Zentr., 1930, ii, 264).—A few hours after intramuscular injection of "lipoid-soluble bismuth" bismuth can be detected in the kidneys. The excretion docs not parallel the bismuth content of the kidneys.

A. A. ELDRIDGE.

Biological effect of bromine. I. Gaseous metabolism of the blood and of the whole organism. II. Oxygen and carbon dioxide dissociation curves of the blood. III. Circulation in rabbits. S. TADA (Tohoku J. Exp. Med., 1930, 15, 236—248, 249—258, 259—266).—The oxygen consumption of rabbit's blood-corpuscles when washed in isotonic sodium bromide solution is less than when sodium chloride is used; the oxygen and carbon dioxide dissociation curves also are below those of unwashed cells or of cells washed in sodium chloride solution. Intravenous injection of sodium bromide reduces the oxygen consumption of the rabbit more than does that of sodium chloride, but the effect is not immediate. CHEMICAL ABSTRACTS,

Fluoride intoxication in white rats. J. CHANELES (Rev. soc. Argentina biol., 1929, 5, 317, 336, 340, 352, 376).—The physiological effects of feeding 50 mg. of fluoride per kg. to young rats are described. The calcium contents of the bones and teeth were diminished; the incisors contained less phosphorus and magnesium than normally. Irradiation with ultra-violet light, however, led to increased values in each case. The bone of treated rats, whether irradiated or not, contained more phosphorus and magnesium than normally.

CHEMICAL ABSTRACTS. Urinary sulphur and thiocyanate excretion in cyanide poisoning. R. G. SMITH and R. L. MALCOLM (J. Pharm. Exp. Ther., 1930, 40, 457-471).-The increase of neutral sulphur in the urine of rabbits subjected to hydrogen cyanide vapour for several weeks is practically all accounted for by the thiocyanate excreted in the urine. A fall in inorganic sulphur usually occurs which equals or exceeds the rise in neutral sulphur. An increase in the total nitrogen and in the N:S ratio of the urine is also observed. Cyanide solution (0.01N) administered to rabbits appears in the urine as thiocyanate, about 72% being accounted for in this way, and when thiocyanate is administered as such an average of 80% is found in the urine. The formation of thiocyanate appears to be the chief method of detoxication of cyanide in the body. W. O. KERMAOK.

Reaction of iodates in vivo. L. C. MAXWELL (J. Pharm. Exp. Ther., 1930, 40, 451-455).—Sodium iodate administered intravenously into rabbits has a toxic action in doses of approximately 75 mg. per kg. body-weight. The effect is apparently not due to the liberation of iodine in the tissues. The toxic action of iodate is much increased by iodide.

W. O. KERMACK.

Action and excretion of nitrates. N. M. KEITH, M. WHELAN, and E. G. BANNICK (Arch. Int. Med., 1930, 46, 797—832; cf. A., 1930, 639).—The diurctic action of ammonium nitrate is confirmed. Data showing its action on normal dogs and normal and codematous humans are given. G. F. MARRIAN.

Biological action of rays of short wave-length on the metabolism of the cell. K. ADLER (Strahlenther., 1930, 36, 1-31; Chem. Zentr., 1930, i, 3078).—The point of attack of X- and radium rays is not to be sought in the metabolism of the cell. The first changes in cell metabolism appear 24 hrs. after irradiation and increase to a maximum after 34-36 days. The respiration of the tissue diminishes, whilst aërobic and anaërobic glycolysis is doubled; an approximation to the type of metabolism of malignant tumours takes place. After 40 days glycolysis falls below normal. Histological investigations showed degenerative changes in the nuclei of the spermatic cells. L. S. THEOBALD.

Hydrogen acceptors and catalase. I. Influence of hydrogen acceptors on human blood catalase in vitro. A. I. ALEXEEV and K. I. RUSINOVA (Bull. inst. recherches biol., Perm, 1929, 6, 425-461).—The activity of catalase is inhibited by aqueous solutions of methylene-blue, 2:4-dinitrophenol, and benzoquinone in proportion to the concentration; the inhibition is maximal at  $p_{\rm u}$  4.7 and vanishes at  $p_{\rm fl}$  7.27. Trinitrophenol inactivates catalase in neutral solution. Salts in dilute solution activate catalase and destroy the inhibiting action of the hydrogen acceptors. CHEMICAL ABSTRACTS.

Irradiation of Dolichos tyrosinase. D. NARA-YANAMURTI and C. V. RAMASWAMI (Biochem. J., 1930, 24, 1655—1658).—The enzyme obtained from Dolichos lab lab is activated by irradiation. Addition of irradiated water causes less marked acceleration than irradiation in glass vessels. The increase in activity diminishes with longer exposure in the case of old solutions. The irradiated enzyme decreases in activity on keeping, and is most active when it is least charged. On longer exposure the positive charge on the enzyme particle is increased, thus causing a slight diminution in activity. S. S. ZILVA.

Detection of methylglyoxal formed by the biochemical fission of sugar. C. NEUBERG and M. SCHEUER (Ber., 1930, 63, [B], 3068-3072).—An alcohol-ether preparation of B. lactis aërogenes is allowed to act on a 4% solution of magnesium hexosediphosphate, which is then centrifuged after addition of fuller's earth and filtered. After addition of 1:2naphthylenediamine hydrochloride, the mixture is agitated for 2 hrs. and subsequently evaporated to dryness at the ordinary temperature. The residue is triturated with alcohol and the extract evaporated in a vacuum at  $37^\circ$ . The residue is mixed with sodium oxalate and oxalic acid solution and extracted with ether. The ethereal solution is shaken with sodium carbonate, dried, and the ether is removed. The residue is treated with cold 20% sulphuric acid, the solution is filtered and poured into about 8% sodium hydroxide, whereby 3-methylnaphthopyrazine, m. p.  $95^\circ$ , is obtained. H. WREX.

Inhibition of esterases by excess of substrate. D. R. P. MURRAY (Biochem. J., 1930, 24, 1890— 1896).—From the observed velocities of the action of the esterase from sheep-liver on different concentrations of ethyl butyrate it is deduced that the inhibition of certain enzymes by excess of substrate is due to the formation of a non-hydrolysable complex of the enzyme with 2 mols. of the substrate. By extending the equation it is possible to predict correctly the effect of competitive inhibitors. S. S. ZILVA.

Kinetics of the stereochemical specificity of human liver-esterase. P. RONA, H. FISCHGOLD, and R. AMMON (Biochem. Z., 1930, 228, 77-88).-Bamann's result (A., 1929, 957) that when human liver-esterase acts on ethyl *dl*-mandelate, the rotation of the acid liberated may be either *d* or *l*, according to the concentration of the substrate, is confirmed with the methyl ester. The rotation obtained does not depend on the ratio of the amounts of enzyme and substrate, but only on the concentration of the latter. The activity- $p_s$  curves are obtained for both d- and *l*-modifications of the methyl ester. No satisfactory explanation for the cause of inversion is available.

P. W. CLUTTERBUCK.

Asymmetric hydrolysis of esters by enzymes. IV. Influence of optically active foreign substances on the configuration specificity of liveresterase of various degrees of purity. E. BAMANN and P. LAEVERENZ (Z. physiol. Chem., 1930, **193**, 201–214; cf. A., 1930, 499).—The age of the enzyme preparation affects the optically selective hydrolysis of dl-ethyl mandelate by human liver-esterase in presence of strychnine. The effect of strychnine on stereochemical specificity is also influenced by the pre-treatment of the enzyme. When the strychnine concentration is maintained constant, a change in the enzyme concentration does not affect the result, but a variation of strychnine concentration coupled with constant enzyme concentration produces varying rotation of the products. The enzyme-strychnine mixture, after long dialysis, has the same effect as the enzyme alone, which indicates that the enzyme-strychnine complex is dissociable.

# J. H. BIRKINSHAW.

Asymmetric hydrolysis of esters by enzymes. V. Configuration-specificity of liver-esterase in its dependence on alterations in enzyme complex. E. BAMANN and P. LAEVERENZ (Ber., 1930, 63, [B], 2939-2948; cf. Willstätter, Kuhn, and Bamann; A., 1930, 499).-It has not been found possible to influence the optical selectivity of the liver-esterase of man by exhaustive purification by the adsorption method. Such influence, previously noted only after addition of suitable optically active material, can be caused by pre-treatment of the enzymic preparations. The enzyme from the untreated dry preparations of the liver of man or rabbit hydrolyses the two components of ethyl dl-mandelate at almost equal rates, whereas an extract from the same dry preparations which has been preserved for some days at 60-65° favours the *d*-ester, and that derived by submitting the extract to protectly the dester. solution for about a week favours the *l*-ester. H. WREN. the extract to proteolytic degradation in faintly acid

Nature of enzyme action. A. FODOR and L. FRANKENTHAL (Biochem. Z., 1930, 228, 101-122).-When dried pancreatic preparations are treated with water, the insoluble residue hydrolyses glycylglycine readily, but glycylglycyl-l-leucine only with difficulty. The filtrate, on the other hand, when incubated for 24 hrs. with glycylglycine initially does not attack, but later shows a strongly autocatalysed hydrolysis of the dipeptide. This period of induction is not obtained either with the tripeptide or with peptone, and is regarded as due to changes in the nature of the enzyme carrier during autolysis of the extract. When amounts of glycyl-l-leucine and glycyl-dl-leucine such that both contain the same amount of glycyl-l-leucine are incubated with yeast macerates, both fresh and 3 days old, the presence of the d-isomerides causes acceleration of hydrolysis. The bearing of these

results on the general nature of enzyme reaction is P. W. CLUTTERBUCK discussed.

Action of degradation products on enzymic proteolysis. P. RONA, H. KLEINMANN, and E. DRESSLER (Biochem. Z., 1930, 228, 6-76).—The contradictory results of Weber and Gesenius (A., 1927, 992), who showed that the solution obtained by digestion of caseinogen with trypsin and pepsin retarded proteolysis of further amounts of caseinogen, and of the authors (A., 1925, i, 473; 1926, 543), who did not obtain inhibition, are shown to depend on the different concentrations of reactants and on the different methods of analysis used by the two sets of investigators. A solution containing only a small amount of protein and enzyme (micro-determination) showed no inhibition of proteolysis (as determined by the nephelometric method) even when 100% of degradation products are added. On the other hand, a solution containing 50 times the amount of substrate and 20 times the amount of enzyme (macro-determination) showed considerable inhibition (as determined by titration of the liberated carboxyl groups) on addition of degradation products. With tryptic hydrolysis, the difference of results depends entirely on the concentration of reactants. When the concentration of enzyme is sufficiently small, the enzymeinhibitor complex is completely dissociated and no inhibition is recorded. With peptic hydrolysis, although inhibition was again obtained using the macro-method and was not obtained using the micromethod, yet the inhibition was dependent only on the method of analysis. When the reaction was followed on the macro-scale by the titration method an inhibition was recorded on adding degradation products, whereas when followed by the nephelometric method (i.e., in terms of unused protein) inhibition was not obtained. These results are reproduced on the same solution, and it seems certain that the two determinations, with peptic digestion, measure different P. W. CLUTTERBUCK. processes.

Formation of diketopiperazine in the enzymolysis of gelatin. A. BLANCHETIÈRE (Compt. rend., 1930, 191, 1479-1481).-Unlike the results obtained with gliadin and ovalbumin (A., 1930, 100) hydrolysis of gelatin occurs less regularly with trypsin than with pepsin and the amount of diketopiperazine formed is only about 66% of that expected from the amino-acids J. W. BAKER. constituting this protein.

Analysis of proteolytic enzyme of Maja squinado by the adsorption method. J. J. MANSOUR-BEK (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 858-870).-Adsorption measurements have shown that the gastric juice of Maja squinado contains several proteolytic enzymes, including a proteinase, a carboxypolypeptidase, an aminopolypeptidase, and a dipeptidase. The proteinase can be purified and is then most active at  $p_{\rm H}$  7.4-8.1, whilst the activity of the crude extract is greatest at  $p_{\rm H}$  6.0-6.1. The proteinase is of a trypsin-like character, degrades peptone and clupeine sulphate, and is activated by enterokinase, but not by hydrocyanic acid, hydrogen sulphide, or zookinase. E. S. HEDGES.

Pathological decomposition of protein. III. Hexone bases and monoaminodicarboxylic acids liberated from caseinogen by the action of coli-protease. M. SCHIERGE (Z. ges. exp. Med., 1929, 62, 141—146; Chem. Zentr., 1930, ii, 756).—In addition to tyrosine, leucine, tryptophan, and phenylalanine, there were also found histidine and lysine; glutamic and aspartic acid were not detected.

A. A. ELDRIDGE.

Purinolytic enzymes of the human organism. R. TRUSZKOWSKI (Biochem. J., 1930, 24, 1681— 1686).—Uricase was absent from the livers of a newborn child and of two adults and from the livers and kidneys of six foctuses from the 12th to the 40th week of pregnancy. Xanthine oxidase was absent from the extracts of the kidneys of the above foctuses but present in all their liver extracts. S. S. ZILVA.

Plasma-phosphatase. I. Determination and properties. II. The enzyme in disease, par-ticularly of bone. H. D. KAY (J. Biol. Chem., 1930, 89, 235-247, 249-266).-I. Blood-plasma is added to excess of a solution of sodium  $\beta$ -glycerophosphate at  $p_{\rm B}$  7.6 and the mixture is kept at 38° for 48 hrs. The difference between the inorganic phosphate content of such a mixture and that of a similar mixture treated at the beginning of the experiment with trichloroacetic acid to remove the enzyme represents the liberation of phosphoric acid brought about by the phosphatase. The optimum  $p_{\rm H}$  for the enzyme is 8.8—9.1; its action is inhibited by calcium ions and by high concentrations of magnesium ions, although low concentrations of the latter have a stimulating effect. Plasma-phosphatase liberates phosphoric acid from sodium hexosediphosphate,  $\alpha$ - and  $\beta$ -glycerophosphate, pyrophosphate, glycophosphate, and guanine nucleotidate at descending rates in the order mentioned. The phosphatase concentration in the blood decreases with the age of the animal.

II. The phosphatase content of the blood-plasma is largely and specifically increased in patients suffering from generalised disease of the bones. The possible rôle of the enzyme in normal bone-formation is discussed. C. R. HARINGTON.

Selective fermentation. II. Fermentation of sugar mixtures by Sauterne yeast. H. SOBOTKA and M. REINER (Biochem. J., 1930, 24, 1783—1786).— This yeast ferments lævulose preferably to dextrose in a mixture, the ratio of the rate of fermentation of lævulose to that of dextrose, which depends on adaptation phenomena, varying from 1.2 to values above 10. It ferments lævulose alone 50—100% faster than dextrose alone. S. S. ZILVA.

Zymatic system of Saccharomyces Johannesberg. I. YAMASAKI (Biochem. Z., 1930, 228, 127-134).—S. Johannesberg, II, either the alcohol-ether or the dried preparation, is able to convert magnesium hexosediphosphate into methylglyoxal and pyruvic acid. The dry preparation ferments pyruvic acid readily. Both the fresh and dry yeast, in presence of toluene, cause phosphorylation of sugar as soon as co-enzyme is added, at least two phosphoric esters being formed, of which one yields a sparingly and the other a readily soluble barium salt.

P. W. CLUTTERBUCK.

Growth of yeast by the aeration method and the increase in its constituents. H. CLAASSEN (Bio-T

a.

chem. Z., 1930, 228, 154—162).—In two fermentations, the hourly increase of yeast in dry weight, protein, nitrogen-free substances, and ash is determined. Formation of protein is greatest when the wort contains sugar and readily assimilable nitrogen, especially ammonia, whereas nitrogen-free constituents are predominantly formed in the later stages of fermentation, *i.e.*, when the wort contains no sugar but still contains amino-acids, alcohol, and nitrogen-free organic acids. Addition of limited amounts of ammonia to a wort containing sufficient assimilable organic nitrogenous material for normal growth does not increase the dry weight of yeast but only causes an increase of the protein fraction and a corresponding decrease of the nitrogen-free substances.

P. W. CLUTTERBUCK.

Conditions of activation of washed zymin. II. A. A. STHEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 889-897; cf. A., 1929, 1107).-When zymin has been exhaustively washed with water it cannot be reactivated without the addition of the co-enzyme of alcoholic fermentation isolated by von Euler. With less washing the inactive preparation may be activated by adding methylene-blue or a mixture of methylene-blue and hexosediphosphate. Von Euler's principle is able to replace hexosediphosphate, although the substitution is not mutual; the principle contains esterified phosphoric acid groups, but also has a specific action of an unknown character. E. S. HEDGES.

Action of sodium monoiodoacetate on the enzymes of zymase and on the fermentation of hexosediphosphate. I. YAMASAKI (Biochem. Z., 1930, 228, 123—126).—Iodoacetic acid, although inhibiting the action of whole zymase, has little effect on the action of glycollase and causes only a 30% inhibition of carboxylase, the chief effect being on the phosphatese. P. W. CLUTTERBUCK.

Activator Z. VI. T. PITLIPSON (Z. physiol. Chem., 1930, 193, 181—192; cf. this vol., 128).— Methods of purification of the Z factor were examined. Dialysis of boiled yeast-juice followed by precipitation with lead and mercury salts increased the activity. By autolysis of bottom yeast, preparations with two to three times the activity of the original material were obtained. The bottom yeast employed contained twice as much Z activator as top yeast. The activator is very stable to acids and alkalis before the mercury treatment, but becomes somewhat sensitive to alkali after the treatment. J. H. BIRKINSHAW.

Bios. VI, VII. B. SUZUKI, K. MATSUSITA, and K. AOKI. VIII. B. SUZUKI and Y. HAMAMURA (Proc. Imp. Acad. Tokyo, 1930, 6, 334—340).—VI, VII. Saccharomyces saké, which forments sugar in the absence of rice-bran bios, S. cerevisiæ, which is active in bios-free media, and several species of yeast of intermediate activity are all incapable of synthesising bios, although propagation is possible in its absence. Aspergillus oryzæ, however, is able to synthesise bios.

VIII. The purification of bios is described, giving a 10% yield having ten times the activity of the starting material. Purified bios appears to be a nonnitrogenous substance containing three hydroxyl groups. The *benzoate* (highest m. p. 116—118°) is not fractionated by decalin or carbon tetrachloride, and is inactive. Activity reappears on hydrolysis with 0.1Nsodium hydroxide. A. COHEN.

Influence of hydrogen sulphide on reproduction rate in *Paramecium caudatum*. M. J. SHARPE (Protoplasma, 1930, 10, 251–252).—Hydrogen sulphide and also sodium sulphide in equivalent sulphur concentration increased the rate of reproduction of *P. caudatum* (cf. Hammett, *ibid.*, 1929, 297; Reimann, this vol., 255). A. G. POLLARD.

Growth of Aspergillus niger and copper content of the nutrient medium. L. K. WOLFF and A. EMMERIE (Biochem. Z., 1930, 228, 443-450). —A. niger absorbs copper from the medium in which it grows, the depth of the colour of the spores being proportional to the amount of copper taken up. For the growth of the organism the presence of at least 0.0002 mg. of copper in 250 c.c. of medium is necessary and for the production of spores at least 0.0003 mg. No degeneration takes place when the organism is propagated in media too poor in copper to promote the production of spores, and this production can at once be initiated in such media by the addition of sufficient copper. W. MCCARTNEY.

Colouring matter of Aspergillus and Mucor. A. BLOCHWITZ (Zentr. Bakt. Par., 1930, II, 80, 201-202; Chem. Zentr., 1930, i, 3066).-Potassium hydroxide extracts from all green conidia of Aspergillus, Penicillium, and Citromyces a characteristic reddish-brown colouring matter which with hydrochloric acid becomes yellow or yellowish-brown according to the concentration. The deep violet conidia of A. purpurea, A. japonicus, and A. violata immediately become deep brown in potassium hydroxide. This brown colour is already present in the conidia. Intense sunlight and high temperature also bring about the change in colour. Young sporangia of Phycomyces, Pilobolus, Pilaira, and Mucor mucedo contain a yellow, oily substance soluble in ether, benzene, and chloroform, but unchanged by potassium hydroxide and hydrochloric acid.

L. S. THEOBALD.

Lipase of Aspergillus niger (Van Tiegh). I, II. Optimum  $p_{\rm H}$  for glycerides of fatty acids. A. JURACEC (Bull. Acad. Sci. Roumaine, 1930, 13, 103—110, 169—176).—The optimum  $p_{\rm H}$  for the action of the lipase on triacetin, monobutyrin, and triolein is 7.8. A more potent enzyme preparation is obtained by extraction of dried mycelium with disodium hydrogen phosphate than by glycerol extraction of fresh mycelium. P. G. MARSHALL.

Citric fermentation caused by Aspergillus niger. L. V. KOTOVSKI (Arkh. Biol. Nauk, 1930, 30, 303-308).—Currie's medium contains too little nitrogen; for cultures 3 cm. deep 5 g. of ammonium nitrate per litre is recommended. Prolonged cultivation produces strains which operate well at the ordinary temperature. CHEMICAL ABSTRACTS.

Variations in the unsaponifiable matter and lipoidal phosphorus of Aspergillus niger as a function of the mineral composition of the culture medium. C. PONTILLON (Compt. rend., 1930, 191, 1367-1369).—The lipoidal phosphorus

content reaches a maximum after 48 hrs. in a normal medium, somewhat later in acid or alkaline media, the formation being greatest as the mineral composition approaches that of Molliard's fluid. Disappearance of lipoidal phosphorus does not run parallel with loss of weight in the mycelium. Sterols are utilised during spore formation.

P. G. MARSHALL.

Esterase and protease of *Penicillium Roqueforti*. N. M. NAYLOR, L. W. SMITH, and H. J. COLLINS (Iowa State Coll. J. Sci., 1930, 4, 465-471).--Optimal conditions for growth, corresponding with increased production of protease and esterase, are recorded. CHEMICAL ABSTRACTS.

Bacterial metabolism. LXXXVIII. Methods for study of "resting" bacteria. LXXXIX. Chemical activity of "resting" Bacillus coli. XC. B. alcaligenes. XCI. B. pyogenesfætidus. XCII. Vibrio H/61. XCIII. Staphylococcus aureus. XCIV. B. pyocyaneus. XCV. Glyoxalase-like action of certain "resting" bacteria. A. I. KENDALL, T. E. FRIEDMANN, and M. ISHIKAWA. XCVI. Utilisation of certain substituted carbohydrates by bacteria. A. I. KEN-DALL and C. E. GROSS. XCVII. Production of histamine by certain strains of the gas bacillus. A. I. KENDALL and E. GEBAUER-FÜLNEGG. XCVIII. Quantitative response of intestine from sensitised guinea-pigs to homologous protein and to histamine. A. I. KENDALL and F. O. SHUMATE. XCIX. Anaphylactic reaction in smooth muscle. A. I. KENDALL (J. Infect. Dis., 1930, 47, 186–193, 194–205, 206–212, 213–218, 219–222, 223–228, 229–236, 237–248, 249–260, 261–266, 267–283, 284-291).-LXXXVIII. Methods for the determination of carbon dioxide, alanine, pyruvic acid, lactic acid, methylglyoxal, dextrose, and volatile acids are described.

LXXXIX. Lactic and pyruvic acids are transformed; the fate of the former is not known, but about 25% of the latter is converted into lactic acid. Alanine is affected only slightly. Dextrose is a good substrate.

XC. Lactic acid is converted into pyruvic acid under aërobic conditions; alanine is readily converted into unknown products. Dextrose is not attacked.

XCI. Dextrose and lactic acid are attacked, particularly under aërobic conditions.

XCII. Lactic acid, but not dextrose or alanine, is utilised.

XCIII. Dextrose, pyruvic acid, and lactic acid are utilised. The action on alanine is pronounced only in presence of oxygen.

XCIV. Pyruvic acid is attacked with production of volatile acids. Alanine and dextrose are attacked in presence of oxygen. Lactic acid is not a favourable substrate.

XCV. Certain "resting" bacteria which ferment dextrose have a glyoxalase-like action.

XCVI. Of carbohydrates dextrose is most readily utilised by bacteria; oxidation to gluconic acid alters the utilisability less than that of the other dextrose derivatives examined. Sorbitol is less readily fer-

mented than mannitol; dulcitol is very resistant. Methyl derivatives of dextrose are refractory to fermentation. isoPropylideneglucose is decomposed by the more vigorous types of bacteria;  $\beta$ -methylglucoside is more readily utilised than a-methylglucoside. Mannose is less readily utilised than dextrose; whereas gluconic acid is nearly as readily utilised as dextrose, the utilisability of mannonic acid is restricted. On the other hand, reduction to mannitol does not greatly reduce utilisability as is the case when dextrose is reduced to sorbitol. Tetramethylmannose and a-methylmannoside are refractory. Lævulose is utilised less readily than dextrose. Methyl and isopropylidene derivatives of lævulose are unfermentable. Galactose is utilised more frequently than mannose or lævulose, but 6-methyl- and isopropylidene-galactose are not fermented. Xylose is fairly readily fermented, whilst  $\gamma$ -trimethylxylose is refractory; d-arabinose is fermented by various bacteria that also ferment *l*-arabinose.

XCVII. Some strains of B. welchii produce histamine in milk. CHEMICAL ABSTRACTS.

Relation of the quantity of cystine in bacterial protein and anaërobiosis. S. KISHINO (Japan. J. Exp. Med., 1929, 7, 575-577).—Cystine could not be found in B. coli; V. choleræ, M. tuberculosis, C. welchii, and C. sporogenes contained 0.144, 0.105, 0.872, and 0.896%, respectively. Sulphur is considered to be essential for the synthesis of bacterial protein of anaërobes. CHEMICAL ABSTRACTS.

Correlation of the oxidation of certain phenols and dimethyl-p-phenylenediamine by bacterial suspensions. F. C. HAPPOLD (Biochem. J., 1930, 24, 1737-1743).—The capacity of bacterial suspension to catalyse the oxidation of pyrocatechol, guaiacol, orcinol, phenol, p-cresol, and tyrosine has been studied. Oxidation of pyrocatechol with the formation of o-benzoquinone is catalysed only by those organisms which give the dimethyl-p-phenylenediamine reaction (cf. Gordon and McLeod, J. Path. Bact., 1928, 31, 185). The suspensions of staphylo-coccus used gave a typical although weak colour change with pyrocatechol and did not deaminate in the system bacterial suspension-alanine-pyrocatechol. The anthracoids, unlike the other oxidase-containing bacteria, catalysed the oxidation of guaiacol to a maroon-coloured compound of unknown type, whilst V. tyrosinatica catalysed the oxidation of phenol and *p*-cresol; pyrocatechol, which is not appreciably autoxidised at slightly acid reactions, is markedly oxidised at  $p_{\rm H}$  9.0, and when the oxidation is carried out in the presence of aniline two distinct crystalline substances, of which one appears to be the anilinoo-quinone, can be isolated. Anilinobenzoquinone is also obtained by the action of washed bacterial suspensions of anthracoid or of V. choleræ on pyrocatechol in the presence of aniline. S. S. ZILVA.

Bacillus thermofibrincolus. III. A. ITANO and S. ARAKAWA (Ber. Ohara Inst. Landw. Forsch., 1930, 4, 457-469).-The influence of several factors on the fermentation of cellulose by B. thermofibrincolus has been studied. Cellulose is best decomposed (88%) at 65° by a 7-day aërobic test-tube culture containing 0.75-2.20% of cellulose, 0.5% of peptone, and calcium

carbonate. Anaërobic flask culture at 50° containing 0.75-3.75% of cellulose, meat extract, and calcium carbonate is most favourable for the production of alcohol and volatile acids. Slight acidity developed in the absence of calcium carbonate greatly impairs the activity of the organism. The organism produces a proteolytic enzyme. Bacterial growth and production of amino-nitrogen are dependent on the A. COHEN. supply of cellulose.

Aërobic soil bacteria which decompose cellulose. A. KALNINS (Latvij. Univ. Raksti, 1930, 1, 11; Proc. Internat. Soc. Soil Sci., 1930, 5, 216-217). -The isolation and morphology of aerobic cellulosesplitting organisms are described. Ammonium salts and nitrates proved the best sources of nitrogen for the bacteria, although organic materials could be utilised. Cellulose, starch, or sugars served as energy sources, but glycerol, mannitol, and calcium salts of organic acids were not utilisable. Acid was produced during the decomposition by the organisms of starch or sugars, but not from cellulose. Among the pro-ducts of decomposition of cellulose was a reducing, osazone-forming substance the formation of which was favoured by limitation of the oxygen supply. The products of cellulose decomposition served as an energy source for Azotobacter chröococcum. Starch and dextrose, in concentrations up to 1% in the medium, retard cellulose decomposition. The optimum temperature for the majority of the organ-isms is  $25-27^{\circ}$  with  $p_{\rm H}$  7.5 approx.

A. G. POLLARD.

Decomposition of peat. II. Symbiosis of cellulose-decomposing and nitrogen-fixing bacteria in the anaërobic decomposition of peat. I. A. MAKRINOV and M. L. STEPANOVA (Arkh. Biol. Nauk, 1930, 30, 293-302).—The two groups of bacteria were grown together on aerobically fermenting peat, and their natural symbiosis is postulated. CHEMICAL ABSTRACTS.

Influence of caffeine on the fixation of free into bacteroids, but does not increase their capacity to fix free nitrogen; there is no correlation between the two processes. CHEMICAL ABSTRACTS.

Influence of silica gel on the assimilation of phosphorus by Azotobacter. J. ZIEMIECKA (Rocz. Nauk Roln. Les., 1929, 22, 343-349).-A discussion of the favourable influence of silica gel on the assimil-ation of phosphorus by plants and micro-organisms of the Azotobacter group. CHEMICAL ABSTRACTS.

Biological determination of dextrose. II. Relation between dextrose concentration and  $p_{\rm H}$ change in media. A. LE VESCONTE, J. H. BUCHA-NAN, and M. LEVINE (Iowa State Coll. J. Sci., 1930, 4, 451-457).-Azotobacter levans acting on replicate media for periods up to 60 hrs. produces uniform  $p_{\rm H}$ values when the media are dextrose (0.01-0.40%) solutions. The most accurate determinations are made by recording data at the minimum  $p_{11}$  value.

CHEMICAL ABSTRACTS. Reduction of nitrates by bacteria. M. P. KORSAKOV (Russ. Microbiol. J., 1929, 9, 108-113).- The reduction of nitrates by bacteria is discussed from the point of view of the theory of oxidation-reduction potential. The oxidation-reduction process can take place only if the compounds in the medium can be activated by the bacteria so that one becomes the donator and another the acceptor of hydrogen, but whether the reduction of nitrates by bacteria in one medium and not in another depends solely on change of the oxidation-reduction potential is an open question. Aërobic bacteria are able to activate, not only the system donator of hydrogen (organic substance)+acceptor (oxygen), but also other systems in which the oxygen is replaced by other acceptors, e.g., nitrates. Thus, B. pyocyaneus, incapable of fermentation when the source of oxygen is citric acid, is able to develop under aerobic conditions at the expense of the system citric acid+nitrate, the acid being oxidised completely to carbon dioxide.

The products formed under aërobic conditions are the final products, these being, for  $B.\ coli$ , lactic, acetic, and formic acids, which cannot be fermented further, as they cannot be activated. Under aërobic conditions, however, lactic and acetic acids form, with the oxygen, systems which  $B.\ coli$  is able to activate, lactic acid being then oxidised to pyrotartaric acid. When nitrates are present in addition to lactic or acetic acid,  $B.\ coli$  oxidises these acids also under anaërobic conditions, since systems of donator and acceptor, capable of activation, are then formed (cf. Quastel and Wooldridge, A., 1929, 355). The general conclusion reached from the available data is that the reduction of nitrates by bacteria represents an oxidation-reduction process, conditioned by the differences of potential which depend on the mutual relationships between the bacteria and the medium and may change with alteration of such relationships. T. H. POPE.

Biological reduction of mineral phosphates. K. I. RUDAKOV (Zentr. Bakt. Par., 1929, II, **79**, 229; Bied. Zentr., 1930, **59**, 543—544; cf. A., 1928, 447).— Phosphate-reducing organisms develop in cultures with  $p_{\rm H}$  range 4-6—7-7, with an optimum reducing power at  $p_{\rm H}$  7-1. Maximum reduction is reached after 2 days. The short period of the reduction process has no relationship to the accumulation of acid in the cultures. The development of the organisms is proportional to the phosphate concentration of the substrate. Simple organic acids and alcohols as well as reduced phosphate compounds are among the products of metabolism of the organisms. The colorimetric method, using quinine sulphomolybdate, serves for the determination of phosphates in the presence of phosphites and hypophosphites.

A. G. POLLARD.

Cholesterol in bacteria. K. MIYOSHI (Sei-ikwai Med. J., 1930, 49, No. 6, 47–49).—No measurable amount of cholesterol is present in *B. coli communis*, *S. pyogenes aureus*, *V. choleræ*, *B. pyocyaneus*, or *B. dysenteriæ*. CHEMICAL ABSTRACTS.

Phosphoric esters produced during lactic fermentation. A. I. VIRTANEN and J. TIKKA (Biochem. Z., 1930, 228, 407–408).—By the action of dried *B. casei*  $\varepsilon$  on dextrose about half of this is converted into lactic acid and half into a mixture of

equal amounts of two phosphoric esters which are formed by the decomposition of Robison's hexosemonophosphoric ester first produced. Neither of the new esters reduces Fehling's solution. One forms a water-soluble barium salt, C12H19O6PBa2,  $[\alpha]_{0} - 8^{\circ}$ , and a crystalline strychnine salt. When boiled with mineral acid this ester loses phosphoric acid only with difficulty and yields a solution which does not reduce Fehling's solution. The other ester forms a barium salt which is sparingly soluble in water and when boiled with dilute mineral acid it also yields a solution which does not reduce Fehling's solution. This ester probably contains a hydroxyl group in place of the aldehyde group of the dextrose molecule. It seems that one ester is an oxidation product, the other a reduction product of dextrose and hence that they are formed by oxido-reduction from Robison's ester (cf. A., 1928, 797). W. MCCARTNEY.

Biochemical preparation of optically active glyceraldehyde. C. NEUBERG (Biochem. Z., 1930, 228, 259—261).—d-Glyceraldehyde is obtained from the racemic aldehyde by the action of *B. lactis aërogenes* and *B. coli*. P. W. CLUTTERBUCK.

Influence of hydrogen-ion concentration on the growth of tubercle bacilli. II. Biochemistry of the acid-resistant bacilli. L. M. MODEL (Zhur. exp. Biol. Med., 1929, **13**, 103—107).—Growth is possible within a wide range of  $p_{\rm H}$  values; the optimal value is  $7\cdot2$ — $7\cdot5$ . In a medium poor in nitrogen the  $p_{\rm H}$  shifts to the acid side, but in one rich in nitrogen and poor in phosphorus it shifts to the alkaline side. Autolysis causes a shift to the alkaline side.

CHEMICAL ABSTRACTS.

Purification of tuberculin. I. E. MASCHMANN and E. KÜSTER (Z. physiol. Chem., 1930, 193, 215— 237).—Tuberculin obtained from cultures on Sauton nutrient solution is purified by 3 days' dialysis (during which there is about 30% loss) and precipitation of proteins by addition of acetic acid to  $p_{\rm H}$  3.8. The specific substance is then adsorbed on electroosmotically purified kaolin, the associated carbohydrates remaining in solution. Elution with dilute ammonia solution regenerates the specific substance, which now shows about twenty times its original activity. It gives the biuret, ninhydrin, sometimes Millon, but no tryptophan or Molisch reaction. A preliminary investigation of the carbohydrate fraction yielded a substance resembling glycogen.

J. H. BIRKINSHAW.

Lipins of tubercle bacilli. XXI. Polysaccharide occurring in the phosphatide from human tubercle bacilli. R. J. ANDERSON and E. G. ROBERTS (J. Amer. Chem. Soc., 1930, 52, 5023— 5029).—Hydrolysis of the phosphatide (A., 1927, 1114) with 1% alcoholic potassium hydroxide solution gives an alcohol-insoluble mixture of the potassium salt of an acid (barium salt) which contains phosphorus, and a polysaccharide termed maninositose,  $[\alpha]_{13}^{34}+57^{\circ}$ in water, which when heated sinters at 100°, froths at 150°, and darkens slowly above 250°. Hydrolysis of the acid with 5% sulphuric acid affords a reducing sugar, whilst maninositose yields mannose and *i*-inositol (cf. A., 1930, 819). H. BURTON.

Reactions relating to carbohydrates and polysaccharides. XXXIII. Synthesis of polysaccharides by bacteria and enzymes. C. F. HARRISON, H. L. A. TARR, and H. HIBBERT (Canad. J. Res., 1930, 3, 449-463).—The formation of polysaccharides from simple sugars by microbiological agents is reviewed.

The production of "gum levan" from sucrose by the subtilis-mesentericus group is confirmed; of these the most active agent is B. mesentericus, Trevisan. A nutrient 20% sucrose broth is inoculated with a culture of this organism and incubated at 37.5° for 6 days. The crude product, obtained by precipitation with alcohol, is purified by electrodialysis and further precipitations from aqueous solution by alcohol; the yield of levan is 55% of the theoretical quantity. Levan is produced both by *B. mesentericus* and *B.* subtilis, Cohn, in nutrient media containing sucrose and raffinose, but not from those containing melezitose, maltose, lactose, dextrose, xylose, or lævulose. The production of levan, which is formulated as a polymeric 2:6-anhydrofructofuranose (cf. Hibbert and Tipson, A., 1930, 1024), is assigned to a specific enzyme, capable of converting the terminal fructofuranose group of sucrose and raffinose, but not the central fructofuranose residue of melezitose, since the production of some polysaccharide is observed in sucrose solutions to which a sterile ultrafiltrate of an active culture has been added. In addition, levan is formed in sucrose solution containing B. mesentericus in the presence of toluene at a time when the concentration of viable cells is rapidly diminishing.

T. H. MORTON.

Molecular size of type III specific polysaccharide of pneumococcus. F. H. BABERS and W. F. GOEBEL (J. Biol. Chem., 1930, 89, 387-394).-Determinations of the diffusion coefficient of the specific polysaccharide from type III pneumococcus lead to the value 118,000 for the mol. wt. C. R. HARINGTON.

Preparation of type-specific polysaccharides of pneumoccocus. W. F. GOEBEL (J. Biol. Chem., 1930, 89, 395-398).-Cultures of pneumococcus were concentrated and precipitated with alcohol; the precipitate was extracted with water and the filtered solution again precipitated with alcohol. The aqueous solution of the precipitate was freed from protein with trichloroacetic acid, neutralised, and treated with alcohol; after one more separation from aqueous solution by addition of alcohol the carbohydrate was dissolved in water and precipitated at 0° by addition of hydrochloric acid (in the case of type III pneu-mococcus) or of alcohol (type I). The yield was 0.197 g. per 1000 c.c. (type III) and 0.053 g. per 1000 c.c. (type I). C. R. HARINGTON.

Chemical alteration of purified antibody proteins. L. REINER (Science, 1930, 72, 483-484).-Diazo-coupling of atoxyl with a type I and II pneumococcus antibody gives a product practically insoluble at the isoelectric point  $p_{\rm H}$  6 and soluble on the acid or alkaline side. Mice infected with 105 lethal doses of virulent pneumococci could be fully protected with the preparation. Normal horse serumglobulin coupled with atoxyl had practically no effect.

L. S. THEOBALD.

(a) Purification and concentration of diphtheria toxin and anatoxin with special reference to active immunisation of man. S. SCHMIDT and A. HANSEN. (b) Purification and concentration of diphtheria toxin and anatoxin by precipitation with acid. S. SCHMIDT and K. A. KJAER (Biochem. Z., 1930, 228, 263-290, 291-299).-(a) Highly concentrated colourless and odourless solutions of diphtheria toxin and anatoxin can be prepared from the original impure materials by adsorption on a mixture of aluminium hydroxide and charcoal. The purified toxin and anatoxin solutions retain the specific immunological properties of the crude materials, contain 500-1000 units per c.c., and have protein contents which do not exceed those of the original solutions.

(b) For practical purposes diphtheria toxin and anatoxin are best purified by precipitation with hydrochloric acid at  $p_{\rm H}$  3.5-4.1, the temperature being kept between 0° and 18° and the acid being allowed to act for as short a time as possible. In this way yields of 50-60% are obtained. The properties of the purified materials differ considerably from those of the original ones, the immunising effect of the anatoxins, for example, being reduced.

W. MCCARTNEY.

Insoluble precipitates in diphtheria and tetanus immunisation. A. T. GLENNY (Brit. Med. J., 1930, ii, 244-245).-The addition of aluminium sulphate or potash alum to diphtheria or tetanus toxoid produces a precipitate with high antigenic CHEMICAL ABSTRACTS. power.

Purification of bacteriophage (Shiga and typhoid phages). S. Hosova, K. Nagase, and T. YOSHIZUMI (Japan. J. Exp. Med., 1930, 8, 1-2).-Bacteriophage was precipitated with zinc chloride; the zinc was removed and the filtrate dialysed. The non-dialysable fraction, concentrated at a low temperature and under reduced pressure, contained nitrogen and was precipitated by tannic and phosphotungstic acids, but did not give the protein colour reactions and was not precipitated by Nessler's reagent, ethyl or methyl alcohol, ammonium sulphate, or picrolonic acid. Treatment of the tannic acid precipitate with barium hydroxide destroyed phage activity. The non-dialysable fraction obtained from vaccine virus was inactive. CHEMICAL ABSTRACTS.

Bactericidal effect of ether and chloroform vapours. S. YASUDA (Sei-i-kwai Med. J., 1930, 49, No. 4, 51-70).-Ether vapour is less toxic towards bacteria than chloroform vapour.

CHEMICAL ABSTRACTS.

Disinfection and sterilisation. II. Constitution of terpenes and their disinfecting properties. P. K. DE. III. Composition of essential oils and their disinfecting properties. V. SUBRAHMANYAN (Indian J. Med. Res., 1930, 18, 83-90, 91-96).-The germicidal power of terpene hydrocarbons, determined by Rideal and Walker's method with Bacillus typhosus, is practically zero; derivatives containing hydroxyl, formyl, carbonyl, and oxygen groups are generally active, alcohols being more effective than ketones. Multiplication of active groups and esterification reduce the phenol coefficients; unsaturation, and increasing length of sidechains, as calculated from the position of active groups, enhance the disinfecting power. The phenol coefficients of essential oils, although largely determined by the nature and proportion of the active constituents, cannot be predicted from the composition alone. CHEMICAL ABSTRACTS.

"Virtual adrenaline": inactivation of adrenaline by formaldehyde. M. PAGET and C. P. LEBLOND (J. Pharm. Chim., 1930, [viii], 12, 531— 536).—The authors have previously demonstrated that suprarenal glands, after keeping for 24 hrs. in a vacuum over sulphuric acid, frequently show a higher adrenaline content than immediately after death, Denigès' reagent being used as a test. The action of formaldehyde on the secondary amino-group of adrenaline causes it to give a negative reaction with Denigès' reagent, but not with those of Vulpian, Folin, or Paget, which react with the pyrocatechol nucleus. The mydriatic action is considerably reduced, but still persists. T. MCLAOHLAN.

Influence of adrenaline and insulin on tissue oxidation. U. VON EULER (Skand. Arch. Physiol., 1930, 59, 123—400; Chem. Zentr., 1930, ii, 937).— For oxygen concentrations of 2—10% adrenaline  $(10^{-8} \text{ to } 10^{-14})$  increases the oxygen demand of intact or minced musculature; that of washed muscle is increased by adrenaline only after addition of glycerophosphates and hexosephosphates. The effect of nerve section is recorded. Adrenaline does not increase the oxygen demand or methylene-blue reduction of erythrocytes even in presence of glycero- or hexose-phosphate. The oxidation-promoting effect of insulin is also observed only in suboptimal oxygen concentrations; the reaction is not observed with aërated muscle. A. A. ELDRIDGE.

Phloridzin and insulin. G. ROSENFELD (Arch. exp. Path. Pharm., 1930, 157, 149-153).—The prevention of accumulation of fat in the liver by administration of insulin to phloridzinised dogs (cf. Wertheimer, Pflüger's Archiv, 1926, 213, 280) was confirmed. A much lower dextrose and nitrogen excretion occurred than in dogs with phloridzin alone. The significance of these changes with respect to the rôle of the pituitary gland is discussed.

F. O. HOWITT.

Initial hyperglycæmia of dogs after administration of insulin. F. RATHERY, R. KOURILSKY, and J. LAURENT (Compt. rend. Soc. Biol., 1930, 103, 563—564; Chem. Zentr., 1930, ii, 1241).—The initial hyperglycæmia is independent of the mode of administration, the preparation, and the dose.

A. A. ELDRIDGE.

Insulin and glycogen. I. Normal dogs. II. Depancreatised, fasting, and phloridzinised dogs. F. RATHERY and B. KOURLSKY [with S. GIBERT and J. LAURENT] (Ann. Physiol. Physicochim. biol., 1930, 6, 32-72, 73-128; Chem. Zentr., 1930, ii, 1240-1241).—I. Blood issuing from the liver after injection of insulin was richest in sugar, that of the portal vein being poorest. Insulin hypoglycamia is not attributed to inhibition of glycogenolysis. Shortly after injection the liver-glycogen diminishes by 45-85%

simultaneously with the hyperglycamia. Muscleglycogen also diminishes, the average fall being 22%.

II. Changes in the liver-glycogen and blood-sugar after injection of insulin are recorded.

A. A. ELDRIDGE.

Oral influence of insulin-bile acid. A. W. ELMER and M. SCHEPS (Münch. med. Woch., 1930, 77, 931—932; Chem. Zentr., 1930, ii, 936—937).—"Cholosulin," when administered orally, has no hypoglycamic action. A. A. ELDRIDGE.

Influence of substances of the thyroid gland on the total creatine content of liver and muscle. I. ABELIN and W. SPICHTIN (Biochem. Z., 1930, 228, 250—256).—Administration of thyroid substances causes in rats a considerable decrease of the total creatinine of liver of muscles as well as loss of glycogen and fat. P. W. CLUTTERBUCK.

Thyroxine and the thyroid. I. ABELIN (Biochem. Z., 1930, 228, 233—249).—A difference in the action of thyroxine and of the whole substance of the thyroid gland is investigated. When rats are given dried thyroid for 8—10 days and again after a rest of 2—3 months, it is found that the second dose is tolerated more readily than the first, the liver being then able to store considerable amounts of glycogen. When thyroxine is injected, both the first and the second treatments render the liver unable to retain carbohydrate as glycogen and the effect on the gaseous metabolism is established more quickly and strongly with the second than with the first injection.

P. W. CLUTTERBUCK.

Effect of long-continued administration of parathyroid on the body-calcium and -phosphorus of albino rats. P. L. DAY (J. Nutrition, 1930, 3, 157-160).—No measurable effect was observed. CHEMICAL ABSTRACTS.

Parathyroid hormone and regulation of calcium level. C. BOMSKOV (Arch. exp. Path. Pharm., 1930, 157, 220—233).—The curve of blood-calcium level before and after oral or subcutaneous administration of calcium gluconate in normal and parathyroidtreated animals and the effect of the hormone on the normal blood-calcium were studied in rabbits. The significance of the results together with those of corresponding serum-phosphorus values are discussed.

F. O. HOWITT.

Growth-promoting hormone of the pituitary body. H. B. VAN DYKE and Z. WALLEN-LAWRENCE (J. Pharm. Exp. Ther., 1930, 40, 413-422).-The finely-ground anterior lobes of the pituitary gland are extracted with dilute sodium hydroxide solution at 0° and the extract is brought by the addition of dilute hydrochloric acid to  $p_{\rm H}$  7.2 and the precipitate removed. The active principle is then precipitated by the addition of sodium sulphate (20 g. per 100 c.c.). The precipitate after washing in 20% sodium sulphate is suspended in distilled water, the mixture brought to  $p_{\rm H}$  7.5, the insoluble residue discarded, and the solution is filtered. For clinical use it is further purified by precipitation with sodium sulphate, dialysis, and treatment with N-acetic acid, which at  $p_{\rm ff}$  4.75 produces a precipitate which is removed. The supernatant fluid is readjusted to  $p_{\rm H}$  7.5–8.0 by N-sodium hydroxide solution. The biological assay of this extract by the use of hypophysectomised or normal adult rats is discussed. It is proposed to name the growth-promoting principle of the anterior lobe "Phyone." These extracts have no effect on the œstrous cycle of normal female rats. When treated with norite the extracts lose their activity.

W. O. KERMACK.

Conditions of action of extract of the posterior pituitary lobe on uterine muscle. H. KNAUS (Zentr. Gynākol., 1929, 1162—1174; Chem. Zentr., 1930, ii, 258).—An examination of the effect of the physiological condition of uterine muscle and of the function of the corpus luteum. A. A. ELDRIDGE.

Hormone of the anterior pituitary lobe. A. BIEDL (Endocrinol., 1928, 2, 241—248; Chem. Zentr., 1930, ii, 1238).—The preparation of the hormone from urine of pregnancy or from the fresh gland, and its biological evaluation, are described.

A. A. ELDRIDGE.

Distribution of the ovarian hormone in the mammalian organism. M. GUTMAN (Monatsschr. Geburtshilfe, 1928, 79, 433—439; Chem. Zentr., 1930, ii, 935).—Only the wall and liquor of ripe follicles of the ox, pig, and horse contain the hormone, which is absent from other parts of the ovary, the corpus luteum, and the placenta; it is absent from the placenta of the dog, cat, rabbit, and guinea-pig, but present in that of the mouse. A. A. ELDRIDGE.

Gastric absorption of the follicular hormone. M. M. MAINO (Arch. Ist. Biochim. Ital., 1930, 2, 495— 504).—Experiments with rats confirm the observation that the mucosa of the digestive apparatus serves well for the absorption of the ovarian hormone. The dose of hormone necessary by this route is treble that required parenterally; the gastric absorption is not influenced by the degree of purity of the solutions used. The nature of the vehicle in which the hormone is ingested affects the amount absorbed, alcoholic solutions being the most active. T. H. POPE.

Female sex hormone: assay; preparation. F. E. D'AMOUR and R. G. GUSTAVSON (J. Pharm. Exp. Ther., 1930, 40, 473-488).—The factors influencing the assay of the hormone producing  $\alpha$ strus in ovariectomised rats have been investigated and the results of Coward and Burn (J. Physiol., 1927, 63, 270) emphasising the variability of individual rats have been confirmed. Crystalline  $\alpha$ strin has been prepared having m. p. 241° after sublimation in a vacuum and recrystallisation from 70% alcohol. On assay 1 rat unit (Coward and Burn) was present in 0.38  $\gamma$ . The compound was apparently identical with that described by Doisy, Veler, and Thayer (A., 1930, 821). W. O. KERMACK.

Rapid (mitogenesis) test for male sexual hormone (androkinin). H. E. Voss and S. LOEWE (Deut. med. Woch., 1930, 56, 1256—1258; Chem. Zentr., 1930, ii, 1237).

The male hormone. IV. C. FUNK and B. HARROW (Biochem. J., 1930, 24, 1678—1680).—Considerable loss of activity takes place when urine is not acidified prior to the extraction of the hormone with chloroform. Ether extracts much of the principle from strongly alkaline solutions obtained by extracting strongly acidified urine with chloroform. S. S. ZILVA.

Nutritive value of fresh grape juice and wine in relation to their vitamin content. L. RANDOIN (Rev. Viticult., 1930, 72, 381—389; Chem. Zentr., 1930, ii, 261—262).—Vitamin-C was present, but the juice was equivalent in antiscorbutic value to half its volume of lemon juice. The amount of vitamin-Bwas insufficient to support life. A. A. ELDRIDGE.

Vitamins of water-cress (Nasturtium officinale). L. B. MENDEL and H. B. VICKERY (J. Home Econ., 1930, 22, 581—587).—Vitamins-A and -E are present in the leaves in larger proportions than in lettuce; vitamin-B is present in amount comparable with that in other green leaves. The leaves are also known to be rich in vitamin-C.

CHEMICAL ABSTRACTS.

Determination of vitamin-A. K. H. COWARD, K. M. KEY, F. J. DYER, and B. G. E. MORGAN (Biochem. J., 1930, 24, 1952—1966).—Two substances to be tested are given to two groups of rats when growth ceases on a vitamin-A-free diet. The mean increases in weight of each of the two groups are referred to a curve relating mean increase to dose of a particular sample of cod-liver oil, whence the relative potencies of the two substances are deduced. With 10 rats in a group the potency of a substance can usually be estimated with an error of less than 30%. The curve relating dose to mean increase of weight in a group cannot be assumed to be applicable to all vitamin-A-free diets.

Vitamin-A content of the livers of normal hogs and of hogs developing experimental rickets. R. GIBBONS and C. B. BARNEY (J. Home Econ., 1930, 22, 491-496).—Liver of rachitic hogs, when fed to rats, produced 52% more growth than that of normal hogs, probably owing to the rachitic hogs requiring 62% more food per lb. of gain than the controls, whereby a larger proportion of vitamin-A was stored. CHEMICAL ABSTRACTS.

Reaction of antimony trichloride with codliver oil and its unsaponifiable fraction. E. L. SMITH and V. HAZLEY (Biochem. J., 1930, 24, 1942— 1951).—The unsaponifiable fraction of cod-liver oil, which can be extracted almost without loss with ether, ethyl acetate, chloroform, or light petroleum, gives with antimony trichloride in chloroform a blue colour proportional to its concentration (cf. Norris and Church, A., 1930, 379, 962). The line representing the dilution effect for the total unsaponifiable fraction is tangential at the origin to the dilution curve for the corresponding cod-liver oil; the intensity of the blue colour is not a linear function of the concentration of the oil. S. S. ZILVA.

Antimony trichloride reaction for vitamin-A. III. Effect of concentration of reagent and stability of chromogen towards light. E. R. NORRIS and A. E. CHURCH (J. Biol. Chem., 1930, 89, 421-435).—With concentrations of oil giving colour values higher than 5 Lovibond units the concentration of antimony trichloride has a marked influence on the intensity of colour developed; further, with high colour values the rate of fading may be such that the intensity of the light employed in making the observations becomes of significance. Exposure of cod-liver oil (whole or unsaponifiable fraction) in chloroform solution to light of wave-length 500 mµ or less causes rapid destruction of the chromogen, particularly in presence of oxygen; light of longer wave-length has no such effect. C. R. HARINGTON.

"Diet 4" for breeding rats for work on vitamin-A. S. V. GUDJÓNSSON (Biochem. J., 1930, 24, 1591-1594).—The diet consists of 30% of skimmed-milk powder, 40% of rice flour, 15% of autolysed yeast, and 15% of hardened coconut oil and shark-liver oil. The young rats are ready for use at the age of 30 days, and, owing to their low reserve of vitamin-A, show deficiency-symptoms early. S. S. ZILVA.

Relation of hydrogen-ion concentration to the precipitation of purified torulin (yeast vita-min- $B_1$ ) by phosphotungstic acid. H. W. KIN-NERSLEY and R. A. PETERS (Biochem. J., 1930, 24, 1856-1863).-The precipitation of the vitamin by this reagent appears to take place between  $p_{\rm H}$  8.0 and 3.5. It is possible to attain a high degree of concentration by precipitating the active fraction several times. Torulin is unstable to alkali in alcoholic solution. Identical results are not obtained in certain stages of a scheme of fractionation when different sources of the vitamin such as rice or yeast are used. S. S. ZILVA.

Maintenance nutrition in the adult pigeon and its relation to torulin (vitamin- $B_1$ ). I, II. C. W. CARTER, H. W. KINNERSLEY, and R. A. PETERS (Biochem. J., 1930, 24, 1832-1843, 1844-1851).-I. A daily dose of marmite of 1.0 g. (equivalent to 4.3 day doses of vitamin- $B_1$ ) is sufficient to convert a falling nutrition on polished rice into maintenance at almost any point between the maximum and minimum weight. Large amounts of vitamin- $B_1$  do not produce this effect, which confirms the authors' previous observation that purified torulin (vitamin- $B_1$ ) does not give maintenance.

II. The factor which supplements  $B_1$  ( $B_5$ ) in the production of maintenance nutrition is present in 50% alcohol extracts of the charcoal process for concentrating vitamin- $B_1$  (Kinnersley and Peters) and centrating vitamin- $B_1$  (Kinnersiev and Peters) and also in alkalised marmite. It is not identical with vitamin- $B_3$ ,  $-B_2$ , or  $-B_4$ . Whole wheat steamed for 5 hrs. gives rising nutrition when supplemented with small doses of vitamin- $B_1$ . Vitamin- $B_3$  is there-fore heat-stable under some conditions. Pigeons receiving up to 36 doses of vitamin- $B_1$  behave nor-mally. Storage of vitamin-B may influence markedly mally. Storage of vitamin- $B_3$  may influence markedly the behaviour of birds up to some 20 days after being placed on polished rice. S. S. ZILVA.

Quantitative comparison of the curative activity of torulin (vitamin- $B_1$ ) on the adult pigeon and the adult white rat. H. W. KINNERS-LEY, R. A. PETERS, and V. READER (Biochem. J., 1930, 24, 1820-1823).-Parallel tests on pigeons and rats by a curative and protective method with torulin (vitamin- $B_1$ ) preparations of different purity indicate that the  $B_1$  factor for the two animals is

identical and show that the dose of vitamin- $B_1$ required by these animals is approximately the same. S. S. ZILVA.

Curative activity of the antineuritic vitamin of rice. B. C. P. JANSEN, H. W. KINNERSLEY, R. A. PETERS, and V. READER (Biochem. J., 1930, 24, 1824-1826).-Curative tests with the Jansen and Donath rice-vitamin crystals (A., 1927, 382) gave the following activity per day dose of vitamin : pigeon 0.007 mg. by injection, 0.009 mg. by mouth; rat, 0.005 mg. Tested on S. corallinus it promoted growth of the organism in a dose of 0.006 mg. per diem. S. S. ZILVA.

Antineuritic vitamin. A. G. VAN VEEN (Rec. trav. chim., 1930, 49, 1178) .- A note on an improved trav. chim., 1950, 40, 40, and  $B_1$ . method for isolating vitamin- $B_1$ . J. D. A. JOHNSON.

Stability of vitamin-B2. N. B. GUERRANT and W. D. SALMON (J. Biol. Chem., 1930, 89, 199-211).-The growth-stimulating effect on young rats of yeast and yeast extracts is diminished by heating at 120° for 4 hrs. or by autoclaving at 20 lb. Concentrated extracts suffer loss of activity when exposed to ultraviolet irradiation or to the action of nitrous acid, although in the latter case disappearance of activity is not proportional to destruction of amino-groups. Exposure to oxygen or to hydrogen sulphide at 85-90° has no effect on the vitamin- $B_2$  content of the extracts. C. R. HARINGTON.

Distribution of the vitamin-B complex. I. Leafy vegetables. M. H. Roscoe (Biochem. J., 1930, 24, 1754-1763).-Watercress, lettuce, spinach, and cabbage (both the outer dark green leaves and inner etiolated ones), when dry weights are considered, have a content of vitamin- $B_1$  and vitamin- $B_2$  about one fourth that of dry brewer's yeast. Their content of vitamin- $B_1$  is lower than that of wheat germ or ox-liver and higher than that of egg-yolk or ox-muscle. The content of vitamin- $B_2$  is lower than that of oxliver, equal to that of milk, ox-muscle; or egg-yolk, and higher than that of the pulses or cereals. In their natural states, however, owing to their high water content, they are relatively poor sources of these vitamins. The onion bulb is poorer in both these vitamins than the green leaves, having about one twelfth to one sixteenth the value of dry yeast. The distribution of vitamin- $B_2$  appears to bear some relation to the greenness of the leaf, being greater in the dark green than in the paler leaves. No such difference is found in the case of vitamin- $B_1$ . The vegetables tested were on the whole richer sources of vitamin- $B_1$  than of vitamin- $B_2$ . In the cooking of spinach by the domestic process about half of both vitamin- $B_1$  and  $-B_2$  is lost in the water and juice. When egg-white is given as a source of vitamin- $B_2$  there is a lack of a third factor (factor Y) necessary for the normal growth of the rat. This factor is present in autoclaved yeast extracts and in all the vegetables tested, but the amounts present in lettuce and etiolated cabbage leaves are less than in the dark green leaves, and the amount present in the onion bulb is still smaller. S. S. ZILVA.

Composite nature of the water-soluble vitamin-B. III. Dietary factors in addition to the antineuritic vitamin- $B_1$  and the antidermatitis vitamin-B2. H. CHICK and A. M. COPPING (Biochem. J., 1930, 24, 1764-1779).-Rats show a failure to sustain growth on a diet containing egg-white as a source of protein and vitamin- $B_2$  and Peters' antineuritic concentrate as a source of vitamin- $B_1$  (diet II). When the protein portion of the diet is replaced by purified caseinogen and vitamin- $B_2$  is supplied in the form of egg-white or concentrates prepared from it, the same result is obtained. This is due to the absence from the ration of a hitherto unknown dietary factor-factor Y (see preceding abstract). Satisfactory but not normal and indefinite development over long periods, including fertility and successful pregnancy, but unsatisfactory lactation, was attained on a similar diet containing purified caseinogen as protein, Peters' antineuritic concentrate as vitamin- $B_1$ , and autoclaved yeast or autoclaved watery yeast extracts (5 hrs.; 120°;  $p_{\rm II}$  about 5.0) as vitamin- $B_2$ . Diet II was rendered satisfactory for growth by addition of a small daily ration of an aqueous yeast extract which had been autoclaved in alkaline solution (4 hrs.; 120—125°;  $p_{\rm H}$  about 10). In this preparation vitamin- $B_0$  was proved to have been destroyed. Factor Y can therefore withstand prolonged heating in alkaline solution, and differs in this respect from vitamin- $B_3$ and  $-B_4$ . It accompanies  $B_1$  and  $B_2$  in nature.

S. S. ZILVA.

Alcohol-solubility of the anti-dermatitis, more heat-stable vitamin- $B_2$  constituent of the vitamin-B complex. H. CHICK and A. M. COPPING (Biochem. J., 1930, 24, 1744—1747; cf. Narayanan and Drummond, A., 1930, 380).—When alcohol to 56% was added to a solution at  $p_{\rm H}$  1.5 of vitamin- $B_2$ prepared from brewer's yeast the precipitate was inactive and the filtrate possessed only one half the potency of the original material. After further addition of alcohol to 70% the solution was completely inactive. When the original solution was less acid ( $p_{\rm H}$  3.2) total inactivation occurred with 56% alcohol. S. S. ZILVA.

Egg-white as a source of the anti-dermatitis vitamin- $B_2$ . H. CHICK, A. M. COPPING, and M. H. ROSCOE (Biochem. J., 1930, 24, 1748—1753).—Hen's egg-white, although a rich source of vitamin- $B_2$ , contains no vitamin- $B_1$ . Growth can be restored in young rats suffering from vitamin- $B_2$  deficiency and the characteristic skin lesions healed by daily doses of a concentrate, prepared by the removal of the heat-coagulable proteins, equivalent to 5—10 g. of the original egg-white. Attempts to purify these concentrates further by alcohol fractionation or precipitation with lead acetate have been unsuccessful. Vitamin- $B_1$  diffuses out when undiluted egg-yolk is kept in a cellophane membrane surrounded by distilled water for 4 days at about 0°. S. S. ZILVA.

Assay of vitamin- $B_4$ . V. READER (Biochem. J., 1930, 24, 1827—1831).—The typical polyneuritis in rats is a mixture of symptoms due to lack of vitamin- $B_1$  and  $-B_4$ . By eliminating vitamin- $B_1$  deficiency at the critical stage the true clinical picture of vitamin- $B_4$  deficiency is revealed and can be used as a curative test. Using this method, vitamin- $B_4$  from 50% alcoholic extract of distillery yeast was concentrated from 500 mg. to 0.4 mg. per daily rat dose. This method also discloses how far a given vitamin- $B_1$  preparation is free from vitamin- $B_4$ . S. S. ZILVA.

Third factor in vitamin-B complex of yeast. G. Z. WILLIAMS and R. C. LEWIS (J. Biol. Chem., 1930, 89, 275-288).—The residue left after exhaustive extraction of yeast with aqueous alcohol contains a heat-stable substance which is necessary, in addition to vitamins- $B_1$  and  $-B_2$ , to promote the normal growth of rats on a diet deficient in the vitamin-B complex (cf. Hunt, A., 1928, 1405).

C. R. HARINGTON.

Toxic effect of fish-liver oils and action of vitamin-B. E. R. NORRIS and A. E. CHURCH (J. Biol. Chem., 1930, 89, 437—449).—The toxic effects of certain cod-liver oils simulate those produced by deficiency of vitamin-B and can be relieved by administration of yeast. The same remarks apply to the toxic symptoms which result from continued administration of small amounts of *iso*amylamine or of choline. An adequate supply of yeast in the diet is therefore of importance in the biological assay of cod-liver oil for its vitamin-A content.

C. R. HARINGTON. Vitamin-B deficiency in the rat. Bradycardia as a distinctive feature. A. N. DRURY, L. J. HARRIS, and C. MAUDSLEY (Biochem. J., 1930, 24, 1632-1649).-Bradycardia, which occurs only in advanced starvation and inanition, appears when young rats are deprived of the vitamin-B complex. The condition can be rapidly cured in the entire absence of food by injection or ingestion of vitamin-B concentrates. Prolonged restoration to normal heart rate is effected by the administration of vitamin-B even when the food consumption is of the same order as that ingested during the last stages of the deficiency. The curative substance was present in various vitamin- $B_1$  concentrates. It is comparatively thermolabile. The heart-rate response is roughly graded to the dose administered. Deficiency of vitamin-A, of vitamin-D, or of both combined has no significant influence. Excess of vitamin-D produces constantly a very slight bradycardia. S. S. ZILVA.

Heart block in pigeons, curative factor. C. W. CARTER (Biochem. J., 1930, 24, 1811—1819).— Whole wheat and yeast contain a factor, or factors, essential for the normal metabolism and nutrition of the pigeon, the absence of which from the polished rice leads to the development of heart block, among other disorders. This factor is destroyed in wheat if the cereal is previously heated at 100° for 5 hrs. and is not extracted with ether from it. The administration of a diet adequate in protein, fat, and inorganic salts instead of polished rice, or of vitamins- $B_1$ ,  $-B_2$ , -A, -D, or -E is incapable of preventing heart block or of clearing up the established condition. There is a similarity in the distribution and in the thermolability between this factor and Williams and Waterman's factor (cf. A., 1928, 1059). S. S. ZILVA.

Antiscorbutic fraction of lemon juice. IX. S. S. ZILVA (Biochem. J., 1930, 20, 1687-1698; cf. A., 1927, 487, 702; 1928, 801; 1930, 256).—In the manipulation of lemon juice variable activity is obtained under presumably the same conditions of fractionation when a volume of a saturated lead acetate solution equal to the volume of the juice is employed for the precipitation of the vitamin. It is, however, possible by adjusting the quantity of the precipitating reagent to prepare from the same juice fractions of higher activity. When the phenolindophenol-decolorising capacity of fractions falls below a certain limit they are antiscorbutically inactive. This reducing property is not an index of antiscorbutic activity itself, but serves rather as an indication that the vitamin has been protected from spontaneous inactivation. The reprecipitation of the antiscorbutic fraction from lemon juice or from cabbage juice with lead acetate in neutral or slightly alkaline zone  $(p_{\rm H} \ \text{S}=9)$  yields an inactive preparation. The addition of an ethereal extract from autoclaved lemon juice (which decolorises iodine but not phenolindophenol), of quinhydrone, or of benzoquinone to unheated lemon juice accelerates markedly the destruction of the reducing principle and of the antiscorbutic factor in a neutral medium in the presence of air. It is possible that a substance of phenolic character oxidisable in the air is formed in the process of autoclaving and that this compound in its oxidised form destroys in conjunction with the peroxidase present in the juice the reducing principle that acts as an agent for the protection of the antiscorbutic factor. Decitrated lemon juice kept aerobically at  $p_{\rm H}$  1 or at 0.6—0.8 for 7 days does not lose its reducing capacity for phenolindophenol to a greater extent than when kept at  $p_{\rm H}$  7 and shows little loss of its antiscorbutic S. S. ZILVA. activity.

Antirachitic properties of shrimp oil. F. P. BROOKS, R. F. ABERNETHY, and F. C. VILBRANDT (J. Amer. Chem. Soc., 1930, 52, 4940—4943).—Rats (suffering from rickets), fed on a rickets-producing diet supplemented by shrimp oil (the ether-soluble oil from shrimp waste), show increased calcium, phosphorus, and ash contents of the bones. H. BURTON.

Formation of antirachitic vitamin under exclusion of light. A. SCHITTENHELM and B. EISLER (Klin. Woch., 1928, 7, 1118—1119; Chem. Zentr., 1930, i, 3075).—No provitamin of the antirachitic active substance is present in barley germ (cf. A., 1928, 1405). No increase in the antirachitic principle results from irradiation with ultra-violet light under various conditions. Ergosterol was not found in the germ nor could an antirachitic substance be prepared from barley germinated in the dark. Thus vitamin-D is formed during germination, but light is not essential for its origin. L. S. THEOBALD.

Action of light and increasing temperature on the assimilation of carbon dioxide by plants. K. NEYDEL (Biochem. Z., 1930, 228, 451-486).—The effects of varying the type and intensity of the light and the temperature to which plants which grow in ordinary light are exposed have been measured and compared with those produced in plants which grow in the shade, the assimilation of carbon dioxide being taken as criterion. As regards the influence of temperature, the results of Lundegårdh (Biochem. Z., 1924, 154, 195) and Johannson (Svensk bot. Tidskr., 1923, 17, 215; 1926, 20) have been confirmed, at least in part. W. MCCARTNEY. Limnological importance of free carbonic acid. E. LINDEMANN (Naturwiss., 1930, 18, 1113).—The carbon dioxide contents of lakes in Sumatra and Java are discussed. The effects of different vegetable organisms on the carbon dioxide content and  $p_{\rm H}$  are also considered. W. R. ANGUS.

Influence of radium on the chrondriome of lower plants. P. F. MILOVIDOV (Protoplasma, 1930, 10, 297—299).—The elements of the chrondriome of *Saprolegnia* were not affected by exposure to  $\beta$ - and  $\gamma$ -radiation for several hours (cf. Compt. rend. Soc. Biol., 1929, 101, 676). A. G. POLLARD.

Hydrogen-ion phenomena in plants. IV. Buffers of potato (tuber and leaf). V. The buffer systems of plant juices. VI. Apparatus for measuring the effect of carbon dioxide on the reaction of plant sap. C. T. INGOLD (Protoplasma, 1930, 9, 441-446, 447-455, 456-458; cf. *ibid.*, 1929, 6, 51).—IV. The buffer action of potato tuber sap is attributed largely to its citrate, malate, and phosphate contents. Proteins, asparagine, and oxalate have but little effect. The substances recorded account for 60-70% of the buffer action between  $p_{\rm H}$  5 and 7, but considerably less in more acid ranges. Citrate, malate, and phosphate are also important buffers in the leaf sap.

V. In any range of  $p_{\rm II}$  the buffer index ( $\beta$ ) of a complex buffer system is the sum of the buffer indices of all single-buffer systems present. The general U-form of  $\beta$  curves is discussed. Proteins are not sufficiently powerful buffers to determine the shape of the  $\beta$  curve of plant sap. The forms of  $\beta$  curves in ranges  $p_{\rm II} < 7$  are considered and their uses in plant physiology discussed.

VI. Suitable electrometric apparatus is described. By colorimetric methods it is shown that the  $p_{\rm II}$  value of distilled water 20% saturated with carbon dioxide is 4.2—4.0 and fully saturated 3.8—3.6. The importance of a consideration of carbon dioxide effects in connexion with the reaction of plant sap is indicated. A. G. POLLARD.

 $p_{\rm H}$  and  $r_{\rm H}$  of the sap of Valonia and the  $r_{\rm H}$  of its protoplasm. M. M. BROOKS (Protoplasma, 1930, 10, 505-509).—The sap of V. ventricosa has  $p_{\rm H}$  $6\cdot02-6\cdot07$ . A new lower limit is set for the minimum value of the  $E_h$  of the sap, and the  $r_{\rm H}$  recalculated from the above lies between 17.9 and 18.4. The  $r_{\rm H}$  of the sap may be taken as approximately that of the protoplasm. A. G. POLLARD.

Surface tension of fresh latex of Euphorbia lathyris. L. BLARINGHEM and M. CHOPIN (Compt. rend., 1930, 191, 1408—1410).—The surface tension of the latex from various parts of specimens of E. lathyris, of varying age but of identical descent, is uniform within limits of experimental error, averaging 30 dynes/cm. Corresponding figures for other plants are : Taraxacum officinalis, 40; Papaver somniferum, var. Mursellii, 20; hybrid Papaver setigerum × somniferum, 31; Chelidonium majus, 21. In the case of the poppies measurements must be made before coagulation sets in. C. A. SILBERRAD.

Development and ripening of peaches as correlated with physical characteristics, chemical

composition, and histological structure of the fruit flesh. II. Histology and microchemistry. III. Macrochemistry. G. T. NIGHTINGALE, R. M. ADDOMS, and M. A. BLAKE (N.J. Agric. Exp. Sta. Bulls., 1930, Nos. 507 and 494).-II. Microchemical examination of ripening peaches failed to demonstrate the presence of pectates in the flesh-cells except in the thick-walled cells adjacent to the epidermis. Protopectin occurs in all cell-walls in intimate association with cellulose, but is not uniformly distributed and tends to accumulate in areas exposed to intercellular spaces. The yellow pigment of ripe peaches is carotenoid in character and the red epidermal colouring is of the anthocyanin group. Dextrose is the principal reducing sugar in the fruit. Softening of fruit during ripening is accompanied by a gradual decrease in protopectin content.

III. A peach tree receiving nitrogenous fertiliser produced greater growth of leaf and twigs than an unfertilised tree, also the fruit ripened later and was less firm. The starch and nitrogen contents of the twigs of the fertilised tree were lower than those of the unfertilised. Fruit from the unfertilised tree had a higher sugar content (especially sucrose), and much lower nitrogen and ash contents than that receiving fertiliser. The tannin content of the green fruit of the unfertilised tree was much higher than the fertilised, but the difference gradually disappeared as the "soft-ripe" condition was approached.

A. G. POLLARD.

Nutrition of fruit trees: some effects of deficiencies of nitrogen, potassium, calcium, and magnesium, with special reference to the behaviour of apple trees. M. B. DAVIS (J. Pomology, 1930, 8, 316-344).-Several varieties of apple trees have been grown under controlled conditions in quartz sand and sand-soil mixtures, and different nutritional treatments studied. All treatments produced significant effects on growth features and chemical composition of the trees. Nitrogen omission was characterised by restricted shoot-growth, yellowed leaves, and delayed bud-break. Potassium omission was associated with restricted shoot-growth in some cases and increased shoot-growth in others, a certain amount of early defoliation, later retention of remaining foliage, leaf scorch, and much earlier bud-break. Phosphorus omission produced earlier defoliation, very restricted shoot-growth in some cases, typical bronzing of the foliage, and delayed bud-break. Calcium omission produced increased shoot-growth and larger leaves in the early stages, breakdown of leaf tissue either near the centre or along the margins. Magnesium omission was characterised by reduced shoot-growth in most cases, earlier defoliation, and marked breakdown of foliage. All omission treatments were reflected in the composition of ash and dry matter of one-year shoots and leaves for the first season. Nitrogen omission resulted in high dry matter in fresh weight; potassium omission showed high dry matter; magnesium omission low dry matter in fresh weight. Nitrogen omission gave high ash in dry matter; potassium omission tended to high ash in dry matter in most cases; calcium omission always gave low ash in dry matter; magnesium omission gave high ash in dry matter. Reductions of potash, phosphoric acid, lime,

and magnesia in ash and in dry matter were usually effected where these elements were omitted. Low potash was associated with high lime and high magnesia; low phosphoric acid was accompanied by low potash and high lime. Low lime was associated with high potash, high magnesia, and low phosphoric acid. Low magnesia was accompanied by high lime. E. HOLMES.

Some effects of potassium deficiency on the histological structure and nitrogenous and carbohydrate constituents of plants. C. T. NIGHTINGALE, L. G. SCHERMERHORN, and W. R. ROBINS (N.J. Agric. Exp. Sta. Bull., 1930, No. 499, 36 pp.).—An accumulation of carbohydrate in potashdeficient tomato plants is ascribed to a retarded nitrogen assimilation. In such plants the translocation of sugars and the digestion of starch can take place freely. The development of mechanical tissue in plants is associated with their carbohydrate content and only indirectly with potash. Potash appears, directly or indirectly, to be essential for the initial stages of nitrate reduction in plants, for cell division, and probably for the protein synthesis in meristematic tissue. Most of the potash in plants is water-soluble and, when limited in amount, is translocated freely from older tissues to regions of active cell division. Stems and storage roots of potash-deficient plants may increase in length, but their diameters remain practically unchanged. Lack of potash frequently causes the premature death of fruiting plants.

A. G. POLLARD.

The organic matter given off by algæ. A. KROGH, E. LANGE, and W. SMITH (Biochem. J., 1930, 24, 1666—1671).—Culture experiments with Scenedesmus in artificial media and with natural lake-water in which the algæ were brought to luxuriant growth show that the organic material synthesised by the assimilation of these organisms is almost quantitatively stored in the cells of the algæ, whilsta fraction amounting at most to 10% may possibly be lost to the surrounding water. These losses are probably mainly due to dead and decomposed organism.

S. S. ZILVA.

Iodine-absorbing (reducing) material in plants. D. MARINE, E. J. BAUMANN, and B. WEBSTER (J. Biol. Chem., 1930, 89, 213—219).—Plant material was steamed, pulped, and extracted with water. The extract was acidified with hydrochloric acid and titrated with 0.01N-iodine solution. The figures obtained varied greatly with different plants and at different stages of growth. In general the highest figures were observed with the growing parts of wild plants and grasses and at the period of most rapid growth. The iodine-absorbing material is reduced in amount when the plant is dried.

C. R. HARINGTON.

Carbohydrate content of the nectar of indigenous flowering plants. R. BEUTLER (Sitzungsber. Ges. Morph. Physiol., 1928, 38, 24-31; Chem. Zentr., 1930, i, 3063).—The carbohydrate concentration of the nectar varies from 8 to 70%according to the kind of plant. Only sucrose, dextrose, and lævulose could be detected, whilst non-volatile substances other than carbohydrate are present only in small amount. With the exception of that of the plum, the nectars react more or less acid; the  $p_{\rm H}$  of Asclepias nectar lies between 2.7 and 4.3.

L. S. THEOBALD. Determination of maltose in plant extracts by maltase. N. NARASIMHAMURTY and M. SREENI-VASAYA (Biochem. J., 1930, 24, 1734—1736).— Maltase and invertase are used as the hydrolysing agents. The method is selective in its action and completely eliminates the errors inherent in the method of acid hydrolysis. S. S. ZILVA.

Occurrence of 2:6-dimethoxy-*p*-benzoquinone in Adonis vernalis, L. W. KARRER (Helv. Chim. Acta, 1930, 13, 1424—1428).—Details are given for the extraction of 2:6-dimethoxy-*p*-benzoquinone (1·3 g.), m. p. 251° after decomp. from 240°, from 200 kg. of A. vernalis. The quinone is synthesised by oxidising pyrogallol trimethyl ether by Graebe and Hess' method (A., 1905, i, 698). 2:6-Dimethoxyquinol has m. p. 160°. H. BURTON.

Frangularoside, a rhamnoside of black alder bark. M. BRIDEL and C. CHARAUX (Compt. rend., 1930, 191, 1374-1376).—The bark is dried, powdered, and macerated with 4 parts of water for 5 hrs. The dried residue is then extracted continuously with ether for 12 hrs. and a crude product obtained, the yield varying from 4.88 to 2.65%, according to the period of the year. The crude product is first crystallised from 66% acetic acid and then from a mixture of 2 vols. of octyl alcohol and 1 vol. of acetic acid. Purification can also be effected, in better yield, by crystallisation from methyl alcohol. The frangularoside separates from octyl alcohol in anhydrous and from methyl alcohol in hydrated form,  $[\alpha]_{5461} - 219^{\circ}$ . With sulphuric acid containing 0.5% of selenious acid it gives a blue colour, and dissolves in dilute sodium hydroxide solution with formation of a yellow fluorescent solution which rapidly changes to an intense red. colour. Hydrolysis gives rhamnose and a product, frangularol, of unknown composition.

P. G. MARSHALL.

Colour changes of plants during desiccation. Chromogen of Orobus niger, L., is arbutin. A. MEUNIER (Compt. rend., 1930, 191, 1471—1473).— From the hot 80% alcoholic extract of the fresh plant of O. niger, L., is isolated a glucoside identical in all respects with arbutin. Hydrolysis of this glucoside with emulsin affords a product which darkens slowly by atmospheric oxidation. Thus the darkening of the foliage of O. niger during desiceation is due to a glucosidic component, unlike that of O. tuberosus, which has been shown to be due to the phenolic substance oroberol. J. W. BAKER.

Composition of consecutive cuttings of Andropogon virginicus and Danthonia spicata. R. B. DUSTMAN and A. H. VAN LANDINGHAM (J. Amer. Soc. Agron., 1930, 22, 719-724).—Consecutive monthly cuttings lessen the normal decline in protein content and increase in fibre content.

#### CHEMICAL ABSTRACTS.

Linum neomexicanum (yellow pine flax) and one of its poisonous constituents. W. W. EGGLE-STON, O. F. BLACK, and J. W. KELLY (J. Agric. Res., 1930, 41, 715-718).—Alcoholic extracts of L. ncomexicanum yielded 6.6% of a substance ("linotoxin") poisonous to animals. It is probably a glucoside. A. G. POLLARD.

Examination of Sida cordifolia, Linn. S. GHOSH and A. DUTT (J. Indian Chem. Soc., 1930, 7, 825—829).—The entire plant contains 0.085% of alkaloids (on air-dried material) in addition to fatty oil, phytosterols, resins, resin acids, mucins, and potassium nitrate. Tannin and glucosides are absent. The seeds contain most alkaloid, the chief constituent of which is ephedrine. H. BURTON.

Hydrocarbons of Echinacea angustifolia. **E.L.** Woods (Amer. J. Pharm., 1930, 102, 611-630).-The crude oil has b. p. 125-240°/5 mm., d<sup>15</sup> 0.801, n<sup>25</sup> 1.4480. The main fraction, b. p. 127-133°/5 mm., gives when redistilled large fractions, (A) b. p. 121-122°/3 mm., d<sup>25</sup>/<sub>25</sub> 0.7873, and (B), b. p. 126-127°/3 mm.,  $d_{25}^{25}$  0.7881. The pure hydrocarbons show little tendency to undergo autoxidation in the dark. Oxidation of A with perbenzoic acid yields mainly a viscous oil, (?) C15H27(OH)3 (oily acetate), with small quantities of an erythrol,  $C_{15}H_{23}(OH)_4$ , m. p. 91°, and a substance, m. p. 135–136°. Oxidation of B with aqueous potassium permanganate gives mainly a mixture of hexoic and heptoic acids, with adipic, pimelic, and myristic acids and traces of acetic acid, a dihydroxytridecoic acid, m. p. 126-127°, and a brown, viscous acid, b. p. 170-205° (decomp.). Oxidation with permanganate in acctone affords the same acids in larger yield, also an unsaturated acid, C13H24O2, b. p. above 160°/15 mm. (silver salt), and a trace of oxalic acid. The main constituent of the oil is therefore probably the hydrocarbon, CHMe<sub>2</sub>·[CH<sub>2</sub>]<sub>3</sub>·CH:CH·[CH<sub>2</sub>]<sub>5</sub>·CH:CH<sub>2</sub>, or a mixture of 

acid indicates that the oil contains 5—10% of a hydrocarbon,  $CH_2:CH\cdot[CH_2]_{12}$ ·Me. The relation of the oil to the other constituents of the plant is discussed (cf. Bischoff, A., 1925, i, 760). H. E. F. NOTTON.

Constituents of essential oil of the bark of Magnolia obocata, Thunb. Y. SUGH and H. SHIN-DO (J. Pharm. Soc. Japan, 1930, 50, 709–714).— The oil contains machilol,  $C_{15}H_{26}O$ , m. p. 83°, which on oxidation affords dihydroxymachilol, m. p. 110° (monobenzoate, m. p. 144–145°), and a hydroxyketone,  $C_{13}H_{22}O_2$ , m. p. 121–122° (semicarbazone, decomp. 216–218°; oxime, m. p. 107–108°). Dihydromachilol has m. p. 84–85°. CHEMICAL ABSTRACTS.

Lipase of the olive and of olive oil. E. PAN-TANELLI and S. VERDESCA (Rend. Accad. Sci. Fis. Mat. Napoli, 1930, [iii], 36, 76-83).—Acidification of the fat of olives is due to the action of a lipolytic enzyme, the activity of which increases rapidly as the cell structure is destroyed by crushing. During the treatment of the olives, the lipase passes from the aqueous magma into the oil, as this dissolves the glycerol; hence the more acid the oil is at the time of crushing, the richer it is in lipase and the more liable to undergo further acidification. This acidification is governed by the glycerol, which determines the introduction of water and lipase into the oil. T. H. POPE.