

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1931.

General, Physical, and Inorganic Chemistry.

Hyperfine structure formulæ for one-electron spectra. G. BREIT (Physical Rev., 1931, [ij], 37, 51—52; cf. Hargreaves, A., 1930, 832; Fermi, *ibid.*, 393).—Mathematical. The energy level separations caused by a nuclear magnetic moment in a one-electron spectrum are derived by a short and rigorous method. N. M. BLIGH.

Variation of spark potential with temperature in gases. H. C. BOWKER (Proc. Physical Soc., 1931, 43, 96—112).—The effect of temperature on the spark potential in hydrogen and nitrogen at ordinary pressures has been investigated up to 860°. The spark potential depends on the density of the gas, but is independent of temperature and pressure for a given density. A. J. MEE.

Continuous spectra of atomic and molecular hydrogen. D. CHALONGE and N. T. ZÉ (J. Phys. Radium, 1930, [vii], 1, 416—425).—When an uncondensed discharge is passed through hydrogen at a pressure of a few mm. the secondary spectrum and a continuous spectrum of molecular origin are emitted. The energy curve of the latter has a maximum at 2350 Å. With sufficiently condensed discharges the secondary spectrum disappears, the Balmer lines become more intense, and the continuous spectrum becomes purely atomic, consisting of two spectra connected with the Balmer and Paschen series. The former is more intense than the latter, the energy in each case being evenly distributed through the spectrum. C. W. GIBBY.

Intensities of Balmer lines. II. L. S. ORNSTEIN and H. LINDEMAN (Z. Physik, 1931, 67, 1—6).—A reply to the criticisms raised by Kopfermann and Ladenburg (cf. A., 1930, 1487) on the authors' earlier work (*ibid.*, 1073). R. W. LUNT.

Influence of traces of hydrogen on the sparking potential of helium. A. GÜNTHER-SCHULTZE and F. KELLER (Z. Physik, 1930, 66, 219—223).—Experiments with commercial types of low-voltage rectifiers consisting of iron electrodes in a helium atmosphere at 20 mm. are described. Spectroscopic examination of the arc under normal and overload conditions has shown that the former is associated with the disappearance of traces of hydrogen which are evolved rapidly under overload conditions. R. W. LUNT.

Fine structure of hydrogen-like atoms in an inhomogeneous electric field. S. GUPTA (Z. Physik, 1930, 66, 246—256).—Theoretical. The Darwin modification of Dirac's equation is used to cal-

culate the Stark effect in an inhomogeneous electric field; the field gives rise to a quadratic as well as a linear term in the potential energy, and the effect of the quadratic term is calculated.

A. B. D. CASSIE.

Extension of simple spectra. F. PASCHEN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1930, 32, 7 pp.).—The simple spectra due to the excitation of a single-valency electron are extended if more than one valency electron is present, and these are simultaneously excited. The two-electron spectra of helium, beryllium, magnesium, and Al II are discussed. A. J. MEE.

Hyperfine structure of S and P terms of two-electron atoms, with special reference to Li⁺. G. BREIT and F. W. DOERMANN (Physical Rev., 1930, [ij], 36, 1732—1751; cf. Goudsmit and Bacher, A., 1930, 265).—Mainly mathematical. An expression is deduced for the interaction energy between the nuclear magnetic moment and the electronic system of a many-electron atom. Results are applied to the Li⁺ 5485 Å. line and to the calculation of the magnetic moment of Li. N. M. BLIGH.

Large displacements in the spectra of ionised nitrogen. K. ASAGOE (Sci. Rep. Tokyo Bunrika Daigaku, 1930, 1, 47—62).—The spectra of N II and N III were studied by a method similar to that employed in the study of the broadening and displacement of the halogen spectra (A., 1927, 2, 602). A. J. MEE.

Excitation of the negative nitrogen band by electron collisions. A. E. LINDB (Z. Physik, 1931, 67, 67—74).—The intensities of the lines of the R branch of the negative nitrogen band have been measured for exciting electrons of 150 and 175 volts energy and at two different current densities. Measurements have also been made of the effective target area of the nitrogen molecule for the excitation of the above band in the range 50—350 volts. The values obtained are much lower than those of Ramsauer and Brode. R. W. LUNT.

Emission bands of sulphur. R. K. ASUNDI (Nature, 1931, 127, 93—94).—Spectrograms of the bands of sulphur emitted in a discharge tube containing sulphur vapour and argon under pressure indicate that argon tends to arrest the predissociation of the sulphur molecule. New bands degraded towards the shorter wave-lengths have been photographed in the region 2100 Å. L. S. THEOBALD.

Spectrum of singly-ionised chlorine (Cl II). K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 15, 41—67).—The first spark spectrum of chlorine was obtained by a condensed discharge through a narrow Geissler tube with tungsten electrodes, one containing a small quantity of sodium chloride. The ground term is given as $3p^3P_2$, and the ionisation potential as 23.115 volts.

A. B. D. CASSIE.

Spectra of doubly-ionised argon, krypton, and xenon. S. C. DEB and A. K. DUTT (Z. Physik, 1931, 67, 138—146).—The spectra of A^{++} , Kr^{++} , and Xe^{++} have been classified, and tables of the multiplets of these spectra are given. The values of the ionisation potentials are 36.75, 31.23, and 28.51 volts, respectively (cf. Déjardin, A., 1924, ii, 284, 709).

W. R. ANGUS.

Zeeman effect for quadrupole lines. E. SEGRÉ (Z. Physik, 1930, 66, 827—829).—The potassium lines $^2S_{1/2}-^2D_{5/2}$ and $^2S_{1/2}-^2D_{3/2}$, at 4642.17 and 4641.58 Å., respectively, may be quadrupole transitions, or may be due to the influence of an inhomogeneous electric field. Photographs of the inverse Zeeman σ and π components of these lines, due to a field of 12,700 gauss, show that the transitions agree with the assumption of a quadrupole electric moment.

A. B. D. CASSIE.

Interferometric measurements in the arc spectrum of iron. C. V. JACKSON (Proc. Roy. Soc., 1931, A, 130, 395—410).—Ten lines in the spectrum of the iron arc in air in the region 4000—4400 Å. have been measured by means of the usual interferometric method and found to be in almost perfect agreement with the values adopted by the I.A.U. in 1928, the mean systematic difference being only ± 0.0003 Å. and the mean accidental difference ± 0.0006 Å. Sixty-eight lines in the region 2300—3100 Å. have also been measured interferometrically.

L. L. BIRCUMSHAW.

Spectrum of doubly-ionised arsenic. K. R. RAO (Proc. Physical Soc., 1931, 43, 68—71).—The doublet system of doubly-ionised arsenic (As^{III}) is considered in detail, and the work of Lang (A., 1929, 112) is amended. It is now possible to evaluate a trustworthy scheme of terms of As^{III} by assuming a probable value for the $5g^2G$ term. The value used is $39,500\text{ cm}^{-1}$. A term table is given. A. J. MEE.

Spectrum of singly-ionised zirconium. C. C. KIESS and H. K. KIESS (Bur. Stand. J. Res., 1930, 5, 1205—1241).—Most of the lines observed in the spark spectrum of zirconium have been classified as combinations between terms of the quadruplet and doublet system of Zr^{II} . The terms which have been found are in all cases those required theoretically for an atom with three outer electrons.

W. E. DOWNEY.

Intensity anomalies in the multiplets of silver and gold. S. SAMBORSKY (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 1025—1027; cf. A., 1930, 831).—The ratio 2 : 1 has been obtained for the relative intensities of the silver lines at 3382.8 and 3280.6 Å. and 2.4 : 1 for those of the second doublet of the principal series ($\lambda=2069.8$ and 2061.2 Å.). When Fermi's theory (A., 1930, 388) is applied to these

results the ratio of the transition probabilities of the $2P$ and $3P$ levels to the ground state (I_2/I_3) is found to be 20, whereas the equivalent ratios for the alkali metals lie between 100 and 200. The intensity ratio of the gold lines $3^2S-2^2P_{3/2}$ and $3^2S-2^2P_{1/2}$ ($\lambda=4241.8$ and 3650.7 Å.) is also the normal value of 2 : 1. The diffuse series 2^2P-3^2D in both silver and gold and the 2^2P-4^2D series in silver show marked departures from the theoretical ratio. This is explained by assuming the existence of a low 2D term. J. W. SMITH.

Spectrum of doubly-ionised iodine. J. B. SETH (Nature, 1931, 127, 165).—Many of the strong lines in the visible and ultra-violet regions originate in terms of $2O_2P_1$, $2O_2P_2$, and $2O_2P_3$ electronic configurations; all the quadruplet terms for these have been recognised. The $2O_2(P_1 \leftarrow P_2)$ and $2O_2(P_2 \leftarrow P_3)$ lines are grouped about 3900 Å. and 3100 Å., respectively. L. S. THEOBALD.

Spectrum of trebly-ionised cerium (Ce IV). J. S. BADAMI (Proc. Physical Soc., 1931, 43, 53—58).—The spectrum of the condensed spark of cerium has been studied in the ultra-violet. The spectrum is simple, being similar in electronic structure to the spectra of Ca^{II} , Ba^{II} , and La^{III} . A table of term values and ionisation potentials of La^{III} and Ce^{IV} is given. A. J. MEE.

Influence of pressure and temperature on the absorption of excited mercury atoms in a neon atmosphere. O. MASAKI (Z. Physik, 1930, 66, 229—240).—The absorption of light corresponding with the transitions $2^3P_{0,1,2}-2^3S_1$ of excited mercury vapour in the presence of an excess of neon has been examined by means of a König-Martens spectrophotometer. The mechanisms suggested in explanation of the phenomena observed are discussed at length. R. W. LUNT.

Optical measurements on the mercury atom. M. SCHEIN (Helv. phys. Acta, 1930, 2, Supp. 1, 3—111; Chem. Zentr., 1930, i, 3009).—As a sensitive method for measuring small spectroscopic wave-length differences the absorption of a monochromatic ray is employed in a monochromatic absorbing medium with the light and absorption frequencies continually out of phase. The method succeeds with mercury resonance fluorescence absorbed in mercury vapour, and has been applied to determine the Stark and Doppler effects. L. S. THEOBALD.

Mercury band system in the neighbourhood of the resonance line. (LORD) RAYLEIGH (Nature, 1931, 127, 125).—Additional bands between that at 2540 Å. and the resonance line 2536.52 have been measured; the bands are shaded from the red and the wave-lengths are 2540.37, 2538.44, and 2537.32 Å. Two bands shaded from the red have also been measured at 2535.82 and 2535.35 Å.

L. S. THEOBALD.

High-frequency discharges in mercury, helium, and neon. C. J. BRASEFIELD (Physical Rev., 1931, [ii], 37, 82—86; cf. A., 1930, 837).—Measurements of the potential drop at the electrodes and the electric force in the positive column of high-frequency discharges in mercury, helium, and neon for a range of gas pressures and oscillation frequencies

of 1.25—22.5 megacycles showed that, in general, the magnitude of the electric force was insufficient to produce electrons of velocity necessary to ionise or excite the gas. N. M. BLIGH.

Intensity determinations with the multiplets of mercury and neon by excitation of the lines by electron collision. W. ENDE (Z. Physik, 1931, 67, 292—293; cf. A., 1929, 1119).—The intensity relationships given in the former paper are corrected.

A. J. MEE.

Intensity distribution in the mercury triplet $2S^3_1-2^3P_{0,1,2}$ and the mean glow period of the triplet components. R. FRISCH and P. PRINGSHELM (Z. Physik, 1931, 67, 169—178).—By irradiation of the lines 5461 and 4047 Å. the fluorescence emission of the visible mercury triplet $2^3S_1-2^3P_{0,1,2}$ was obtained. The relative intensity of the three lines is independent of whether the green or the violet component is used for the excitation. It is concluded that the inequality observed by Randall (A., 1930, 970) in the life period of the three lines cannot be cleared up by consideration of hyperfine structure (cf. Richter, this vol., 8). A. J. MEE.

Polarisation of the continuous X-rays from single electron impacts. B. DASANNACHARYA (Physical Rev., 1930, [ii], 36, 1675—1679).—Polarisation increased exponentially with decreasing thickness of aluminium targets, indicating nearly complete polarisation at 6×10^{-6} cm. thickness, and diminished with increasing velocity of the exciting electrons. Results are in agreement with Sugiura's theory of the polarisation of continuous X-rays (cf. A., 1930, 4).

N. M. BLIGH.

Scattering of short X-rays by molecular hydrogen. H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1931, 27, 77—85; cf. Debye, A., 1930, 843).—Mathematical. From the formula deduced by Waller (cf. A., 1929, 746) the intensities of short X-rays scattered from molecular hydrogen are calculated.

N. M. BLIGH.

Spectrum of the radiation from a high potential X-ray tube. C. C. LAURITSEN (Physical Rev., 1930, [ii], 36, 1680—1684; cf. *ibid.*, 988).—Using a Seeman type spectrograph, a spectrogram with the tube at 600 kilovolts shows a continuous spectrum with a maximum intensity at about 200 kilovolts, and a short wave-length limit at about 600 kilovolts, the range covered being 100—20 Å.

N. M. BLIGH.

Origin of L-absorption edges of heavier elements. A. SANDSTROM (Z. Physik, 1930, 66, 784—789).—The known L-absorption and emission spectra for the elements tungsten to uranium indicate that L edges are due to a transition from the L level to the first incomplete group or sub-group of extra-nuclear electrons.

A. B. D. CASSIE.

Accuracy of interference determinations with molecules with X- and cathode rays. L. BEWLOGUA (Physikal. Z., 1931, 32, 114—117).—The accuracy attainable by the use of X-rays and of cathode rays in determinations based on interference is discussed. X-Rays provide a more accurate result than

cathode rays, although the latter possess the advantage of requiring shorter exposure time.

A. J. MEE.

Discontinuous absorption of X-radiation. B. B. RAY (Z. Physik, 1930, 66, 261—268).—X-Radiation scattered in a direction inclined to a primary beam suffers a change in wave-length depending on the vector change in momentum, *i.e.*, the change in wave-length is due to the Compton effect, and broadens the spectral line in the direction of longer wave-lengths. Any Raman line is therefore obscured. Radiation scattered in the direction of the primary beam shows no Compton modification in wave-length, but might show an anti-Stokes Raman line due to atoms excited by Compton collisions. $CuK\alpha$, $NiK\alpha$, $NiK\beta$, $WL\alpha$, and $FeK\beta$ radiations scattered by carbon, nitrogen, and oxygen were examined, and anti-Stokes lines corresponding with $CK\alpha$, $NK\alpha$, and $OK\alpha$ were found.

A. B. D. CASSIE.

Angular intensity distribution of the continuous X-ray spectrum. Y. SUGIURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 15, 37—39).—Mathematical.

A. B. D. CASSIE.

Change of wave-length of X-rays on traversing an absorbing medium. J. M. CORK (Compt. rend., 1931, 192, 153—155).—The new lines stated by Ray (cf. A., 1930, 972) to be produced on passing copper $K\alpha$ radiation through carbon etc. were not obtained when his experiment was repeated, nor could any such effect be obtained with boron.

C. A. SILBERRAD.

Vacuum spectrograph for precise measurements of X-rays of long wave-length. C. E. HOWE (Rev. Sci. Instr., 1930, [ii], 1, 749—757).—A plane grating spectrograph and special features of design for securing high precision are described.

N. M. BLIGH.

Multiple scattering in the Compton effect. J. W. M. DUMOND (Physical Rev., 1930, [ii], 36, 1685—1701).—Theoretical. Possible errors due to the neglect of multiple scattering in a study of the spectral distribution of X-radiation scattered by light elements are reviewed.

N. M. BLIGH.

Double-crystal spectrometer. J. W. M. DUMOND and A. HOYT (Physical Rev., 1930, [ii], 36, 1702—1720).—The uses, theory, design, and technique of operation of the double-crystal spectrometer are described.

N. M. BLIGH.

Infra-red absorption bands in the spectra of the greater planets. R. WILDT (Naturwiss., 1931, 19, 109—110).—The spectra of Neptune and Jupiter were photographed up to 8600 Å. and compared with the spectra of the sun and Capella obtained in the same way.

W. R. ANGUS.

Photo-electric and thermionic properties of rhodium. E. H. DIXON (Physical Rev., 1931, [ii], 37, 60—69).—A thin ribbon of pure rhodium was submitted to rigorous heat treatment in a pyrex tube at 950—1450° for 1050 hrs. in a vacuum. During heating, the long-wave limit shifted from 2530 to 3150 and back to 2509 Å.; the photo-electric current, measured by a Compton electrometer, increased about 130% for the temperature range 25—950°, with a

sudden increase at 240° . The thermionic current curve showed an irregularity at 1100° .

N. M. BLIGH.

Photo-electricity. J. WERNER (Z. Physik, 1931, 67, 207—226).—Metals and salts show, in a high vacuum, an increase in the photo-electric emission with time, which is independent of the radiation. The cause of this increased sensitivity, shown only by the unsaturated emission, is the removal or diminution of the layer of gas adsorbed on the metal or salt.

A. J. MEE.

Connexion between the effect of nitrogen-oxygen compounds and that of their components on the photo-electric sensitivity of potassium. R. FLEISCHER and H. TEICHMANN (Z. Physik, 1931, 67, 184—191; cf. A., 1930, 391).—An examination of the effect of nitrogen dioxide, nitric oxide, nitrogen, and oxygen on the sensitivity of the potassium cell shows that the change in position of the selective maximum from 334 to 365 m μ is due to the formation of nitrogen dioxide.

A. J. MEE.

Temperature relationship of the unidirectional layer photo-effect. H. TEICHMANN (Z. Physik, 1931, 67, 192—193; cf. this vol., 9).—In the temperature range down to -180° , emission of the copper-copper oxide cell reaches a maximum between -80° and -110° .

A. J. MEE.

Avoidance of an infinite singularity at the electron. W. ANDERSON (Z. Physik, 1930, 66, 712—720).—Ambarzumian and Ivanenko concluded (cf. A., 1930, 1335) that electrons in crystal formation could not approach closer than $6.34e^2/m_0c_2$, and this is precisely the minimum diameter possible for electrons when considered as gas of compressible electric particles (cf. A., 1929, 1137). No explanation of this coincidence could be found.

A. B. D. CASSIE.

New method for recording electrons. P. H. CARR (Rev. Sci. Instr., 1930, [ii], 1, 711—743).—The use of photographic plates for recording electrons is reviewed. Using a slightly modified apparatus, the experiments of Cole (cf. A., 1926, 1189) were repeated, and it was found that photographic plates are rendered more sensitive to electrons by the application of small amounts of certain oils, provided the electrons strike the plate at speeds not less than 25 equivalent volts. The sensitivity is mainly due to cathodo-luminescence of the oil, and the failure at low speeds is due to the high electrical resistance of the photographic emulsion. The regions of metal surfaces bombarded by electrons react differently from the unbombarded regions towards certain vapours, the effect being observed for electron speeds down to 12 equivalent volts. Experimental details are given for gold and silver, for which mercury and iodine vapours, respectively, were found the most satisfactory developers. The effect was also investigated for other metals, and possible explanations are discussed. The advantages and scope of the two methods are compared.

N. M. BLIGH.

Longitudinal distribution of photo-electrons. L. SIMONS (Nature, 1931, 127, 91—92).—Assuming the wave-mechanical principle of interference $P(\theta) \propto \sin^2\theta$ and that independent groups of photo-electrons originate from a small, plane circular area of

radius b normal to the ray, and a small spherical volume, radius a , the probability $P(\theta)d\theta \propto (A^1\pi a^2 + B^1\pi b^2 \cos \theta) \sin^3 \theta d\theta$, where A^1 and B^1 are independent of θ , is obtained. This expression must be regarded as unilateral and integrable only between the limits 0 to $\pi/2$. Experiment has confirmed the existence of longitudinal symmetry.

L. S. THEOBALD.

Electron diffraction at oxygen adsorbed on tungsten. W. BOAS and E. RUPP (Ann. Physik, 1930, [v], 1, 983—1000).—An apparatus for studying the diffraction of electrons of 100—2000 volts energy at surfaces the temperature of which could be raised to 3000° , is described, and the possible errors are discussed. Results are given for pure tungsten and for tungsten with an adsorbed layer of oxygen.

A. B. D. CASSIE.

Capture of electrons by protons. K. WOLF (Ann. Physik, 1930, [v], 7, 937—946).—An apparatus which brings protons and electrons of variable relative velocity into the same stream is described. The stream is subsequently analysed into electrons, protons, and hydrogen atoms. According to Davis and Barnes' results for α -particles (A., 1929, 971), neutral hydrogen atoms should appear at definite relative velocities. No such phenomenon was observed.

A. B. D. CASSIE.

Angular scattering of electrons in gases. F. L. ARNOT (Proc. Camb. Phil. Soc., 1931, 27, 73—76; cf. A., 1930, 1493).—The error introduced into experiments on the angular scattering of electrons in gases by the potential gradient between the electron beam and a point outside it resulting from the slight difference in concentration between the positive ions and electrons due to the greater mobility of the former is discussed.

N. M. BLIGH.

Diamagnetism of the free electron. C. G. DARWIN (Proc. Camb. Phil. Soc., 1931, 27, 86—90).—Mathematical. Landau, in his calculation of the diamagnetic effect due to the motion of electrons in a magnetic field (cf. A., 1930, 1355), made an allowance for boundary considerations. A special case is considered, admitting of exact solution, in which the boundary is replaced by a weak field of force. The result reduces to Landau's formula, and shows Bohr's argument of the creeping of the electron round the boundary wall.

N. M. BLIGH.

Diffraction of an electron wave at a single layer of atoms. M. VON LAUE (Physical Rev., 1931, [ii], 37, 53—59).—A mathematical examination of the treatment by Morse of the incidence and reflexion of electrons at the surface of a space lattice (cf. A., 1930, 976).

N. M. BLIGH.

Effect of resolving power on measurements of the absorption coefficient of electrons in gases. R. R. PALMER (Physical Rev., 1931, [ii], 37, 70—81).—Using a Mayer type apparatus with an opening of variable aperture at the end of the scattering chamber, the absorption coefficient of electrons in helium and mercury vapour for the range 20—135 volt electrons was studied as a function of the aperture for $2-11^\circ$.

N. M. BLIGH.

Photographic detection of asymmetrical angular distribution of doubly-reflected elec-

trons. E. RUPP (Naturwiss., 1931, 19, 109).—Using a non-rotating analyser an asymmetry has been observed in the angular distribution of doubly-reflected electrons. A pencil of electrons was reflected by gold foil of a fibrous structure inclined at 45° to the incident pencil. Using 220-kilovolt electrons diffraction patterns have been obtained showing definite asymmetrical intensity distribution of the doubly-reflected electrons, the intensity being greatest in the plane of the incident and reflected pencils and towards the side of the electron source. The intensities at right angles to this plane were equal. This asymmetry was not due to the fibrous structure of the foil, since the same effect was observed with the foil turned through 90° . The effect is not observable when aluminium foil is substituted for gold. J. W. SMITH.

Discrete range groups of *H*-particles expelled from aluminium. II. Dependence of sharing and energy of *H*-particles on the angle between the primary and secondary rays. H. POSE (Z. Physik, 1931, 67, 194–206; cf. A., 1930, 1086, 1232).—It is shown that the backward sharing is about 30% smaller than that in the forward direction. The velocities of the *H*-particles calculated from the ranges decrease as the angle between the primary and secondary ray increases. A. J. MEE.

Recoil atoms in gases. L. GOLDSTEIN (Compt. rend., 1930, 191, 1450–1452; cf. A., 1929, 1358).—The curve showing the relation of yield of activation to pressure shows a rapid rise to a maximum of 50% for a pressure of about 2 cm. mercury, followed by an asymptotic decline to about 26% for pressures in excess of 45 cm. It is suggested that the maximum occurs when the field is just strong enough to bring all recoil atoms on to the electrode, the subsequent decline being caused by increased ionic density due to increased pressure resulting in more complete utilisation (in ionisation) of the α -particles. C. A. SILBERRAD.

Method of ion counting in the free atmosphere. Y. ITIWARA (Physikal. Z., 1931, 32, 97–106).—The use of the ion counting tube for determining the number of ions in the free atmosphere is discussed. It is shown that if it is used by the charge method, *i.e.*, the outer electrode of the cylindrical condenser is raised to a constant potential, then the charge on the inner electrode which was originally earthed measures only a fraction of the total number of ions. The counting tube of Gockel, as used by Hess, counts only the large ions, and if a suitable correction is applied to his figures, they agree more closely with those of other observers. A. J. MEE.

[Method of ion counting in the atmosphere.] V. F. HESS (Physikal. Z., 1931, 32, 106).—Doubt is cast on the quantitative value of the work of Itiwara (cf. preceding abstract). The experiments of Itiwara in no way touch the work of Hess on the ionisation balance of air over land and open sea. A. J. MEE.

Formation of negative ions in gases. W. HEY and A. LEIPUNSKY (Z. Physik, 1930, 66, 669–685).—Experiments to determine the probability of the formation of negative ions in argon, mercury, and iodine vapours as a function of the electron velocity are

described in which care has been taken to eliminate the sources of error to which are attributed the discrepancies in the data of other workers. The probability in all cases is of the order of 10^{-5} in the range 0–20 electron volts. Iodine vapour exhibits a well-defined maximum in the neighbourhood of 2.5 volts and thereafter the probability attains an approximately constant value. Below 10 volts the probability in argon and mercury vapour is very small and rises rapidly in the range of 10–20 volts. R. W. LUNT.

Production of high-speed canal rays without the use of high voltages. E. O. LAWRENCE and D. H. SLOAN (Proc. Nat. Acad. Sci., 1931, 17, 64–70).

Value of M/m . W. N. BOND (Nature, 1931, 127, 164).—Evidence against Eddington's suggested value of 1849.6 for M/m is quoted. L. S. THEOBALD.

Masses of the electron, the proton, and the universe. (SIR) A. S. EDDINGTON (Proc. Camb. Phil. Soc., 1931, 27, 15–19; cf. A., 1930, 518).—An extension of the theory of the value 137 for the constant $hc/2\pi e^2$ is outlined; it gives satisfactory values for the masses of the electron, proton, and universe. N. M. BLIGH.

Eleventh report of the German commission on atomic weights. M. BODENSTEIN, O. HAHN, O. HÖNIGSCHMID, and R. J. MEYER (Ber., 1931, 64, [B], 1–21).—The report follows the general lines of its predecessors. The following changes are adopted: As=74.93 instead of 74.96; Ta=181.36 instead of 181.5; Re=186.31 instead of 188.7. H. WREN.

Fundamental at. wts. IX. At. wt. of sulphur. Synthesis of silver sulphide. O. HÖNIGSCHMID and R. SACHTLEBEN (Z. anorg. Chem., 1931, 195, 207–227; cf. A., 1929, 370).—By direct combination of silver and sulphur vapour at 250° the value of 1.148621 has been obtained for the ratio $\text{Ag}_2\text{S}:2\text{Ag}$, which gives 32.0664 for the at. wt. of sulphur. Silver sulphide does not dissociate at $150\text{--}300^\circ$. R. CUTHILL.

Revision of at. wt. of calcium. At. wt. of calcium from sylvine. O. HÖNIGSCHMID and K. KEMPTER (Z. anorg. Chem., 1931, 195, 1–14).—Determination of the ratios $\text{CaCl}_2:2\text{Ag}$ and $\text{CaCl}_2:2\text{AgCl}$ has given the value 40.085 ± 0.00060 for the at. wt. of calcium. The at. wt. of calcium obtained from sylvine is normal, indicating the absence of any appreciable amount of the calcium isotope Ca^{41} . R. CUTHILL.

At. wt. of uraninite lead from Wilberforce, Ontario, Canada. G. P. BAXTER and A. D. BLISS (J. Amer. Chem. Soc., 1930, 52, 4851–4853).—The at. wt. of lead extracted from uraninite is found to be 206.195 and on certain assumptions the thorium/uranium constant is computed to be 0.27. J. G. A. GRIFFITHS.

At. wt. of uranium lead from Swedish kolm. G. P. BAXTER and A. D. BLISS (J. Amer. Chem. Soc., 1930, 52, 4848–4851).—The at. wt. of uranium lead extracted from Swedish kolm, in which thorium could not be detected, is 206.01. J. G. A. GRIFFITHS.

Determination of the isotope ratio from intensity measurements of the boron monoxide spectrum. A. ELLIOTT (Z. Physik, 1931, 67, 75—

88).—The intensity of a spectral line depends on the number of molecules in the original state, and on the transition probabilities. If the curve showing the number of molecules with a given energy is selective to a range of energies, as is the case with boron monoxide in an active nitrogen discharge tube, then because of the difference between the energies of vibration of two isotopic molecules, the isotope ratio may not be proportional to the relative intensities of the corresponding lines. The error in assuming this proportionality for boron monoxide isotopes is 4–7%. The corrected isotope ratio is 3.63 ± 0.02 , and the corresponding at. wt. is 10.794 ± 0.001 . The effective temperature of active nitrogen in such a discharge tube is 470° .
A. B. D. CASSIE.

Isotopic constitution and at. wts. of zinc, tin, chromium, and molybdenum. F. W. ASTON (Proc. Roy. Soc., 1931, A, 130, 302–310).—With the object of determining the relative abundance of isotopes in a number of elements, attempts have been made to measure the photometric intensity of mass spectra lines. The use of cadmium methyl and germanium ethyl led to unsatisfactory results for these metals. In the experiments on zinc, zinc methyl was used. The packing fraction of Zn^{64} was found to be -9.9 , the percentage of this isotope being 48.0. The at. wt. of the metal was calculated to be $65.38_0 \pm 0.02$, in exact agreement with the best chemical determinations. The methyl compound was also used for tin, which gave a packing fraction of -7.3 for Sn^{120} and at. wt. 118.72 ± 0.03 . Chromium hexacarbonyl was used for chromium, and four isotopes, 50, 52, 53, and 54, were discovered, 52 being much the strongest. A provisional value for the packing fraction of Cr^{52} is -10 , giving at. wt. 52.011 ± 0.006 . The hexacarbonyl was also used for molybdenum and seven isotopes, 92, 94, 95, 96, 97, 98, and 100, were observed. This group shows a similarity of abundance more striking than that of any other element of such complexity. The packing fractions of Mo^{98} and Mo^{100} were found to be the same, -5.5 (approx.), giving at. wt. 95.97 ± 0.06 .
L. L. BIRCUMSHAW.

Constitution of osmium and ruthenium. F. W. ASTON (Nature, 1931, 127, 233).—The mass spectrum of osmium tetroxide indicates that the metal has four strong and two weak isotopes, one of the latter being isotopic with tungsten, W^{186} . The mass numbers and % relative abundances (provisional) are 186 and 1.0, 187 and 0.6, 188 and 13.5, 189 and 17.3, 190 and 25.1, and 192 and 42.6, respectively. The packing fraction is -1.0 ± 2.0 and the deduced at. wt. is 190.31 ± 0.06 , suggesting that the accepted value of 190.9 is too high. The behaviour of ruthenium tetroxide in the discharge makes the following data uncertain, but six isotopes, with possibly a faint seventh, appear to be present. The mass numbers and percentage abundances are 96 and 5, (98) and —, 99 and 12, 100 and 14, 101 and 22, 102 and 30, and 104 and 17, respectively. Assuming a packing fraction of approximately -6 , these give an at. wt. of 101.1, but the divergence from the accepted value of 101.7 can be partly explained in this case.
L. S. THEOBALD.

Isotopes and living organisms. W. VERNADSKY (Compt. rend., 1931, 192, 131–133).—To determine whether living organisms have the power of separating isotopes, compounds of potassium, iron, magnesium, zinc, calcium, silicon, and sulphur have been prepared from them and the at. wts. are to be determined (cf. Lowry, this vol., 141).
C. A. SILBERRAD.

Removal of radon from an emanation chamber after use. C. L. UTTERBACK and D. DEVAPUTRA (Rev. Sci. Instr., 1931, [ii], 2, 53–54).—An apparatus and method are described for the rapid removal of radon after work on solutions containing radium up to 10^{-7} g. per litre, by alternate evacuation of the emanation chamber and sweeping out with specially dried air.
N. M. BLIGH.

Magnetic spectra of α -rays. S. ROSENBLUM (J. Phys. Radium, 1930, [vii], 1, 438–444).—Two pieces of apparatus are described. It is shown that all the α -rays from thorium-C do not travel with identical speeds, but in groups.
C. W. GIBBY.

Anomalous scattering of α -particles by light nuclei. E. GUTH and T. SEXL (Z. Physik, 1930, 66, 577–580).—A method is indicated for the exact calculation of anomalous scattering of α -particles by a Gamow–Gurney–Condon potential field, instead of by the usual successive approximation method.
A. B. D. CASSIE.

Capture of electrons by α -particles. H. C. WEBSTER (Proc. Camb. Phil. Soc., 1931, 27, 116–130).—The capture of one and two electrons by swift α -particles, reported by Davis and Barnes (cf. A., 1929, 971; 1930, 393), was investigated, using an electrical counter instead of a scintillation screen, with completely negative results. Detailed considerations of various aspects of the experimental conditions and interpretation of data show no possibility of reconciliation with the reported effect.
N. M. BLIGH.

Scattering of slow α -particles by helium. P. M. S. BLACKETT and F. C. CHAMPION (Proc. Roy. Soc., 1931, A, 130, 380–388).—Mott has shown (A., 1930, 269), from consideration of the symmetry of the wave functions, that the scattering of particles by an inverse square field is quite different from that of the classical theory when the scattering and scattered particles are identical. By using an automatic Wilson chamber containing a mixture of helium and oxygen, the scattering of α -particles by helium has been followed down to a velocity of 10^8 cm. per sec., corresponding with a range of 0.5 mm. in air at N.T.P.
L. L. BIRCUMSHAW.

Attempt to demonstrate the existence of short-range α -particles from radium-C. G. H. HENDERSON and J. L. NICKERSON (Proc. Nova Scotia Inst. Sci., 1930, 17, 256–258).—An attempt to detect short-range particles from radium-C by the Wilson chamber method showed that no group of particles of definite range could be detected above the general background.
H. BURTON.

Absorbable radiation accompanying α -rays from polonium. (MME.) I. CURIE and F. JOLIO (J. Phys. Radium, 1931, [vii], 2, 20–28).—A more detailed account of work already noted (A., 1930, 130).

Loss of energy by β -particles, and its distribution between different kinds of collisions. E. J. WILLIAMS (Proc. Roy. Soc., 1931, A, 130, 328—346).—Theoretical. The requirements of the classical and quantum theories are compared, and it is shown that the quantum theory is in general agreement with experiment and provides an explanation of several previously obscure effects, particularly in connexion with primary ionisation.

L. L. BIRCUMSHAW.

Rate of loss of energy by β -particles in passing through matter. E. J. WILLIAMS (Proc. Roy. Soc., 1931, A, 130, 310—327).—Most of the previous experimental work which has been carried out on β -particles is vitiated by the effects due to scattering and straggling. Experimental values which are practically free from these effects are now given for the rate of loss of energy by β -particles with velocities ranging from about 0.1 to 0.97c.

L. L. BIRCUMSHAW.

Photographic effects of γ -rays. J. S. ROGERS (Proc. Phys. Soc., 1931, 43, 59—67).—Although slow, a photographic method can be used for measuring intensities of γ -rays, even when very small. The photographic action of γ -rays from radium and radon in equilibrium with their short-lived products has been investigated. The variation of photographic density with time of exposure (using constant intensity) and the variation of density with intensity (constant time) were examined for γ -rays filtered through lead screens of different thicknesses. The index in the Schwarzschild relation is unity for all lead filters. A photographic method has been developed for the determination of absorption coefficients. The absorption coefficient of lead for γ -rays is 0.533 cm^{-1} for thicknesses of lead from 1 to 7 cm. This is the same value as was found by Kohlrausch for the harder rays from radium-C, but is somewhat less than that obtained by Ahmad with a filter of lead 1 cm. thick.

A. J. MEE.

Absorption coefficients of γ -radiation from radium-D and -E, and the number of emitted quanta. (MISS) S. BRAMSON (Z. Physik, 1930, 66, 721—740).—Absolute measurements have been made of ionisation currents due to γ -radiation from radium-D and -E, after passage through aluminium and copper. Radium-D showed absorption coefficients corresponding with the wave-length $2.6 \times 10^{-9} \text{ cm.}$, and radium-E the wave-lengths 1.55 and $0.5 \times 10^{-9} \text{ cm.}$ The longer radium-E wave-length is a $K\alpha$ radiation from polonium, but the shorter probably arises in the radium-D nucleus. The magnitude of ionisation currents showed that every 100 disintegrating radium-D atoms emitted 3.1 ± 1.2 , and every 100 disintegrating radium-E atoms emitted 0.5 ± 0.25 γ -quantum. The internal absorption coefficient is known for radium-D, and indicates that every disintegrating radium-D nucleus emits one γ -quantum.

A. B. D. CASSIE.

Number of γ -quanta emitted from radium-D. E. STAHEL and G. J. SZOOS (Z. Physik, 1930, 66, 741—747).—The number of γ -quanta emitted from radium-D due to disintegration was determined by means of an ionisation chamber containing methyl iodide. L-Radiation from excited atoms was ab-

sorbed by 1 mm. of aluminium and β -radiation was deflected by a magnetic field. Energy absorbed by the methyl iodide that does not contribute to ionisation was allowed for. Every 100 disintegrating radium-D atoms emit 2.4 ± 0.7 γ -quanta.

A. B. D. CASSIE.

Methods of investigating the intensities of γ -rays. C. D. ELLIS and D. SKOBELEZYN (Nature, 1931, 127, 125).—The methods of Skobelzyn (A., 1930, 8) and of Ellis and Aston (*ibid.*, 1339) for measurements of the intensities of the γ -rays of radium-B and -C are discussed in relation to each other and are shown to be complementary. Confidence in the values of the individual intensities of the γ -rays measured by the photo-electric method is also given by this agreement. L. S. THEOBALD.

Photo-electric absorption of γ -rays. L. H. GRAY (Proc. Camb. Phil. Soc., 1931, 27, 103—112).—Available data for the derivation of a formula for the photo-electric absorption coefficient of X-rays and γ -rays are reviewed.

N. M. BLOCH.

Absorption law for short wave-length γ -rays. L. MEITNER and H. H. HUPFELD (Z. Physik, 1931, 67, 147—168).—The absolute scattering coefficient of γ -rays of wave-length 4.7 X from thorium-C'', filtered through 4 cm. of lead, was determined for different substances and was found to correspond with that calculated from the formula of Klein and Nishina (A., 1929, 373) for carbon only; in general, σ_e increases with increasing nuclear charge. For γ -rays from radium-C the scattering coefficients for aluminium and carbon are identical and accord with the theory.

A. J. MEE.

Theory of atomic disintegration. II. G. BECK (Z. Physik, 1931, 67, 227—239; cf. A., 1930, 1233; this vol., 16).—The case of a heavy nucleus is considered where the incident α -rays cannot penetrate far, and the excitation of a nucleus by direct collision with α -rays is discussed.

A. J. MEE.

Present status of theory and experiment as to atomic disintegration and atomic synthesis. R. A. MILLIKAN (Science, 1931, 73, 1—5).—An address.

L. S. THEOBALD.

Microcalorimetric measurements of a thermic effect varying with time. A. DORABIALSKA (Roczn. Chem., 1931, 11, 35—39).—The increase in heat production of 2.2 mg. of radium separated from emanation and from slowly disintegrating products can be measured by means of an adiabatic microcalorimeter, and is a measure of the accumulation of emanation.

R. TRUSZKOWSKI.

Radiation and molecular properties. R. D. KLEEMAN (Z. anorg. Chem., 1931, 195, 164—172).—Theoretical. It is shown that the author's theory of a static atom is capable of affording a comprehensive explanation of the phenomena of photochemistry (cf. A., 1930, 1340). It also yields a satisfactory physical interpretation of radiation and ionisation potentials.

R. CUTHILL.

Quantum-mechanical motion of free electrons in electromagnetic fields. E. H. KENNARD (Proc. Nat. Acad. Sci., 1931, 17, 58—63).

Transfer of energy between atoms on collision. O. N. RICE (Proc. Nat. Acad. Sci., 1931, 17, 34—39).—Mathematical. An outline is given of a modification of Born's treatment of the question of energy exchange between atoms or molecules which takes into account the relative translational energy and also meets the objections raised by Kallmann and London (A., 1930, 395) to Frenkel's view that Born's method may be applied directly (*ibid.*, 132). The method yields in any given case an upper limit for the radius of action which is considerably smaller than that found by Kallmann and London (A., 1929, 487).

H. F. GILLBE.

Absorption coefficient of earth radiation in air. G. A. SUCKSTORFF (Naturwiss., 1931, 19, 87—88).—The absorption coefficient of earth radiation for free air (10 metres above ground level) was found to be $3.4 \times 10^{-5} \text{ cm.}^{-1}$; for air in an iron tower 10 metres high the value was $4.5 \times 10^{-5} \text{ cm.}^{-1}$. The absorption curve in free air can be represented by the addition of three absorption curves with coefficients, 4.6, 3.2, and $2.6 \times 10^{-5} \text{ cm.}^{-1}$, which correspond with the ionising influences of radium, thorium-C'', and potassium, respectively.

W. R. ANGUS.

Transformation of light into heat in solids. I. J. FRENKEL (Physical Rev., 1931, [ii], 37, 17—44; cf. A., 1930, 126, 132).—Mainly mathematical. From the analogy between a crystal and a molecule the electronic excitation forming the first step in the process of light absorption is distributed among the atoms in the form of "excitation waves," similar to sound waves, which are used to describe the heat motion in the same crystal.

N. M. BLIGH.

Building up of elements in stars. W. ANDERSON (Z. Physik, 1931, 67, 294—295).—The statement of Atkinson and Hontermans (A., 1929, 738) that the temperature of stars is of the order of 4×10^7 and that the density is about 10 g. per c.c. does not agree with Milne's value of 10^{11} .

A. J. MEE.

Van der Waals forces for hydrogen and helium at large inter-atomic distances. H. R. HASSÉ (Proc. Camb. Phil. Soc., 1931, 27, 66—72; cf. Eisen-schitz, A., 1930, 525; Lennard-Jones, this vol., 17).—Mathematical. The interatomic force at large distances is calculated from the principle of minimum energy by a method based on that used for the polarisability of helium (cf. this vol., 14).

N. M. BLIGH.

Separation of the two types of iodine molecule and the photochemical reaction of gaseous iodine with hexene. R. M. BADGER and J. W. URMISTON (Proc. Nat. Acad. Sci., 1930, 16, 808—811).—Wood and Loomis (J. Franklin Inst., 1928, 205, 481) found that the fluorescence spectrum of iodine excited by the green mercury line (5461 Å.) contained only half the number of lines of the fluorescence spectrum excited by white light. The lines appearing under excitation by 5461 Å. are ascribed to an "ortho" type of iodine molecule. Therefore by irradiating iodine with 5461 Å. it is possible to activate selectively "ortho" molecules. Experiments were performed in which the activated "ortho" molecules reacted with hexene are discussed. It is claimed that after irradiating a mixture of iodine

and hexene with 5461 Å. for 24 hrs., the residual iodine consists largely of molecules which cannot absorb the mercury green line.

W. R. ANGUS.

Photometric properties of ground and frosted glass. J. DOUGNON and P. WAGUET (Compt. rend., 1931, 192, 155—156).

C. A. SILBERRAD.

Highly-attenuated flames of alkali metal vapours with halogen hydrides. G. SCHAY (Z. physikal. Chem., 1930, B, 11, 291—315; cf. A., 1930, 832).—Reactions between opposing streams of halogen hydrides and vapours of sodium or potassium have been studied by the methods described in earlier papers. The primary reaction is $M + HX = MX + H$, and the luminescence observed is due to subsequent reaction of the hydrogen atoms. A part of the emitted light is due to a reaction $H + HX = H_2 + X$ and the remainder probably to combination of hydrogen atoms with sodium adsorbed on the walls of the tube, and subsequent reaction of the hydride with atomic hydrogen. The light emitted by the sodium flames is that of the sodium D line, whereas the potassium flames give a continuous spectrum.

F. L. USHER.

Ammonia discharge tube. G. I. LAVIN and J. R. BATES (Proc. Nat. Acad. Sci., 1930, 16, 804—808).—The active products in the exit tube of an ammonia discharge tube have been examined and seem to consist of atomic hydrogen and NH or NH₂. The catalytic effects of certain substances and the characteristic luminescences at various surfaces have been examined (A., 1930, 659) and are discussed.

W. R. ANGUS.

Band spectrum intensities for symmetrical diatomic molecules. II. E. HUTCHISSON (Physical Rev., 1931, [ii], 37, 45—50).—Mathematical. The approximate expression previously deduced (cf. A., 1930, 1331) is extended, using the Schrödinger perturbation theory and removing the restriction of linear oscillations.

N. M. BLIGH.

Theoretical values of the quantum of energy of vibration of unexcited gaseous alkali iodides. H. J. VAN LEEUWEN (Z. Physik, 1930, 66, 241—245).—Theoretical. Brück's method (A., 1929, 381) is used to calculate the energy of interaction of a comparatively small positive ion and the electrons of a completed O shell, where the O shell moves in a field of force due to a nucleus of effective charge Z. Examples discussed are lithium, sodium, and rubidium iodide.

A. B. D. CASSIE.

Analysis and interpretation of hydrogen chloride bands in the ultra-violet. M. KULP (Z. Physik, 1931, 67, 7—23).—The band spectrum obtained by a Geissler discharge in streaming gaseous hydrogen chloride was measured (cf. A., 1930, 1089; this vol., 19).

W. R. ANGUS.

Influence of the crystal lattice on the absorption spectrum of a compound. H. FESEFELDT (Z. Physik, 1931, 67, 37—41).—Absorption spectra between 180 and 600 mμ are given for silver and thallium iodides at one temperature below the inversion point, and at another above the inversion point. Variation of the absorption constant with temperature of silver iodide at 480 mμ is also given.

The curves indicate that silver and thallium iodides have not simple ionic lattices like those of the alkali halides.

A. B. D. CASSIE.

Intensity relationships in the spectra of alkali mixtures and the possibility of quantitative spectral analysis of these elements. H. LUCAS (*Z. anorg. Chem.*, 1931, 195, 321—337).—With the object of establishing a technique for the spectroscopic determination of sodium and potassium in a mixture of salts the intensity ratios of suitable spectral lines of the two metals have been measured. When the carbon arc is used not only the intensities but also the ratios of the intensities vary from point to point in the arc; in the coolest region, where the field strength is small, the more readily excited potassium spectrum becomes relatively more intense. By measuring the emission always from the same zone of the arc and maintaining constant voltage, current, and length of arc the intensity ratios of sodium or potassium lines of different series but of which the upper terms have approximately the same excitation potential are constant to within 10%. For lines of the same series the error may be 40—50%, and deviations of this order are obtained also when comparing the lines of sodium with those of potassium. The intensity ratio, however, bears a definite relationship to the composition of the salt mixture, and by employing the doublet ratios of either metal as a control, the error of a determination may be reduced to about 20—25%. The error is of the same order if the spark at the surface of a solution of the salts be employed as the source of light.

H. F. GILLBE.

Emission spectra of benzene derivatives. J. B. AUSTIN and I. A. BLACK (*J. Amer. Chem. Soc.*, 1930, 52, 4755—4762; cf. A., 1930, 660; McVicker, Marsh, and Stewart, *J.C.S.*, 1923, 123, 642, 2147).—The ultra-violet emission band spectra of the vapours of toluene, *o*-, *m*-, and *p*-xylene, and ethylbenzene, excited in a Tesla discharge, have been photographed and the wave-lengths of bands between 2600 and 3000 Å. determined to within ± 0.5 Å. The toluene and ethylbenzene bands are displaced towards the red, as compared with those of benzene, and those of *o*-, *m*-, and *p*-xylene exhibit progressively larger displacements. The application of these spectra to qualitative and quantitative analysis is limited.

J. G. A. GRIFFITHS.

Simple relations between molecular spectra and structure. H. DESLANDRES (*Compt. rend.*, 1930, 191, 1404—1407). The formula $\nu = qd_1/rs \pm q'd_1/r's'$ (cf. A., 1925, ii, 1023) and the theory of a fundamental frequency ($d_1 = 1062.5$) are examined in regard to their applicability to certain vibration bands, residual rays, and Raman spectra. The frequencies are shown to be integral multiples of various fractions (from $\frac{1}{2}$ to $1/160$) of the fundamental frequency.

C. A. SILBERRAD.

Absorption spectra of dibenzyl and its derivatives. (MME.) RAMART-LUCAS and J. HOCH (*Compt. rend.*, 1931, 192, 53—55).—Dibenzyl prepared in hexagonal plates by the action of sodium and magnesium on three specimens of benzyl chloride of different origins showed the *a* and *b* absorption bands observed by Baly and by Castille (A., 1927, 186, 608),

the former varying in intensity. Condensation of two specimens of bromoethylbenzene and benzene in the presence of aluminium chloride gave prismatic needles of dibenzyl showing only the *b* band (2700—2300 Å.). The differences in absorption and crystal structure are accounted for by the presence in the former specimen of about 0.05% of stilbene.

J. GRANT.

Ultra-violet absorption spectra of the quinoline group. C. S. HICKS (*Austral. J. Exp. Biol.*, 1930, 7, 171—181).—The following ultra-violet absorption bands have been determined: quinine $\lambda\lambda$ 3268—3058, 2805—2570, 2390—? Å. (in alcohol); quinine hydrochloride, $\lambda\lambda$ 3295—3035, 2800—2580, 2325—? (in water); methylquinine sulphate, $\lambda\lambda$ 3285—3020, 2776—2581, 2385—? (in water); cinchonine, $\lambda\lambda$ 3150—3125, 2818—2450, 2240—? (in alcohol); cinchonine hydrochloride $\lambda\lambda$ 3150—3125, 2850—2470, 2280—? (in water); cinchotoxin, $\lambda\lambda$ 3100—2630, 2376—2322, 2174—? (in alcohol); cupreine, $\lambda\lambda$ 3340—3040, 2815—2578, 2190—? (in alcohol); hydrocupreine $\lambda\lambda$ 3335—3049, 2840—2685, 2413—? (in alcohol); optochin hydrochloride, $\lambda\lambda$ 3355—3400, 2872—2570, 2840—? (in water); eucupine dihydrochloride, $\lambda\lambda$ 3305—2700, 2350—? (in water); euquinine, $\lambda\lambda$ 3305—3005, 2800—2575, 2300—? (in alcohol); hydrochinotoxin, $\lambda\lambda$ 3390—2865, 2265—? (in water); hydrochinone, $\lambda\lambda$ 3465—2840, 2265—? (in alcohol); yohimbine $\lambda\lambda$ 2745—2445, 2190—? (in water). The absorption bands of the quinine alkaloids are determined almost entirely by the quinoline nucleus and not by the quinuclidine group. W. O. KERMAK.

Infra-red spectra of water, hydrogen sulphide and selenide. W. MISCHKE (*Z. Physik*, 1931, 67, 106—126).—The spectra of hydrogen sulphide and selenide were plotted between 0.8 and 18 μ . Hydrogen sulphide showed bands at 14.6, 8.1, 4.27 μ (fundamental frequencies), and at 2.70, 1.92, and 1.57 μ (combination frequencies); hydrogen selenide showed bands at 8.5, 4.25, 3.33, and 2.3 μ . Partial resolution was obtained for most of the bands. *P-R* branch separations give a moment of inertia 2.0×10^{-40} g.-cm.² Hund's model (A., 1925, ii, 479) of hydrogen sulphide gives $J_1 = 3.5$, $J_2 = 1.3$, $J_3 = 4.8 \times 10^{-40}$ g.-cm.², and the mean value $\sqrt[3]{J_1 J_2 J_3}$ agrees with 2.0×10^{-40} g.-cm.². An alternation in the intensities of resolved lines in the 8.1 μ band is ascribed to two forms of hydrogen sulphide corresponding with parallel and with anti-parallel hydrogen nuclear spins.

A. B. D. CASSIE.

Absorption of ultra-violet rays by transparent liquids. J. CLUZET and T. KOFMAN (*Compt. rend. Soc. Biol.*, 1930, 103, 783—785; *Chem. Zentr.*, 1930, ii, 12).—Using a cadmium cell, the ultra-violet absorption in the region 3000—2300 Å. has been investigated for the commoner organic solvents and acids, and for aqueous solutions of common inorganic salts.

L. S. THEOBALD.

Ultra-violet absorption spectrum of lignin derivatives. E. HÄGGLUND and F. W. KLINGSTEDT (*Z. physikal. Chem.*, 1931, 152, 295—312).—The positions of the maxima and minima in the absorption spectra, and the molecular extinction coefficients, are given for methyl-, ethyl-, and isoamyl-lignin, for

lignosulphonic acid, and for alkali lignins derived from different species of wood. There is comparatively strong selective absorption. F. L. USHER.

Optical effects (absorption and fluorescence) caused by salt formation of substituted cinnamic acids. H. LEY and R. DREINHÖFER (Z. wiss. Phot., 1930, 29, 134—154).—Quantitative measurements of the absorption of *o*-hydroxy- and *o*-amino-cinnamic acids and their alkali salts show that the spectra in the region down to 220 m μ consist of two bands, one of long and the other of short wave-length. The fluorescence centres in the molecules are the groups C₆H₄·OH (or C₆H₄·O' in the more strongly fluorescing alkali *o*-hydroxycinnamate) and C₆H₄·NH₂. The absorption of rays in the long-wave-length bands produces the fluorescence. J. W. GLASSETT.

Thermoluminescence in glasses which contain two activators. B. E. COHN and W. D. HARKINS (J. Amer. Chem. Soc., 1930, 52, 5146—5154; cf. Nyswander and Cohn, A., 1930, 520).—The progressive addition of manganese to zinc borate glass containing cerium at first increases and then decreases the thermoluminescence. Similar affects are produced by the addition of cerium to the glass containing manganese. As to whether the addition of a definite proportion of cerium will activate or damp the luminescence depends on the concentration of the manganese. The emission spectrum from zinc borate glass containing manganese is a band occupying the green, yellow, and red. The ultra-violet absorption bands of zinc borate glass containing cerium, manganese, or thorium have single ends on the longer wave-length side and the energy of luminescence may be derived from near these boundaries. It is concluded that different light sources will excite thermoluminescence of different relative intensity with different solutes in the same solvent. Absorption curves of these glasses are given and that of zinc borate containing manganese is anomalous.

J. G. A. GRIFFITHS.

Decay of phosphorescence in sylvine containing thallium chloride and its dependence on temperature. W. BÜNGER and W. FLECHSIG (Z. Physik, 1931, 67, 42—53).—A method for determining the decay of phosphorescence at different wave-lengths is described. The total radiation emitted as phosphorescence decays exponentially with time. It has a definite physical significance, and with this is associated a threshold energy necessary for emission of phosphorescence. This is calculated to be 1.5 μ , where preliminary experiments have shown the excited KCl-TlCl system to have high absorption.

A. B. D. CASSIE.

Raman spectrum of nitric oxide. F. RASETTI (Z. Physik, 1930, 66, 646—649).—An exposure of 72 hrs. gave a plate with displacements corresponding with ${}^2\Pi_{1/2} \rightarrow {}^2\Pi_{3/2}$ and indicates that the doublet separation is 122 cm.⁻¹ The instrument did not resolve individual rotation lines, but the photographs suggest that the transitions $\Delta J = \pm 1$ and ± 2 occur, as theoretically predicted for a Π level.

A. B. D. CASSIE.

Raman effect and constitution of molecules.
III. The fundamental frequencies of molecules

of type XY₄. **Effect of mixed halides.** B. TRUMPY (Z. Physik, 1930, 66, 790—806; cf. A., 1930, 1499).—Raman displacements due to the molecules CCl₄, SiCl₄, TiCl₄, SnCl₄, and SnBr₄ were obtained, and the corresponding infra-red frequencies calculated. The chlorides each show four intense infra-red fundamental frequencies, which diminish regularly as the mass increases from carbon to tin. Dennison's expressions (A., 1926, 659) for the normal vibration frequencies of such tetrahedral molecules are used to deduce ratios of the fundamental frequencies, and these ratios show that theory and experiment agree to within 10%. The infra-red fundamental frequencies of SnBr₄ are less than those of SnCl₄, agreeing with the greater mass of bromine. Mixtures of SnCl₄ and SnBr₄ in the ratios 1 : 1, 1 : 3, and 3 : 1 were investigated and showed new Raman displacements. The lines due to SnCl₄ and SnBr₄ were considerably weakened, and new lines were even more intense than the original lines. Results support the hypothesis that SnCl₂Br₂, SnBr₃Cl, and SnBrCl₃, respectively, are the chief intermediate products in these mixtures.

A. B. D. CASSIE.

Chemical constitution and the Raman effect : ethylenic compounds. R. LESPIEAU and BOURGUEL (Bull. Soc. chim., 1930, [iv], 47—48, 1365—1376; cf. A., 1930, 1091).—When the double linkings are of different types, i.e., closed or open chain, numerous lines appear in the neighbourhood of the frequency 1600 cm.⁻¹ The substitution by methyl of a hydrogen atom attached to an ethylenic carbon atom causes an increase of the characteristic Raman frequency, but the effect is less marked than in acetylenic compounds. The existence of conjugated double linkings is indicated by increased intensity of the lines due to each linking. Comparison of the Raman spectra of phenyltrimethylene with those of allyl- and propenyl-benzene shows that the first-named contains a three-membered ring, in confirmation of the view previously expressed (A., 1930, 1041).

H. F. GILLBE.

Chemical constitution and the Raman effect : acetylenic compounds. BOURGUEL and P. DAURE (Bull. Soc. chim., 1930, [iv], 47—48, 1349—1365).—A detailed account of work mostly published elsewhere (A., 1930, 978). In addition to the lines previously reported, there appears to be a fairly strong line of frequency about 350 cm.⁻¹ due to the triple linking, but its position depends on the nature of the compound under investigation. The linking :C≡Me is characterised by a rather strong line of frequency 1375. The effect of substitution in an acetylenic side-chain in aromatic compounds is described.

H. F. GILLBE.

Raman effect in monohalogen derivatives of methane. G. N. BALL (Z. Physik, 1930, 66, 257—260).—The Raman spectra due to methyl chloride, bromide, and iodide were investigated with a spectrometer of dispersion 50—90 Å. per mm. in the range 3650—4916 Å. Methyl chloride gave displacements corresponding with 13.85, 7.36, and 3.37 μ , methyl bromide 16.8 and 3.38 μ , methyl iodide 19.6, 8.00, and 3.38 μ . Thus only the fundamental frequencies of vibration appear. The 16.8 μ displacement for the

bromide and 19.6μ for the iodide were predicted, from infra-red measurements, by Bennett and Meyer (A., 1929, 239).

A. B. D. CASSIE.

Ionisation of air by the oxidation of phosphorus. J. TAUSZ and H. GÖRLACHER (Physikal. Z., 1931, 32, 91—97).—The dependence of the ionisation on the velocity of streaming of the gas over the phosphorus, the temperature, and the area of the phosphorus surface is examined. For air it was found that there was a marked increase of ionisation with time. When the oxidation has once begun there is a rise of temperature which increases the ionisation. With increasing velocity of streaming, the ionisation increases. It appears that when the gas is still the oxidation zone is round the phosphorus, but when the gas is in motion the oxidation zone is inside the ionisation chamber. In moist streaming oxygen, there is no increase in ionisation at atmospheric pressure. For dry oxygen, however, there is an increase, the increase depending on the degree of dryness. With dry oxygen and dry phosphorus there was strong ionisation and cloud formation, but no glow. The effect on the ionisation of the admixture of foreign substances (isoprene, cyclohexene, cyclohexane, and benzene) with the air was determined. There was smaller ionisation with isoprene and cyclohexene than with cyclohexane and benzene. The ionisation decreases with increasing concentration of the foreign substance.

A. J. MEE.

Influence of adsorbed gas layers on the photo-effects of salts. J. KLAEPHECKE (Naturwiss., 1931, 19, 87).—The properties arising from an adsorbed layer of gas in Geiger counting chambers is discussed (cf. Bosch and Klomb, this vol., 142). Water vapour promotes the escape of electrons from salts. Salts which have been heated strongly in a vacuum show little or no photo-electric effect on cooling. If a salt is produced by sublimation and then introduced into a photo-cell, a certain photo-stream is obtained which is increased ten-fold by treating the salt for a short time with water vapour; the same salt prepared from an aqueous solution gives a much higher photo-stream. Therefore adsorbed and occluded water both act as promoters for the escape of electrons. The influence of gases on the phenomena which concern the escape of surface electrons has been examined, but the results are not conclusive. The gases may have been imperfectly dried or small quantities of hydrogen and oxygen present in the gas may have united. If adsorbed layers of gases, other than water vapour, exert a similar effect, its magnitude will be considerably less than that of water vapour.

W. R. ANGUS.

Conductivity of liquid hydrocarbons in thin layers. L. BRÜNINGHAUS (Compt. rend., 1931, 192, 151—153; cf. A., 1930, 282).—The conducting stage has been further examined with means for more accurately measuring the distance between the electrodes.

C. A. SILBERRAD.

Polarisation in photo-electric conductivity arising from X-ray excited rock-salt. P. TARTAKOVSKI (Z. Physik, 1930, 66, 830—833).—A thin plate of rock-salt was placed between the poles of an electromagnet, and the Hall effect was used to give a

preponderance of free electrons towards one side of the plate. When the magnetic field was removed, the corresponding half of the plate showed a lower conductivity. Hence free electrons increase the polarisation.

A. B. D. CASSIE.

Dielectric constant and conductivity of ionised gases. J. V. JONESCU and C. MIHUL (Compt. rend., 1930, 191, 1436—1438).—An apparatus is described by means of which variations in dielectric constant and conductance ($1/\rho$) of a gas due to change in degree of ionisation are determined. It is shown that the conductance is proportional to the intensity of ionisation when the square of the wave-length of the oscillator is taken into account.

C. A. SILBERRAD.

Dielectric constant of supercooled sulphur and some sulphur solutions. S. ROSENAL (Z. Physik, 1930, 66, 652—656).—A condenser consisting of a double-walled glass vessel is described. The outside and inside of the vessel are metal-coated, and the substance to be investigated is contained between the walls. Sulphur, supercooled to 25° below f. p., showed a linear relation between dielectric constant and temperature. At 130° , the dielectric constant is 3.720 ± 0.003 ; on solidification it rose by 5—10%. Solutions in benzene followed the Clausius-Mossotti relation, but in carbon tetrachloride small increases in polarisation occurred with rise in temperature.

A. B. D. CASSIE.

Dielectric constant of liquid bromine. D. DOBORZYŃSKI (Z. Physik, 1930, 66, 657—668).—The condenser described by Rosental (see preceding abstract) and the resonance method were used to determine the dielectric constant of bromine in the range $0-53.8^\circ$. The experimental method and possible errors are discussed. The dielectric constant is given by $\epsilon = 1.0730 + 671.42/T$. Bromine, which can be considered as a non-associated liquid, has therefore a dipole moment of 0.49×10^{-18} e.s.u.

A. B. D. CASSIE.

Dielectric measurements on vapours of amines. O. STEIGER (Helv. phys. Acta, 1930, 3, 161—162; Chem. Zentr., 1930, ii, 1343).—The following dipole moments ($\times 10^{-18}$ e.s.u.) have been determined: methylamine 1.23 ± 0.02 , dimethylamine 0.96 ± 0.01 , trimethylamine 0.60 ± 0.02 .

A. A. ELDRIDGE.

Electrical moments of certain organic compounds. A. SÄNGER (Helv. phys. Acta, 1930, 3, 162; Chem. Zentr., 1930, ii, 1343).—The following values ($\times 10^{-18}$ e.s.u.) are recorded: dimethyl ether 1.316 ± 0.012 , methyl chloride 1.861 ± 0.008 , ethyl chloride 2.019 ± 0.025 , propyl chloride 2.040 ± 0.08 . Hence the polarising effect of the chlorine atom reaches only to the second carbon atom in the chain.

A. A. ELDRIDGE.

Change of the electric polarisation of ethyl ether with temperature. M. WOLFKE and J. MAZUR (Nature, 1931, 127, 236; cf. A., 1930, 1501).—The value of the dielectric polarisation of ethyl ether, calculated by means of the Clausius-Mossotti formula, increases slowly with a fall in temperature from the value 0.5858 at 35° to a maximum of 0.9209 at -105.4° , and then decreases rapidly. This marked change suggests that the structure of the molecule of

ethyl ether suffers a modification at -105.4° (cf. A., 1930, 1554).
L. S. THEOBALD.

Dense space charges (polarisation) in calcite. A. JOFFÉ, D. ROJANSKI, and K. SINELNIKOV (Z. Physik, 1930, 66, 143—171).—Measurements relating to the dielectric polarisation in calcite due to continuous potentials are described. Polarisation is confined to a very thin region, a few μ , in the neighbourhood of the cathode. The polarisation is conveniently expressed in terms of that capacity which may be regarded as proportional to the total charge per cm^2 in those layers adjacent to the cathode in which the space charge falls from its maximum value to $1/\text{eth}$. When an equilibrium state of polarisation is attained the conductivity of the medium attains a constant value which is much smaller than the normal conductivity. Related data are given for a large number of materials.
R. W. LUNT.

Electrical conductivity and [high-tension] polarisation in sodium nitrate crystals. B. HOCHBERG and V. JOFFÉ (Z. Physik, 1930, 66, 172—191).—The experiments on dielectric polarisation described in the preceding abstract have been extended to sodium nitrate. The polarisation is again found to be confined to regions in the neighbourhood of the electrodes. The temperature variation of the conductivity in the polarised state is found to have the same form as that of the normal state.
R. W. LUNT.

Dielectric properties of potassium sodium tartrate. P. KOBÉKO and J. KURTSCHATOV (Z. Physik, 1930, 66, 192—205).—The abnormally high values of the dielectric constant of potassium sodium tartrate reported by earlier workers has been confirmed, and provided that a good contact is made between the electrodes and the specimen values up to 20,000 may be obtained. The dielectric constant of a given specimen diminishes as the potential across the specimen is increased. It is shown that these abnormal values cannot be attributed to the polarisation effect in the neighbourhood of the electrodes such as is observed in calcite (cf. preceding abstracts).
R. W. LUNT.

Refractive indices of some heavy metal halides in the visible, and determination of interpolation formulæ for the dispersion curves. H. SCHRÖTER (Z. Physik, 1931, 67, 24—36).—The refractive indices of silver chloride and bromide, and of thallium chloride and bromide, were measured in the range 4500—7000 Å. accurately to the third decimal place. The prisms of silver bromide and chloride were single crystals; those of thallium consisted of three or four crystals. The method of obtaining these crystals is described.
A. B. D. CASSIE.

Dispersion of potassium bromide crystals in the infra-red. E. GUNDELACH (Z. Physik, 1930, 66, 775—783).—The refractive index of crystalline potassium bromide was determined between 0.8 and 18μ with two Wadsworth prism spectrometers, using either rock-salt or sylvine prisms, and between 18 and 28.5μ by means of an étalon interferometer and a prism of potassium bromide. A radiometer was used to measure intensity of radiation. The refractive

indices are accurate to one unit in the third decimal place.
A. B. D. CASSIE.

Mechanical double refraction of liquids in relationship to the molecular form. II. D. VORLÄNDER and U. KIRCHNER (Z. physikal. Chem., 1931, 152, 47—66).—Data are given relating to the specific double refraction of unitary anisotropic "oils," including glycerol, aliphatic and aromatic esters, and aromatic aldehydes and ketones, and of homogeneous mixtures of isotropic "oils," solutions of colloids in oils, and a variety of aqueous solutions. The measurements show the influence of double linkings, *p*-substituents, chain length, and branched molecules such as tolyl phosphate. The simple aliphatic alcohols do not exhibit mechanical double refraction; glycol, despite its high viscosity, is also inert, and cannot be of the simple structure expressed by its formula. Among the normal monobasic fatty acids the effect first becomes evident with nonoic esters, and among the dibasic acids with succinic esters. Aqueous solutions, even of high viscosity, of simple inorganic compounds such as calcium and zinc chlorides do not exhibit the effect to any marked extent, whereas with potassium acetate solutions there is a definite positive effect which reverses sign as the chain length of the anion increases.
H. F. GILLBE.

Measurement of circular dichroism. J. P. MATHIEU (Compt. rend., 1931, 192, 156—158).—A method is described for measuring circular dichroism by which both rotation and ellipticity are determined with the same apparatus, the essential point being the use as compensator of one birefringent plate for the whole visible spectrum.
C. A. SILBERRAD.

Photo-elastic dispersion of vitreous silica. L. N. G. FILON and F. C. HARRIS (Proc. Roy. Soc., 1931, A, 130, 410—431).—By means of a modification of the spectrometer method previously described (Filon, Proc. Camb. Phil. Soc., 1902, 12, 55), measurements have been made of *C*, the stress-optical coefficient of vitreous silica for light of wave-length λ , and the formula $C = C_0/(1 - \lambda_0/\lambda)$ is found to hold with fair accuracy.
L. L. BIRUMSHAW.

Magnetic rotation of gaseous halogen derivatives of saturated hydrocarbons. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1931, 192, 278—280).—Magnetic rotations of eleven halogen derivatives of the lower paraffins have been determined in the liquid and gaseous states. From these results and those previously obtained (cf. this vol., 148) the following values have been deduced for the atomic rotations ($\times 10^2$) of H, C, Cl, Br, and I respectively: 5.5, 10, 33, 66, and 143. The figure for hydrogen is but slightly lower than that for the free gas; the figures for the halogens are very much lower than those for the corresponding ions (Cl' 108, Br' 208, and I' 450).
C. A. SILBERRAD.

Magnetic rotatory power of a uniaxial crystal in directions oblique to the axis; determination of the rotation of tysonite in a direction approximately that of a binary axis, at the temperature of liquid nitrogen. J. BECQUEREL (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 913—925).—An

extension of the work on tysonite at the ordinary temperature. A compensation method is used. The optical and magnetic axes are in a horizontal plane and different orientations are given to the crystal and to the field. With a magnetic field of given orientation and constant intensity, the rotation of the principal axis of the emerging elliptically polarised light is measured for different orientations of the crystal. An equation is deduced for the magnetic rotation of tysonite under the conditions of the experiment, which is verified by the results. The ratio of the rotatory powers normal and perpendicular to the optical axis is much less at liquid nitrogen temperatures than at the ordinary temperature.

J. FARQUHARSON.

Determination of the paramagnetic rotatory power of a crystal of tysonite in a direction normal to the optical axis at the temperature of liquid hydrogen. J. BECQUEREL and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 926—936).—Two methods of measurement may be used: (a) a compensation method (see preceding abstract), (b) the field is oriented perpendicularly to the optical axis and the component of the effect is measured directly in a direction normal to the optical axis. Experiments were made by both methods at 20° and by method (a) at 14°. J. FARQUHARSON.

Magneto-optical anisotropy in a plane normal to the optical axis of a hexagonal crystal. Paramagnetic rotatory powers in directions approximating to the binary axes at very low temperatures. J. BECQUEREL and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 937—948).—At the temperature of liquid helium, method (b) (see preceding abstract) is applicable. Measurements are made with two tysonite plates of different thicknesses. After correction for the thickness of the plates curves are obtained for the magnetic rotation as a function of H/T . The magnetic rotations in the directions of the two species of binary axes are different; the deviation of the two curves is greater than can be ascribed to experimental error. This is the first example of an optical anisotropy in a plane normal to the optical axis of a uniaxial crystal. The anisotropy has a paramagnetic origin, for the saturation rotations in the directions of the binary axes are the same, showing that the uniaxial crystal is optically isotropic for all directions normal to the optical axis. J. FARQUHARSON.

General theory of paramagnetic rotation in crystals. H. A. KRAMERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 959—972).—Theoretical. If the divergence from isotropy is small, the introduction of a rotation vector permits a simple explanation of the properties of a beam of light in any direction. An atomic system of odd number of electrons, in a purely electrical external field, has doubly degenerate energy levels. The magnetisation produced in such an atom by a magnetic field in any direction is discussed, as is the paramagnetic rotation in a crystal containing these atoms. J. FARQUHARSON.

Theory of Kossel and Magnus. ALLARD (Bull. Soc. chim., 1930, [iv], 47, 1333—1342).—A lecture describing the Kossel-Magnus theory, and particu-

larly its bearing on the structure of hydrates and ammines. H. F. GILLBE.

Structural principles of compounds of boron and hydrogen. E. WIBERG (Z. anorg. Chem., 1931, 195, 288).—A correction (cf. A., 1930, 524).

R. CUTHILL.

Molecular structure of triatomic gases. II. H_2O , H_2S , and N_2O . P. C. MAHANTI (Physikal. Z., 1931, 32, 108—110; cf. A., 1929, 1365).—The available data for dipole moments, Raman spectra, and infra-red absorption bands for these three molecules are discussed with a view of settling their structure. The H_2O molecule has a triangular structure which explains the existence of three moments of inertia. The H_2S molecule has a finite dipole moment and hence there can be no central symmetry, so that again the molecule has a triangular structure. For the N_2O molecule, the dipole moment is 0.249×10^{-18} , which is very small. All observations point to a linear symmetrical structure for this molecule.

A. J. MEE.

Natural classification of chemical compounds. F. M. SCHEMJAKIN (Z. physikal. Chem., 1931, 152, 235—244).—Theoretical. An attempt is made on the basis of Grimm's method to develop a system of classification of inorganic and organic compounds.

F. L. USHER.

Chemistry and geochemistry of the titanium group. G. VON HEVESY (J.C.S., 1931, 1—16).—A lecture. N. M. BLIGH.

Surface tension in a magnetic field. H. AUER (Z. Physik, 1930, 66, 224—228).—A discussion of the effect of surface tension in the capillary method of measuring magnetic susceptibility and a method for controlling it. J. FARQUHARSON.

Parachors of two isomeric chlorodinitrobenzenes. S. A. MUMFORD and J. M. C. PHILLIPS (J. Amer. Chem. Soc., 1930, 52, 5295—5297; cf. A., 1929, 1219).—A correction of statements by and polemical against Sickman and Menzies (A., 1930, 1279). J. G. A. GRIFFITHS.

Parachors of isomeric chlorodinitrobenzenes. D. V. SICKMAN and A. W. C. MENZIES (J. Amer. Chem. Soc., 1930, 52, 5297).—A reply (see preceding abstract). J. G. A. GRIFFITHS.

Parachor and chemical constitution. XVI. Silicon compounds. S. SUGDEN and H. WILKINS (J.C.S., 1931, 126—128).—Owing to divergent values of the atomic parachor of silicon from existing data for silicon tetrachloride, measurements of surface tension and density were made for methyl and ethyl orthosilicate and for tetra-ethyl-, -propyl-, and -phenylsilicane. Results give 28 for the parachor.

N. M. BLIGH.

Determination of atomic distances in gas molecules by means of Röntgen and cathode rays. J. M. BIJVOET and H. J. VERWEEL (Chem. Weekblad, 1930, 27, 648—650).—A discussion of recent results obtained with chloroform and ethylene chloride vapours; the existence of *cis*- and *trans*-forms in the latter is not regarded as established.

S. I. LEVY.

Part-absorption phenomena of X-rays. R. C. MAJUMDAR (Nature, 1931, 127, 92; cf. A., 1930, 1334).—Details of part-adsorption of iron and nickel radiations by carbon, nitrogen, and aluminium are recorded and discussed. L. S. THEOBALD.

Dependence of the width and intensity of Debye lines and rings on the dimensions of the X-ray source, of the preparation, and of the camera. W. BUSSE (Z. Physik, 1930, 66, 285—288; cf. A., 1930, 1240).—Results deduced in the earlier paper are applied to an apparatus of average dimensions, and the conditions for its most efficient use are given. A. B. D. CASSIE.

Dependence of width and intensity of Debye lines and rings on tube-focus etc. W. BUSSE (Z. Physik, 1931, 67, 296; cf. A., 1930, 1240).—The criticism made by Bredig (*ibid.*, 1502) of the form of apparatus used previously has been applied.

A. J. MEE.

Relation of the liquid to the crystalline state. K. BANERJEE (Nature, 1931, 127, 92—93).—The partial "crystallinity" of liquids manifested by the maximum, shown by X-ray diffraction, in the molecular arrangements in liquids corresponding with the crystalline structure of the substance in the solid state is responsible for the modified scattering reported by Gross (A., 1930, 1237). Gross' explanation of the broadening of Raman lines is criticised and another explanation is advanced. L. S. THEOBALD.

Theory of recrystallisation. J. A. M. VAN LIEMPT (Z. anorg. Chem., 1931, 195, 366—386).—A mathematical attack on the problem of recrystallisation in metals. By consideration of the velocity of interchange of position of the atoms in uni-crystalline materials as a function of the temperature, the equation $D = (\pi p^2 \nu / 6) e^{-k b^2 T_s / T}$ is derived, where D is the diffusion coefficient of a metal A , of relatively low m. p., into another metal, B , at temperature T , p is the minimum distance between the atoms of B , ν is the characteristic atomic frequency and T_s the m. p. of A , $b = +2$, and k is theoretically 3, but is subject to deviations from Dulong and Petit's law. The recrystallisation process in mixed crystals is discussed and the influence of impurities on the recrystallisation temperature of metals is to some extent elucidated. H. F. GILLBE.

Growth and dissolution of non-polar crystals. I. N. STRANSKI (Z. physikal. Chem., 1930, B, 11, 342—349; cf. A., 1928, 1178).—A theoretical discussion of the differences between homopolar and heteropolar crystals with reference to their growth, dissolution, and function in heterogeneous catalysis. F. L. USHER.

Crystal etchings. G. T. FAUST (Bull. Wagner Inst. Sci., 1930, 5, 35—41).—The results of etch figure studies of the quartz trigonal pyramid s (1121) are given and establish a symmetry identical with that previously indicated by the etchings of the commoner forms. The symmetry of orthoclase was also investigated by the etching method. W. GOOD.

Fractional precipitation. V. Inclusion of foreign matter in the crystal lattice. O. RUFF

(Z. anorg. Chem., 1931, 195, 60; cf. A., 1930, 286).—A correction. R. CUTHILL.

Recrystallisation of rock salt. K. PRZIBRAM (Z. Physik, 1931, 67, 89—105).—Recrystallisation of rock-salt can be followed by use of a radium preparation. Discoloration due to radiation from the radium follows crystal planes, and only extends throughout recrystallised portions. Dependence of rate of recrystallisation on temperature and pressure (400—3000 kg./cm.²) was thus studied.

A. B. D. CASSIE.

Crystalline structure of the inert gases. Krypton. A. NASINI and G. NATTA (Atti R. Accad. Lincei, 1930, [vi], 8, 141—147).—Application of the powder method of X-ray analysis to krypton indicates a face-centred cubic lattice; the cells containing four atoms have edges of 5.78 Å., corresponding with a volume of 193×10^{-24} c.c.; $d_{\text{calc.}}$ 2.83.

F. G. TRYHORN.

Physical properties of rhenium. C. AGTE, H. ALTERTHUM, K. BECKER, G. HEYNE, and K. MOERS (Naturwiss., 1931, 19, 108—109).—Rhenium crystallises hexagonally in the densest packing. The lattice constants are a 2.765, c 4.470 Å., c/a 1.616. The smallest atomic distance being 2.765 Å., the atomic radius is 1.382 Å. The m. p. determined by the drill-hole method is $3440 \pm 50^\circ$ Abs. The coefficient of linear expansion measured by the X-ray method is 12.45×10^{-6} in the direction of the hexagonal axis and 4.67×10^{-6} in the direction perpendicular to this axis. The density of a highly-sintered rod was measured as 20.9, the density from X-ray measurements being 21.4. This indicates at. wt. 186.31 ± 0.02 . The tensile strength of a rhenium wire of 0.25 mm. cross-section with a tungsten core of 0.03 mm. cross-section was 50.6 kg./mm.² The extension was 24%. The specific electrical resistance at the ordinary temperature is 0.21×10^{-4} ohm $\pm 15\%$, and the temperature coefficient of the resistance 3.11×10^{-3} between 0° and 100° and 1.98×10^{-3} between 0° and 2710° . The ratio of the specific resistances at 2710° and 0° is 6.34. Measurements of the electron emission between 1900 and 2700° Abs. give the following values for the constants in Richardson's emission equation $i = AT^2 e^{-b/T}$: $A = 200$ amp./cm.² degree²; $b = 59,500$, and the work of evaporation of electrons calculated therefrom is 5.1 volts. J. W. SMITH.

Crystal structure of thallium. S. SEKITO (Z. Krist., 1930, 74, 189—201; Chem. Zentr., 1930, ii, 1945).— α -Thallium, stable below 225° , hexagonal, has a 3.450 Å., c/a 1.600, $d_{\text{calc.}}$ 11.83; β -thallium, stable above 225° , cubic face-centred, has a 4.841 Å., d 11.86. Measurements were also made with various thallium alloys. A. A. ELDRIDGE.

Crystal structure of ice. E. BRANDENBERGER (Z. Krist., 1930, 73, 429—430; Chem. Zentr., 1930, i, 3528).—Polemical (cf. Barnes, A., 1930, 20).

A. A. ELDRIDGE.

X-Ray diffraction in water: the nature of molecular association. G. W. STEWART (Physical Rev., 1931, [ii], 37, 9—16).—Using a method previously described (cf. A., 1927, 1015) the X-ray diffraction intensity-angle distribution for water and its variation for the temperature range 2 — 98° was

investigated. Periodicities were found at 3.24, 2.11, and 1.13 Å. in agreement with Meyer (cf. A., 1930, 1097). N. M. BLIGH.

Crystal structure of molybdenum trioxide. N. WOOSTER (Nature, 1931, 127, 93).—Small, thin, lustrous plates parallel to b (010) of sublimed molybdenum trioxide show orthorhombic symmetry with a 3.93 ± 0.02 Å., b 13.91 ± 0.05 Å., and c 3.57 ± 0.02 Å. There are four mols. per cell and the space-group is Q_h^{11} (bmm). With the centre of symmetry as origin, the co-ordinates of the molybdenum atoms are $uv \frac{1}{4}$: $\bar{u} + \frac{1}{2}$, $v + \frac{1}{2}$, $\frac{1}{4}$; $u + \frac{1}{2}$, $\bar{v} + \frac{1}{2}$, $\frac{3}{4}$; $\bar{u}\bar{v} \frac{3}{4}$, where $u = 36^\circ$, and $v = 30^\circ$, approximately. L. S. THEOBALD.

X-Ray investigation of potassium fluoborate. B. PESCE (Gazzetta, 1930, 60, 936–939).—Examination of the two supposed dimorphous forms of potassium tetrafluoborate by means of X-rays shows that they are identical. For the precipitated product dried at 100° d^{15} is 2.555. O. J. WALKER.

X-Ray analysis of the structure of potassium dihydrogen phosphate. J. WEST (Z. Krist., 1930, 74, 306–332; Chem. Zentr., 1930, ii, 1658).—Hendricks' view (A., 1927, 1013) is supported after some modification. A. A. ELDRIDGE.

Pearlite: its structure and mechanical properties. N. T. BELAIEV (Rev. Mét., 1930, 27, 680–685).—A review of recent work of the author and of Green in which expressions are deduced for determining the width of the lamellæ of cementite and ferrite in the pearlite eutectic. A. R. POWELL.

Structure of silicates. W. L. BRAGG (Z. Krist., 1930, 74, 237–305; Chem. Zentr., 1930, ii, 1657).—A discussion. A. A. ELDRIDGE.

Crystallographic relationships between epidote-zoisite and orthite-allanite. F. MACHAT-SCHKI (Zentr. Min. Geol., 1930, A, 89–96, 154–158; Chem. Zentr., 1930, ii, 536).

Crystal structure of loparite and pyrochlore. H. R. VON GAERTNER (Neues Jahrb. Min., 1930, A, 61, 1–30; Chem. Zentr., 1930, ii, 536).—The pseudocubic unit cell of loparite has a 3.854 ± 0.018 Å. Pyrochlore has a 10.34 Å., with 8 mols. in the unit cell; space-group O_h^1 . A. A. ELDRIDGE.

Structural and molecular unit of eudialyte. B. GOSSNER and F. MUSSGUG (Zentr. Min. Geol., 1930, A, 81–88; Chem. Zentr., 1930, ii, 537).—The rhombohedral unit cell has a 14.31 , c 30.15 Å. A. A. ELDRIDGE.

Structural and molecular unit of petalite. B. GOSSNER and F. MUSSGUG (Z. Krist., 1930, 74, 62–66; Chem. Zentr., 1930, ii, 1355).—The unit cell, a 11.77 , b 5.13 , c 15.17 Å., β $112^\circ 44'$, contains 4 mols. of $\text{LiAlSiO}_4 \cdot 3\text{SiO}_2$; space-group C_{2h}^2 . The crystals are monoclinic pseudocubic. The constituents, particularly lithium, are subject to replacement. A. A. ELDRIDGE.

Structure of melilite. B. E. WARREN (Z. Krist., 1930, 74, 131–138; Chem. Zentr., 1930, ii, 1964).—Melilite, $(\text{Ca}, \text{Na})_2(\text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_7$, tetragonal, has a 7.73 , c 5.01 Å., the unit cell containing 2 mols.; space-group D_{2d}^2 (V_8^2). A. A. ELDRIDGE.

Structure of sodalite and helvine. L. PAULING (Z. Krist., 1930, 74, 213–225; Chem. Zentr., 1930, ii, 1965).—Sodalite, cubic, has a 8.870 Å.; the unit cell contains 2 mols.; d 2.290 ; space-group T_d^1 . Helvine has a 8.25 Å., space-group T_d^1 . A. A. ELDRIDGE.

Crystal structure of benoitite, $\text{BaTiSi}_2\text{O}_6$. W. H. ZACHARIASEN (Z. Krist., 1930, 74, 139–146; Chem. Zentr., 1930, ii, 1964–1965).—Benoitite has a 6.60 ± 0.01 , c 9.71 ± 0.01 Å.; the trigonal unit cell contains 2 mols.; space-group D_{3h}^1 . The ionic condition of the ions is discussed. A. A. ELDRIDGE.

Spinel. III. Cobalt and zinc titanates. L. PASSERINI (Gazzetta, 1930, 60, 957–962; cf. A., 1930, 1007).—Cobalt orthotitanate, Co_2TiO_4 , and zinc orthotitanate, Zn_2TiO_4 , which were prepared by heating a mixture of 2 mols. of the corresponding nitrate and 1 mol. of titanate acid at 900° , are shown to crystallise in the cubic system with a lattice of the spinel type. Co_2TiO_4 , a 8.420 ± 0.005 , v 596.94×10^{-24} c.c., $d_{\text{calc.}}$ 5.12 , and Zn_2TiO_4 , a 8.410 ± 0.005 , v 594.82×10^{-24} c.c., $d_{\text{calc.}}$ 5.43 ; the unit cell contains 8 mols. in each case. O. J. WALKER.

Influence of shape and polarity of molecules on the X-ray spectra of liquids. III. Appearance of two intense "amorphous rings" in substances the molecules of which are probably disc-shaped. J. R. KATZ and J. SELMAN (Z. Physik, 1930, 66, 834–857; cf. A., 1928, 222).—Experiments on colloidal solutions of disc-shaped colloidal particles have shown that these particles tend to orient in parallel layers, separated by a definite distance. Experiments described suggest that disc-shaped molecules, such as naphthalene, quinoline, isoquinoline, coumarin, and like molecules with short side-chains also form groups of parallel molecules, when at a temperature considerably below the critical temperature. This parallel grouping of molecules gives rise to a second amorphous ring, the comparatively large width of which shows that the group is small in size, and the intensity of which indicates that few, if any, of the molecules are not in groups. As the critical temperature is approached, the outer ring becomes more diffuse, and finally disappears; that for quinoline disappears at 150° . Hydration of the molecules also tends to destroy the outer ring. Molecular dimensions deduced from the diameter of these rings are given. A. B. D. CASSIE.

Centres of addition as centres of co-ordination. E. HERTEL (Z. physikal. Chem., 1930, B, 11, 279–290; cf. A., 1930, 668).—*C*-Diethylbarbituric acid crystallises in rhombic bipyramids; translation-group Γ_0' , space-group V_8^{17} , molecular symmetry C_{2v} , a 7.11 , b 14.4 , c 9.7 Å. The unit cell contains four molecules. Structural models are given. F. L. USHER.

Molecular layers of fatty acids. A. JOFFÉ and P. LUKIRSKY (J. Phys. Radium, 1930, [vii], 1, 405–410).—Measurements have been made by an ionisation method of the changes of potential at layers of stearic acid 1, 2, and 3 mols. thick, on a gold-plated surface. The values obtained are $+0.13$, 0, and $+0.09$ volt, respectively, showing that the molecules in adjacent layers lie with similar ends adjacent. If the

gold surface is first washed with acid, -0.14 volt is obtained for a unimolecular layer, in agreement with Frumkin and Guyot (cf. A., 1926, 1093), showing that the first layer is then attached by the other end of the molecule. C. W. GIBBY.

Alternation in properties of long-chain carbon compounds. T. MALKIN (Nature, 1931, 127, 126—127).—Theoretical. It is suggested that the essential feature of an alternating series is that the zig-zag chain is tilted with respect to the terminal planes; non-alternating series possess vertical as opposed to tilted chains. L. S. THEOBALD.

X-Ray study of mannitol. G. W. MCCREA (Nature, 1931, 127, 162—163).—X-Ray analysis gives for *d*-mannitol *a* 8.66, *b* 16.58, *c* 5.50 Å.; space-group Q^4 ; d_{calc} 1.522 g./c.c.; 4 mols. per unit cell (cf. Marwick, this vol., 152). L. S. THEOBALD.

X-Ray examination of liquid-crystalline substances. I. *p*-Azoxyanisole. P. W. GLAMANN, K. HERRMANN, and A. H. KRUMMACHER (Z. Krist., 1930, 74, 73—94; Chem. Zentr., 1930, ii, 1493).—X-Ray photographs of *p*-azoxyanisole in the liquid-crystalline and amorphous phases show two liquid-rings; the liquid-crystalline phase oriented in a magnetic field also gives the two rings, but modified in a manner which is not observed in the amorphous phase. When $\text{MoK}\alpha$ radiation is used a third ring is observed. A. A. ELDRIDGE.

X-Ray investigations of optically active compounds. II. Diphenyl and its active and inactive derivatives. G. L. CLARK and L. W. PICKETT (J. Amer. Chem. Soc., 1931, 53, 167—177).—Rotation and oscillation photographs of diphenyl, dimesityl, *d*- and *l*-3:3'-diaminodimesityl, hexachlorodiphenyl, diphenic acid, and *o*-tolidine are used for the determination of the crystal structures. The systems, unit cell dimensions, space-group, and number of mols. per unit cell are given. Of the compounds examined, only diphenyl has a centre of symmetry. H. BURTON.

Influence of impurities on some physical and crystallographical properties of hemimellitic acid. V. AGAFONOV (Compt. rend., 1931, 192, 99—101).—The ultra-violet polychroism of hemimellitic acid is probably due to the distribution in the crystal lattice of small quantities of α - and β -acids. These were isolated by fractional crystallisation as flat plates or elongated yellow prisms (α), and as needles (β), *d* 1.54 and 1.66, n_D 1.63 and 1.68, respectively, *m. p.* (α) 182—185°, β infusible. The former contained about 0.5% of ash (calcium, aluminium, and manganese), whilst the β -crystals were calcium hemimellitate. Crystallographic data are also given, and show the birefringence of the acid to be greater than that of the α - or β -crystals. J. GRANT.

Transformation of lattice of cellulose nitrate. General phenomenon in cellulose compounds. J. J. TRILLAT (Compt. rend., 1930, 191, 1441—1443).—X-Ray examination of cellulose nitrate (12.95% N) as prepared and in the form of film obtained by evaporation of an acetone solution shows, respectively, the usual crystalline cellulose nitrate diagram, and a modified form also crystalline, due to

an admixture of what may be merely a new form of the nitrate, or of a combination thereof with acetone—of which about 1% is obstinately retained (cf. A., 1930, 1519). Films of cellulose nitrate containing 10—12% N are amorphous; undissolved nitrate shows a crystalline structure diminishing in definiteness with decrease in content of nitrogen. It is inferred that only the trinitrate is a well-defined compound (cf. Hess etc., *ibid.*, 750). C. A. SILBERRAD.

Structure of cellulose nitrates. DESMAROUX and MATHIEU (Compt. rend., 1931, 192, 234—236).—Cellulose nitrates of nitrogen contents between 13.9 and 11.5% give, on X-ray examination, Debye-Scherrer diagrams in each of which there appears a clearly-defined ring corresponding with a lattice spacing which increases from 6.6 to 7.5 Å. with increasing nitrogen content. Cellulose nitrate containing 13.9% N gives two definite intense rings corresponding with lattice spacings of 4.5 and 4 Å., respectively. The intensity and definition of these rings diminish with decreasing nitrogen content. The homogeneity of nitration can thus be investigated. In the X-ray diagrams of films prepared from cellulose nitrate of 12.10% N the definite internal ring has become a feeble halo and the external bands have coalesced. A. RENFREW.

Volta effect. E. DUBOIS (Ann. Physique, 1930, [x], 14, 627—725).—Detailed investigations of the Volta effect for a number of metals are described with reference to the degree of heating, influence of time, and presence of impurities. The effect shows a positive variation for moderate heating, becoming negative for higher temperatures, and a variation with the time elapsing after heating. The temperature variations are due to the elimination of impurities, in particular oxygen and water vapour. On heating, oxygen is expelled first and a positive variation results; water vapour is removed on raising the temperature, and a negative variation is observed. Traces of salts of the alkali metals distilled on to the metallic electrodes rendered them more electro-positive. The variation with time is found even after heating the metal in argon, and corresponds with a decrease in density of electron emission of the pure metal. N. M. Blich.

Measurements of contact potentials between pure metals. H. KÖSTERS (Z. Physik, 1930, 66, 807—826).—Contact potentials between tungsten, molybdenum, nickel, copper, and chromium were measured in a high vacuum by Mönch's method (*ibid.*, 1926, 47, 522). The metals were freed from adsorbed and occluded gases by induction heating. This heating and the measurements of potential were carried out with the apparatus surrounded by liquid air. Tungsten, tantalum, and molybdenum gave results in good accord with the work required to transfer an electron across the surface, but nickel and copper gave uncertain results. A. B. D. CASSIE.

Theory of the polarity effects in solids during passage of currents. P. BÖNING (Z. Physik, 1930, 66, 581—597).—A theory of the mechanism of the partial unidirectional conductivity characteristic of some crystalline materials which are relatively poor

conductors of electricity is developed with particular reference to the rôle played by polarisation in such phenomenon. It is claimed that the theory has important bearings on the mechanism of the electrical breakdown of insulating materials. R. W. LUNT.

Contact potentials. I. The contact potentials between metals and insulators. F. POLEDNIK (Z. Physik, 1930, 66, 619—631).—A method involving the use of Henkel's thread electrometer has been developed for the determination of the contact potential between a metal and glass or fused quartz in a vacuum. The following values in volts are given for quartz or glass, respectively: platinum +2.22, +1.15, iron +1.99, +1.15, copper +1.60, +0.58, gold +1.42, +0.58, silver +1.42, +0.14, aluminium +0.93, +0.14, magnesium, +0.93, +0.14, zinc +0.45, -0.29, lead +0.16, -0.60, and tin -0.30, -1.14. When these values are plotted against the m. p. of the metal the points are found to lie on two smooth curves approximately parabolic.

R. W. LUNT.

Contact potentials. II. Contact potential between salts and their saturated (aqueous) solutions. (FRL.) M. LEDERER (Z. Physik, 1930, 66, 632—645).—The possibility of measuring the contact potential between a salt and its saturated solution has been examined, to which end a special form of Dolezalek electrometer was designed. The errors inherent in the method do not permit absolute values to be obtained; it has, however, been possible to determine the absolute value of the difference between the potential for salt-solution pairs. The following data are given: sodium chloride-potassium chloride, -0.18 ± 0.08 ; sodium chloride-sodium nitrate, -0.04 ± 0.07 ; sodium nitrate-barium nitrate, -0.21 ± 0.06 .

R. W. LUNT.

Conductivity of thin metal foils. L. TISZA (Naturwiss., 1931, 19, 86—87).—The specific resistance of thin metal foils slowly increases as the thickness of the foil is diminished until at a limiting thickness of 10—20 μ , when there is a sudden increase in its value. Theories propounded to account for this behaviour take no account of the relation between conductivity and temperature. The conductivity of silver at -253° is 150 times that at the ordinary temperature. Limiting thicknesses are expressed as a function of the mean free path in the compact metal, on the assumption that surface electrons are reflected diffusely and thereby lose a forward impulse.

W. R. ANGUS.

Curie points. L. F. BATES (Proc. Physical Soc., 1931, 43, 87—95).—Three temperatures may require to be specified in a description of the magnetic behaviour of a ferromagnetic substance. The term "Curie point" is loose and it is better to call it the ferromagnetic critical point, since it is not enough to state that a change in specific heat occurs at the Curie point. The second important temperature is the ferromagnetic Curie point at which the intrinsic magnetisation may be considered to become zero. It is obtained by extrapolation of the curve of intrinsic magnetic moment against temperature, that portion of the curve being used where the rate of change is a maximum. The third temperature is the para-

magnetic Curie point, and comes into account when the variation of susceptibility with temperature after the substance has passed into the paramagnetic state is considered. This temperature may vary considerably from the ferromagnetic Curie point. In the case of iron, the separation is 80° . There are cases where the paramagnetic Curie point is lower than the ferromagnetic Curie point; e.g., the ferrocobalts. The significance of these two points in connexion with a theory of ferromagnetism is discussed. An extension of the view that ferromagnetism is due to the association of atoms in groups may account for the paramagnetic behaviour of iron, cobalt, and nickel, and of more complex substances such as the ferrocobalts, magnetite, and manganese arsenide. The experimental evidence in the case of the elements iron, nickel, and cobalt leaves some doubt as to the existence of a true paramagnetic Curie point, but it may be assumed for the purpose of an approximate calculation of the Weiss constant of the internal molecular field.

A. J. MEE.

Critical anisotropic point of ferromagnetic crystals. N. S. AKULOV (Physikal. Z., 1931, 32, 107—108).—Theoretical.

A. J. MEE.

Paramagnetism independent of temperature. Existence of electronic isomerides in polyatomic ions. S. FREED and C. KASPER (J. Amer. Chem. Soc., 1930, 52, 4671—4679; cf. A., 1930, 1102).—The susceptibilities of uranyl sulphate, sodium tungstate, and potassium dichromate have been determined at temperatures between 70° and 293° Abs. The susceptibility of the uranyl ion decreases slightly and uniformly with depression of the temperature. The permanganate ion (Ishiwara, A., 1915, ii, 141) probably behaves similarly. The susceptibilities of the tungstate and dichromate ions are 5.93×10^{-6} and 62.1×10^{-6} per g.-mol., respectively, and within experimental error ($< 0.1 \times 10^{-6}$) these susceptibilities exhibit no variation with temperature. The properties of these ions indicate that the least stable electrons are localised near the metallic kernel and are shielded from the external fields of neighbouring ions. Hence, modern theories of magnetism may be applied (van Vleck, A., 1928, 572) and as a consequence the existence of electronic isomerides in these polyatomic ions is recognised.

J. G. A. GRIFFITHS.

Thermal analogy of the Barkhausen effect. B. DEL NUNZIO (Atti R. Accad. Lincei, 1930, [vi], 11, 125—129).—Measurements of the magnetisation of nickel at temperatures between 0° and 400° in a constant magnetic field show that the magnetisation falls slowly up to 300° , and then abruptly to almost zero near the Curie point 357° .

F. G. TRYHORN.

Thermomagnetic property of manganese. Y. SHIMIZU (Sci. Rep. Tôhoku, 1930, 19, 411—417).—The magnetic susceptibility of 99.9% manganese is 7.55×10^{-6} at 20° and falls in a smooth curve to 5.22×10^{-6} at 805° . At 810° the change to β -manganese is accompanied by a rise in the susceptibility to 6.0×10^{-6} ; this is followed by a slow fall to 5.4×10^{-6} at 1090° , when there is a sudden increase to 8.41×10^{-6} at 1100° corresponding with the change to γ -manganese.

A. R. POWELL.

Range of brittleness of iron at low temperatures. F. SAUERWALD, B. SCHMIDT, and G. KRÄMER (Z. Physik, 1931, 67, 179—183).—For technical soft iron there was a sharp limit to the brittleness at -155° . For a two-crystalline system of a special soft iron, the limit for brittleness can be raised to -90° to -98° . A. J. MEE.

Determination of mol. wt. in liquid ammonia. H. H. STRAIN and J. H. C. SMITH (J. Amer. Chem. Soc., 1930, 52, 5291—5293).—The method is similar to those of Schwarz (A., 1929, 1416) and Signer (A., 1930, 531), involving the diffusion of a vapour, in this case ammonia, until two solutions (one is the unknown, the other a standard) have the same molecular concentration. Ammonium chloride appears to exist in the bimolecular form in liquid ammonia. The results for levulose are low, probably owing to interaction with the solvent. Results are given for 21 substances. H. BURTON.

Vapour-pressure determination of the mol. wt. of sucrose. S. OGURI (Mem. Fac. Sci. Eng. Waseda, 1930, 7, 93—96).—A current of dry air is saturated first in an aqueous sugar solution of known concentration and secondly in pure water. If p' is the vapour pressure of the solvent and p that of the sugar solution at the temperature of experiment, the losses in weight of the solution and of the solvent are proportional to p and to $p' - p$, respectively. Application of the usual molecular vapour-pressure depression equation to the above weight losses enables the mol. wt. of the sugar to be calculated directly. The apparatus used is described. E. A. RYDER.

Thermoanalysis of metal single crystals and a new thermoelectric effect of bismuth crystals grown in magnetic fields. A. GOETZ and M. F. HASLER (Physical Rev., 1930, [ii], 36, 1752—1781).—Crystals of bismuth having any desired orientation predetermined by a seed crystal were grown by the method previously described (cf. A., 1930, 401), one half normally, and the other under a transverse magnetic field, by the continuous and discontinuous process. A thermoanalyser is described for measuring and localising changes of the thermoelectric properties along the crystal length by progressive local heating without application of mechanical stress. It was found that the normal half of a crystal has a thermo-*E.M.F.* against the magnetic half; this effect was investigated in relation to the orientation of the crystal to the magnetic field and thermoelectric current, the method of growth, the presence of impurities, the strength of the applied field, and the temperature. The results obtained are brought into relation with the diamagnetic anisotropy of bismuth. N. M. BLIGH.

Measurements with the aid of liquid helium. XI. Resistance of pure metals at low temperatures. W. MEISSNER and B. VOIGT (Ann. Physik, 1930, [v], 7, 761—797).—Measurements of the electrical resistance of the metals in the first and second groups of the periodic table and of boron, aluminium, indium, and thallium in the third group down to temperatures of about 1.1° Abs. have been made and superconducting metals determined.

W. GOOD.

Measurements with the aid of liquid helium. XI. Resistance of pure metals at low temperatures. W. MEISSNER and B. VOIGT (Ann. Physik, 1930, [v], 7, 892—936).—Tables showing the resistance between 1.2° and 273° Abs. are given for all elements in the fourth group excepting hafnium, for vanadium, tantalum, arsenic, antimony, and bismuth, for chromium, molybdenum, tungsten, uranium, selenium, and tellurium, manganese and rhenium, iron, ruthenium, cobalt, rhodium, iridium, nickel, palladium, and platinum. A. B. D. CASSIE.

Properties of pure nickel. L. JORDAN and W. H. SWANGER (and others) (Bur. Stand. J. Res., 1930, 5, 1291—1307).—Fairly pure electrolytic nickel was further purified by annealing in hydrogen. The ingots finally prepared were of a purity of 99.94% and contained not more than 0.001% O. The density as cast is 8.907 g. per c.c. at 23° . The length of the side of unit cube is 3.525 \AA . The m. p. is 1455° . Electrical resistivity is 7.236 microhms-cm. at 20° with a temperature coefficient of 0.0067 ohm per 1° per ohm at 0° . Saturation value of intrinsic induction is 6150 gauss. Magnetic transformation takes place at 370 — 380° and thermal transformation at 350° . The thermal *E.M.F.* against platinum (towards which nickel is negative) are 1.485 millivolts at 100° , 6.165 millivolts at 500° , 12.130 millivolts at 1000° . The average coefficient of thermal expansion is 13.3×10^{-6} (25— 100°), 14.4×10^{-6} (25— 300°), 16.5×10^{-6} (300— 600°), and 17.8×10^{-6} (600 — 900°). W. E. DOWNEY.

Damping of sound waves in a homogeneous gaseous medium. Y. ROCARD (J. Phys. Radium, 1930, [vii], 1, 426—438).—Theoretical.

C. W. GIBBY.

Equation of state of easily liquefiable hydrocarbons. IV. Density and compressibility of *n*-butane. M. BECKERS (Bull. Soc. chim. Belg., 1930, 39, 470—495; cf. A., 1930, 25).—Methods available for the preparation and purification of *n*-butane have been critically examined. The progress of purification by fractional distillation may be followed accurately by measurement of the vapour pressure of the liquid before fractionation and of the initial and final fractions obtained; the usual criterion of purity, viz., constancy of pressure during distillation, is untrustworthy. Measurements with *n*-butane by the balloon method previously described yield for the density at 0° mean values of 2.5185 (710 mm.), 1.79876 (510 mm.), and 1.07568 (310 mm.). The extent to which the vapour deviates from the gas law has been calculated. The mol. wt. of *n*-butane, calculated from the density, is 58.188, giving at. wt. of carbon 12.0275. H. F. GILBE.

Magnetic susceptibility and absorption spectra of complex cyanides. L. SZEGÖ and P. OSTINELLI (Gazzetta, 1930, 60, 946—957).—Measurements have been made of the magnetic susceptibility and of absorption spectra of the following complex cyanides: $\text{K}_3\text{Cr}(\text{CN})_6$; $\text{K}_4\text{Cr}(\text{CN})_6$; $\text{K}_3\text{Mn}(\text{CN})_6$; $\text{K}_4\text{Mn}(\text{CN})_6$; $\text{K}_5\text{Mn}(\text{CN})_6$; $\text{K}_3\text{Co}(\text{CN})_6$; $\text{K}_4\text{Co}(\text{CN})_6$; $\text{K}_2\text{Ni}(\text{CN})_4$, and $\text{K}_2\text{Ni}(\text{CN})_3$. As in the case of ferro- and ferri-cyanides, greater optical activity is associated with the paramagnetic than with the diamagnetic state, except with the complex cyanides of bivalent

cobalt and of uni- and bi-valent nickel. Potassium cobaltocyanide, for example, is diamagnetic, but shows a greater absorption than the cobaltcyanide. The results are discussed in terms of the electronic theory.

O. J. WALKER.

Determination of the susceptibility of cerium fluoride at low temperatures. W. J. DE HAAS and C. J. GORTER (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 949—952).—The susceptibility of cerium fluoride has been measured from very low temperatures up to the ordinary temperature. At higher temperatures the Curie-Weiss law is followed. At the temperature of liquid nitrogen and at lower temperatures deviations occur. The result is in disagreement with the theory of Becquerel and Kramers as applied to tysonite, which has the same crystal structure and the same central atom as cerium fluoride.

J. FARQUHARSON.

Dependence of certain electrical and electro-optical constants of nitrobenzene and nitrotoluene on the purity. W. ILBERG (Z. tech. Physik, 1930, 11, 283; Chem. Zentr., 1930, ii, 1342).—Polemical (cf. Hehlgers, A., 1930, 142). F. HEHLGERS (*Ibid.*, 283—285).—A reply. A. A. ELDRIDGE.

Quantum theory of null-point temperature. G. BECK, H. BETHE, and W. RIEZLER (Naturwiss., 1931, 19, 39).—The absolute null point is characterised by a cessation of all motion within the lattice. Each electron, according to Eddington, possesses $1/\alpha$ degrees of freedom, where α is the Sommerfeld fine-structure constant. Besides electrons the crystal also contains protons, for which, obviously, the number of degrees of freedom is the same, since, according to Dirac, a proton can be considered as a hole in electron gas. To arrive at the absolute null point it is necessary to subtract $2/\alpha - 1$ degrees of freedom for each neutron (=1 electron+1 proton). By doing this the expression for the null point temperature is obtained, $T_0 = -(2/\alpha - 1)$ degrees. Substitution of 273° for T_0 gives the value 137 for $1/\alpha$, which agrees, within the limits of error, with values previously deduced in other ways. A hexagonal crystal was studied, but the same result is obtained irrespective of the type of crystal structure.

W. R. ANGUS.

F. p. of nickel as a fixed point on the international temperature scale. H. T. WENSEL and W. F. ROESER (Bur. Stand. J. Res., 1930, 5, 1309—1318).—The f. p. of nickel was determined by measuring with an optical pyrometer the ratio of brightness of red light of wave-length 0.6533μ emitted by black bodies at the f. p. of nickel and gold, respectively. The nickel was frozen in magnesia crucibles in a vacuum. The f. p. was found to be $1455 \pm 1^\circ$ on the International temperature scale based on the value 1063° for the f. p. of gold and 1432 cm.-degree for C_2 .

W. E. DOWNEY.

Christiansen three-plate method for the determination of the heat conductivity of gases. H. DIERKES (Physikal. Z., 1931, 32, 84—91).—This method has been investigated in an endeavour to increase its accuracy so as to render it a precision method. The apparatus is accordingly modified in several ways, the temperatures being determined by

thermo-elements. Results are given for the heat conductivity of hydrogen and carbon dioxide relative to air. The results obtained were for hydrogen, 5.3, and for carbon dioxide, 0.71. Compared with the generally accepted values the former is too small, and the latter too great. If the Schleiermacher method is correct, and there appears to be no doubt of this, there must be other errors in the Christiansen method. It may be that the temperature inside the plates is not identical with that at the surfaces, and adsorption of gas on the plates may occur.

A. J. MEE.

Specific heats of gases at high pressures. II. Method and apparatus at high temperatures. N. W. KRASE and B. H. MACKAY (J. Amer. Chem. Soc., 1930, 52, 5111—5114; cf. A., 1930, 403).—The constant-temperature, adiabatic, flow calorimeter described may be used for the determination of the specific heats of gases at temperatures as high as 350° and at pressures up to 1000 atm. Data for nitrogen are recorded.

J. G. A. GRIFFITHS.

I. Specific heats of thallium, calcium, and magnesium at 10° Abs. II. Entropy and chemical constants of magnesium from spectroscopic data. K. CLUSIUS and J. V. VAUGHEN (J. Amer. Chem. Soc., 1930, 52, 4686—4699; cf. A., 1929, 635).—I. The specific heats have been determined at temperatures between 10° and 250° Abs. in the apparatus described. Previous values recorded for thallium are too low, whilst those for calcium and magnesium are too high. At temperatures above 17° Abs., the results for thallium are reproduced by inserting the characteristic temperature $\theta = 94^\circ$ in the Debye function; at lower temperatures, θ decreases to 84° . With calcium, θ approaches a constant value, 219, at low temperatures. With magnesium, the values of θ increase with fall of temperature, but above 30° Abs. θ is about 322.

II. The vapour-pressure constant of magnesium is 0.443 ± 0.1 as compared with the value 0.493 calculated statistically. The entropy of the monatomic vapour at 1 atm. and 25° is 35.29 g.-cal./ 1° (cf. theoretical value 35.5).

J. G. A. GRIFFITHS.

Specific heat of liquid diphenyl. R. F. NEWTON, B. D. KAURA, and T. DE VRIES (Ind. Eng. Chem., 1931, 23, 35—37).—The specific heat of liquid diphenyl determined over the range 100 — 300° was $0.388 + 0.00057t$ (t in $^\circ\text{C}$). An accuracy of 1% is claimed for the results.

H. INGLESON.

Specific heat of diphenyl. H. O. FORREST, E. W. BRUGMANN, and L. W. T. CUMMINGS (Ind. Eng. Chem., 1931, 23, 37—39).—The specific heat of diphenyl has been measured from 77° to 347° by two methods. A curve of the variation of specific heat with temperature reproduces the experimental results with an accuracy of about 2%.

H. INGLESON.

Measurement of the true specific heats of solid and liquid metals at high temperatures. H. SEEKAMP (Z. anorg. Chem., 1931, 195, 345—365).—A method has been developed for measuring the specific heats of metals at temperatures up to 600 — 700° . A hollow cylinder of the metal encloses an insulated tungsten spiral which can be heated electrically;

after passage of the current for a known time with a measured fall of potential the temperature of the metal is measured with a thermocouple inserted in a hole in the wall of the cylinder. Results for the specific heat of copper (18–700°), aluminium (18–600°), and magnesium (18–500°) agree in general with those of other observers. Measurements with thallium at temperatures up to 500° yield for the transition temperature 226.7° and for the heat of transition 98 g.-cal./g.-atom, and show the existence of minima in the temperature-specific heat curve at about 254° and 380°.

H. F. GILLBE.

Influence of period of heating on b. p. of liquids used in ebullioscopy. Testing purity of volatile liquids by isothermal distillation. S. L. WRIGHT, jun., and A. W. C. MENZIES (J. Amer. Chem. Soc., 1930, 52, 4699–4708).—A pair of differential isothermometers (Smith and Menzies, A., 1910, ii, 1036) is employed to determine directly any differences of the vapour pressure of two samples of a liquid, one having been maintained at the b. p. for several hours and the other having been elevated to the b. p. immediately before the determination. The results obtained with acetic acid, bromine, benzene, and carbon tetrachloride are taken to indicate that the vapour pressure is independent of the above treatment, and delay in the attainment of internal equilibrium is therefore without influence on the b. p. The purity of the liquids was verified by isothermal distillation in the apparatus. The presence of impurities in quantities too small to be detected by ordinary means causes errors in vapour-pressure measurements when circumstances favour fractionation (cf. Washburn, A., 1928, 10).

J. G. A. GRIFFITHS.

Vapour pressure of ice at low temperatures. C. DEI (Atti R. Accad. Lincei, 1930, [vi], 11, 119–124).—Measurements have been made of the potential required to produce an explosive discharge in water vapour at a series of known low pressures. The curve giving the relationship between discharge potential and pressure of water vapour was then applied to calculate the vapour pressure of ice at low temperatures from measurements of the discharge potential over ice. At the temperatures –22.3°, –55°, and –66° the respective vapour pressures of ice are 0.58 ± 0.023 , 0.0166 ± 0.0008 , and 0.0037 ± 0.0002 mm.

F. G. TRYHORN.

Vapour pressures of selenium tetrachloride. Existence of selenium dichloride. D. M. YOST and C. E. KIRCHER (J. Amer. Chem. Soc., 1930, 52, 4680–4685; cf. Simons, A., 1930, 1356).—The vapour pressure of selenium tetrachloride at temperatures between 109° and 181° is given by $\log_{10} P(\text{mm.}) = 11.2040 - 0.05223 \times 73,990/T$. By means of vapour-pressure measurements with excess of chlorine and vapour density determinations it is found that between 109° and 226° the vapour consists of chlorine and selenium dichloride. The heat of the reaction $\text{SeCl}_4(s) = \text{SeCl}_2(g) + \text{Cl}_2(g)$ is (ΔH) 35,380 g.-cal. and the heat of formation of $\text{SeCl}_2(g)$ is (ΔH) –10,780 g.-cal.

J. G. A. GRIFFITHS.

B. p. and vapour-pressure formulæ for organic liquids. E. W. MADGE (Z. anorg. Chem., 1931, 195,

338).—It is shown that the formula derived by Herz (A., 1930, 1104) must be applicable to substances which obey Trouton's rule.

H. F. GILLBE.

M. p. of pure chromium. F. HOFFMANN and C. TINGWALDT (Z. Metallk., 1931, 23, 31–32).—The m. p. of electrolytic and of aluminothermic chromium has been determined by melting the metal in a magnesia crucible and by observing the temperature of a hole in a bar of chromium during melting in a vacuum by the passage of a high current. The first method gave $1800 \pm 10^\circ$ and the second $1765 \pm 10^\circ$.

A. R. POWELL.

Heat of dissociation of fluorine. H. VON WARTENBERG and J. TAYLOR (Nachr. Ges. Wiss. Göttingen, 1930, 119–123; Chem. Zentr., 1930, ii, 1660).—The heat of dissociation of fluorine, calculated from the band spectrum, is 63.5 ± 0.7 kg.-cal. Irradiation with ultra-violet light does not accelerate the union of hydrogen and fluorine.

A. A. ELDRIDGE.

Entropy of hydrogen and the third law of thermodynamics. Free energy and dissociation of hydrogen. W. F. GIAUQUE (J. Amer. Chem. Soc., 1930, 52, 4816–4831; cf. Giauque and Johnston, A., 1929, 138).—Band spectrum data for the hydrogen molecule are employed in conjunction with the equations previously developed (this vol., 295) to evaluate the proportions of ortho- and para-hydrogen present in equilibrium at temperatures between 0° and 298° Abs. The energy contents and heat capacities of para- and ortho-hydrogen, their equilibrium mixtures, and mixtures of para and ortho in the ratio 1 : 3 have been calculated for the range 0–298° Abs. The free energy of dissociation, equilibrium constants, and percentage dissociation of the hydrogen molecule at temperatures between 298° and 5000° Abs. have been calculated and are in satisfactory agreement with Langmuir's data. The absolute entropy of hydrogen is 33.98 g.-cal./1° per mol. In agreement with the experimental value, the ordinary application of the third law of thermodynamics gives 29.59, based on the assumption that the lowest levels of ortho- and para-hydrogen, with their total of 10 quantum species, are present in the solid state as a perfect solution, the relative proportions being those determined by the equilibrium at the ordinary temperature. It is concluded that for most substances (e.g., Giauque and Wiebe, A., 1929, 755) the absolute entropy resulting from nuclear spin will persist to temperatures below those at which measurements are ordinarily made, and hydrogen is probably the only exception. A value, 31.23, is derived for the entropy of hydrogen and may be used in conjunction with data obtained for other substances by the ordinary methods.

J. G. A. GRIFFITHS.

Superheating and intensive drying of liquids.

E. COHEN and W. A. T. COHEN-DE MEESTER (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 1003–1014).—From many experiments it is found that the true b. p. of water, benzene, or carbon tetrachloride can never be obtained when a heating bath is used, even when all the precautions detailed by Smits are introduced (cf. A., 1930, 1102). Heating with a free flame always led to a slight degree of superheating, but this was less than that which appeared when a

heating bath was used. No superheating whatever occurs when an electrically heated platinum wire in the liquid is used. The b.p. measurements of Baker and of Smits are believed to be inconclusive (cf. Lenher, A., 1929, 1372).

J. W. SMITH.

Second virial coefficient for gases: critical comparison between theoretical and experimental results. H. MARGENAU (Physical Rev., 1930, [ii], 36, 1782—1790).—Mainly mathematical. From London's recent theory of the attractive forces between molecules (cf. A., 1930, 1239) the second virial coefficient is computed for the gases: hydrogen, neon, argon, helium, nitrogen, oxygen, carbon dioxide, ammonia, and water vapour. For the two last named, which have a dipole moment, the contribution of the dipole interaction is also calculated (cf. Margenau, *ibid.*, 1349). Results are compared graphically with experimental values computed from Beattie and Bridgeman's constants; agreement is satisfactory except in the case of helium and hydrogen, where the discrepancy can be accounted for by the presence of zero point energy.

N. M. BLIGH.

Lattice energy from the thermodynamic view point. J. H. HILDEBRAND (Z. Physik, 1931, 67, 127—134).—Theoretical. Restrictions on the electrostatic equation giving lattice energies are pointed out. The thermodynamic equation determines these energies from the elastic properties of the crystal at the ordinary temperature. The lattice energy calculated for potassium iodide agrees with Mayer's value (A., 1930, 836).

A. B. D. CASSIE.

Equation of state explicit in the volume. G. SCATCHARD (Proc. Nat. Acad. Sci., 1930, 16, 811—813).—Beattie (A., 1930, 534) has derived an equation of state in the virial form $V/n = RT/p + \beta/RT + \gamma p/(RT)^2 + \delta p^2/(RT)^3$ as an approximation of the Beattie-Bridgeman equation, $p = RT(n/V) + \beta(n/V)^2 + \gamma(n/V)^3 + \delta(n/V)^4$ (A., 1927, 819), where β , γ , and δ are functions of the temperature. A new approximation of the Beattie-Bridgeman equation has been derived, $V/n = RT/p + \beta/RT + [\gamma/(RT)^2 - \beta^2/(RT)^3]p + [\delta/(RT)^3 - 3\beta\gamma/(RT)^4 + 2\beta^3/(RT)^5]p^2$. The accuracy of the two approximate equations in reproducing the values obtained by using the Beattie-Bridgeman equation is compared for hydrogen, oxygen, nitrogen, methane, ethylene, and carbon dioxide; the new approximation fits more closely. The limitation of the approximation at higher pressures is indicated.

W. R. ANGUS.

Chemical constant of hydrogen vapour and the entropy of crystalline hydrogen. T. E. STERN (Proc. Roy. Soc., 1931, A, 130, 367—379; cf. Fowler, A., 1928, 469).—Mathematical. By the use of the Einstein-Bose statistics, a result is obtained for the vapour pressure of hydrogen crystals at low temperatures which yields a value for the chemical constant of hydrogen in even closer agreement with experiment than that obtained by Fowler (*loc. cit.*). As the result of the Einstein-Bose statistics, slight variations are found to occur in the composition of the mixed crystal of ortho- and para-hydrogen as it is allowed to build up from the gas at low temperatures. Thus at temperatures very near the absolute zero the ratio of the two kinds of molecules, when the crystal is

small, may be as great as 3:2:1, whilst at higher temperatures the ratio is always nearly 3:1. The vapour-pressure equation which is correct at low temperatures is followed through to the ordinary temperature.

L. L. BIRCUMSHAW.

Calculation of free energy from spectroscopic data. W. F. GIAUQUE (J. Amer. Chem. Soc., 1930, 52, 4808—4815; cf. Lewis and Mayer, A., 1929, 648).—Theoretical. A general expression for the absolute entropy of ideal gases is derived and includes terms for molecular rotation, vibration, electronic excitation, nuclear spin, and other states which the molecule may assume. The equations given afford a basis for the evaluation of the free energy of gases and equilibrium constants from spectroscopic data.

J. G. A. GRIFFITHS.

Specific gravities of liquid and solid sulphuric acid. D. MCINTOSH (Proc. Nova Scotian Inst. Sci., 1930, 17, 259—261).—Sulphuric acid of d 1.7—1.84 is denser in the solid (frozen) state than in the liquid. The f.-p. diagram of the system water-sulphuric acid is given.

H. BURTON.

Determination of critical temperatures. Critical temperature of hydrogen fluoride. P. A. BOND and D. A. WILLIAMS (J. Amer. Chem. Soc., 1931, 53, 34—37).—The substance to be investigated is enclosed in a monel metal tube 15 cm. long, 1 cm. diameter, inclined at about 20° to the horizontal and supported at its centre by knife edges; the lower end is attached to the arm of a sensitive balance by a vertical wire which passes through the top of the oven enclosing the tube. When the oven has cooled to the critical temperature, the formation of the liquid phase in the lower end of the tube sets the balance in motion. The critical temperature of hydrogen fluoride is 230.2° (cf. Van Laar, A., 1921, ii, 83).

J. G. A. GRIFFITHS.

Measurement of very small vapour pressures. Vapour pressure of mercury and potassium. III. H. MAYER (Z. Physik, 1931, 67, 240—263).—A method for the determination of vapour pressures of the order 10^{-7} to 10^{-2} mm. is described. The vapour pressure of potassium (2.0×10^{-6} mm. at 69.8° and 4.78×10^{-4} at 143.2°) is given by $\log p \cdot T = -21087/4.571T + 10.418$. The results in general agree with those of Weiler and of Killian (A., 1926, 653), but the values of Edmondson and Egerton (A., 1927, 103) are 20—30% lower.

A. J. MEE.

Vapour pressure of Ramsay greases. H. MAYER (Z. Physik, 1931, 67, 264—269; cf. preceding abstract).—The vapour pressure of the gum grease of Ramsay at ordinary and higher temperatures has been determined by means of the apparatus previously described. It is shown that these greases can be regarded as having a definite and constant vapour pressure only if left in a vacuum desiccator at a temperature above m. p. for some time in order to outgas them. The vapour pressure of a grease so treated was 1.1×10^{-5} mm. at 12.6°.

A. J. MEE.

Density of mixtures of chloroform (U.S.P.) and benzyl alcohol. S. M. GORDON (J. Amer. Pharm. Assoc., 1931, 20, 15—17).—A graph of the densities of mixtures of chloroform and benzyl

alcohol is a straight line joining the densities of the two components, 1.4843 and 1.0468, respectively, at $20 \pm 0.5^\circ$. E. H. SHARPLES.

Viscosities of binary mixtures. L. PIATTI (Z. physikal. Chem., 1931, 152, 36—46).—The viscosity isotherms of binary mixtures of *m*-cresol and of anisole with ethyl alcohol and with benzene have been determined at temperatures from 0° to 60° . In the cresol systems the curves are continuous, with neither maxima nor minima, but the viscosities are much lower than the values calculated additively, and indicate that the strongly associated cresol molecules are largely dissociated in presence of the second component. The anisole-alcohol isotherms exhibit minima at all temperatures, but in the anisole-benzene system the curves follow closely the additive law, especially at temperatures above 50° . The b.p. curves of the four systems have been determined, and the results are compared with the viscosity measurements. H. F. GILLBE.

Theory of concentrated solutions. M. HOEPFNER and A. VON ANTROPOFF (Z. physikal. Chem., 1931, 152, 95—109).—The vapour pressure, density, and composition of the vapour phase in equilibrium with liquid mixtures of benzene and carbon tetrachloride have been determined at 15° . The deviations of the saturated vapour from the ideal gas law amount to about 3.5%. The deviations from the Raoult law for the vapour pressure of solutions, from Henry's law, and from the Nernst law when expressed in terms of the fractional molar concentration, are of the same order. H. F. GILLBE.

Empirical correction of Raoult's law applied to concentrated solutions. G. A. ROSNER (Rocz. Chem., 1931, 11, 13—18).—The empirical formula $a/N_1 = 1 + KN_2$ is derived, in which $a = p'/p$, where p and p' are the partial pressures of the solvent and the solution, respectively, $N_1 = N/(n+N)$ and $N_2 = n/(n+N)$, where n and N are respectively the number of molecules of solvent and solute present, and K is a constant. R. TRUSZKOWSKI.

Influence of b. p. on composition of azeotropic mixtures. B. KAMIENSKI (Rocz. Chem., 1931, 11, 1—12).—The expressions $\Delta p' = p' \Delta p'_0 / p'_0$ and $\Delta p'' = p'' \Delta p''_0 / p''_0$ are derived, in which $\Delta p'$ and $\Delta p''$ represent the increase in the partial pressures p'_0 and p''_0 of the components of a binary azeotropic mixture, occasioned by a rise in temperature of 1° above the b. p., and p' and p'' are the partial pressures at the higher temperature. The application of these formulae to the calculation of the composition of azeotropic mixtures of various b. p. gives results in better agreement with experiment than those given by Merriman's formula (J.C.S., 1913, 103, 1801). R. TRUSZKOWSKI.

Mol. wt. of nitrosobenzene in solid solution. C. DRUCKER and T. FLADE (Z. wiss. Phot., Schaum Festschr., 1930, 29, 29—41).—The mol. wt. of nitrosobenzene has been determined cryoscopically with dried nitrobenzene as the solvent. The results indicate that the compound is almost dimeric in dilute solid solutions. Pure nitrosobenzene is therefore at least dimeric and probably exists in a higher state of

association. The sublimation pressure, heat of sublimation, and heat of combustion have also been determined. J. W. GLASSETT.

Miscibility and variation in the properties of supersaturated silver-copper alloys. N. AGEEV, M. HANSEN, and G. SACHS (Z. Physik, 1930, 66, 350—376).—The influence of concentration and annealing temperature on the hardness and electrical resistance of the alloys has been studied by X-ray measurements. The mixing and annealing processes are the same for alloys at the copper and silver ends of the series, although copper dissolved in silver separates at a temperature about 100° above that at which silver separates from copper. The velocity of reaction is determined primarily by the concentration, and has a negative temperature coefficient. When separation takes place, an abnormal increase in resistance occurs. Experimental results are insufficient for a theoretical discussion of this, and of the abnormal hardness effects. A. B. D. CASSIE.

Heat of mixture in molten metals. M. KAWAKAMI (Sci. Rep. Tôhoku, 1930, 19, 521—549; cf. A., 1928, 21).—The heat of mixing has been measured for twenty-five systems of binary alloys containing magnesium, antimony, aluminium, silver, copper, or gold. The results show that the intermetallic compounds which exist in the solid state up to their m. p. do not decompose into their components on melting, but exist as such in the liquid phase. W. E. DOWNEY.

Thermal [and X-ray] analysis of the system lithium-copper. S. PASTORELLO (Gazzetta, 1930, 60, 988—992; cf. A., 1930, 1359).—Thermal and X-ray analyses of the above system show that no compounds or solid solutions are formed between lithium and copper. The eutectic point is at the m. p. of pure lithium, which is given as 180° . O. J. WALKER.

System bismuth-selenium. N. PARRAVANO and V. CAGLIOTI (Gazzetta, 1930, 60, 923—933).—The existence of two bismuth selenides (cf. A., 1913, ii, 415), Bi_2Se_3 and BiSe , is confirmed by X-ray examination of pure bismuth and selenium and of a series of alloys of the two elements. Taking the most probable values of the axial ratio shown, the following lattice constants are obtained: Bi , c/a 2.706, a_0 4.531; Se , c/a 1.14 or 2.66, a_0 4.360; Bi_2Se_3 , c/a 1.68, a_0 6.702; BiSe , c/a 1.60, a_0 5.021. For the two selenides in the above order the values of d are 7.398 and 7.98. O. J. WALKER.

Equilibrium diagrams of the aluminium-manganese, copper-manganese, and iron-manganese systems. T. ISHIWARA (Sci. Rep. Tôhoku, 1930, 19, 499—519).—As a preliminary to the investigation of ternary systems containing manganese, the above binary systems have been examined thermally, microscopically, and dilatometrically and also by electrical resistance measurements and X-ray observations. Equilibrium diagrams which differ from those of earlier workers are given. W. E. DOWNEY.

System iron-carbon. E. L. DUPUY (Rev. Mét., 1930, 27, 686—692).—Modern knowledge of the equilibria at the iron end of this system is summarised,

and the development of the equilibrium diagram from that first proposed by Roberts-Austen to that now generally accepted is traced. A. R. POWELL.

Equilibrium diagram of the iron-vanadium-carbon system. M. ŌYA (Sci. Rep. Tôhoku, 1930, 19, 449—472).—The system has been investigated by X-ray, micrographic, and thermal analysis up to a content of 9.9% C. The system contains no ternary compounds. There are five liquidus surfaces, six binary eutectic reactions, one binary peritectic reaction, two ternary eutectic reactions, and a ternary peritecto-eutectic reaction. The composition and temperature of the non-variant points are: (a) liquid $\rightleftharpoons \gamma + [\text{Fe}_3\text{C}] + \epsilon$; 3.4% V, 4.2% C, 92.4% Fe, 1122°; (b) liquid $\rightleftharpoons \alpha + \beta + \epsilon$; 35% V, 1% C; (c) $\delta + \text{liquid} \rightleftharpoons \gamma + \epsilon$; 7% V, 2.3% C, 1330°. In the field of existence of the γ -phase there are three solubility surfaces in which α , ϵ , and $[\text{Fe}_3\text{C}]$, respectively, begin to separate and three binary eutectoid curves along which the following reactions occur: $\gamma \rightleftharpoons \alpha + \epsilon$, $\gamma \rightleftharpoons \alpha + \text{Fe}_3\text{C}$, and $\gamma \rightleftharpoons \text{Fe}_3\text{C} + \epsilon$. The complete and various sectional diagrams as well as several characteristic micrographs of the alloys are included.

A. R. POWELL.

Solubility of hydrogen fluoride in benzene and in octane. J. H. SIMONS (J. Amer. Chem. Soc., 1931, 53, 83—87).—Data are recorded between 20° and 65°. The vapour pressure of hydrogen fluoride over benzene solutions exhibits negative deviations from Raoult's law at very low concentrations and large positive deviations at higher concentrations. This phenomenon is attributed to the strong polarity of the hydrogen fluoride molecule. J. G. A. GRIFFITHS.

Solubilities [of salts] in hydrogen fluoride. P. A. BOND and V. M. STOWE (J. Amer. Chem. Soc., 1931, 53, 30—34; cf. Fredenhagen and Cadenbach, A., 1930, 421).—Solubility data for lithium hydrogen fluoride at 0—40° are recorded. The solubility of calcium, zinc, and magnesium fluorides is less than 0.01 at 0°.

J. G. A. GRIFFITHS.

Solubilities of silver salts. K. MASAKI (Bull. Chem. Soc. Japan, 1930, 5, 345—348).—Solubilities of some sparingly soluble silver salts have been determined potentiometrically. The values obtained are: cyanide 2.1×10^{-7} , thiocyanate 1.10×10^{-6} , bromide 7.0×10^{-7} , and carbonate 1.1×10^{-4} mol. per litre.

F. L. USHER.

Reaction between polyhydric alcohols or phenols and arsenic compounds, in particular arsinoacetic acid. III. B. ENGLUND (J. pr. Chem., 1931, [ii], 129, 1—23).—The constant L (cf. A., 1930, 330) has been evaluated for the increase in solubility of arsenious oxide in 95% *n*-butyl alcohol in presence of propane- $\alpha\beta$ - and - $\alpha\gamma$ -, meso- and *r*-butane- $\beta\gamma$ -, hexane- $\alpha\zeta$ -, heptane- $\alpha\eta$ -, octane- $\alpha\theta$ -diols, and pinacone, the results being parallel to those already described.

The comparatively small increases in the solubility of arsinoacetic acid in glacial acetic acid caused by the aliphatic glycols $(\text{CH}_2)_n(\text{OH})_2$, where $n=4-10$, show an irregular oscillating effect when plotted against n . *cis*- α -Glycols of cyclic hydrocarbons exert a greater

effect than corresponding aliphatic glycols, but the *trans*-compounds are much less effective, the ratio *Ltrans* : *Lcis* being 1:11, 5, 10, and 22, respectively, for cyclopentane, cyclohexane, hydrindene, and tetrahydronaphthalene. The results are in general agreement with those required on stereochemical grounds, assuming the formation of a five-membered heterocyclic ring, except that ease of addition to the two forms of cyclohexane-1:2-diol should be about the same in the two cases.

Arsenic and arsinoacetic acid derivatives of ethylene glycol are found to be unimolecular in boiling acetone. Similar derivatives of pinacone, in contrast to those of ethylene glycol, are stable to alcoholic alkali; with phenolphthalein as indicator they behave as monobasic acids. The arsenic acid complex of pinacone in addition shows marked stability towards aqueous alkali, with which it can be titrated at 0°; it is rapidly and completely hydrolysed in aqueous solution, however, with regeneration of arsenic acid. A kinetic study by titrimetric and conductometric methods indicates also that hydrolysis is markedly accelerated by small quantities of mineral acids.

The preparation of butane- $\alpha\delta$ -, pentane- $\alpha\epsilon$ -, octane- $\alpha\theta$ -, and nonane- $\alpha\iota$ -diols, by reduction of the corresponding dicarboxylic acids with sodium and alcohol (cf. A., 1903, i, 597; 1928, 43), is described.

H. A. PIGGOTT.

Laws of distribution of small amounts of substances in crystalline precipitates. O. HAHN, H. KADING, and R. MUMBRAUER (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1930, 30, 11 pp.).—The separation of small quantities of a foreign substance which is admixed with a crystalline precipitate may take place in two ways. It may separate in the mass of the precipitate so as to be independent of the area of surface of the precipitate, its polar nature, and its charge; by this method, mixed crystals are formed. In the second case, the separation is greatly dependent on the surface properties, and is in fact an adsorption phenomenon. The method used to study the separation of foreign substances was to crystallise salts (especially barium salts) from a radioactive solution. In this way it was possible to determine how the radium had been taken up. Mixed crystals may be formed under these conditions, even if, in the macroscopic state, no isomorphism is known.

A. J. MEE.

Frenkel and Hückel's theories of adsorption. A. GANGULI (Z. Physik, 1930, 66, 704—707).—Frenkel and Hückel's adsorption formulæ are both contained in the formula deduced by Kar and Ganguli (A., 1930, 151).

A. B. D. CASSIE.

Correction for adsorption in physico-chemical determinations of mol. and at. wts. E. MOLES (Anal. Asoc. Quím. Argentina, 1930, 18, 114—123).—An historical account is given of the part played by adsorption in earlier work with gases, and of the corrections which have been applied to the data. Adsorption corrections cannot be eliminated by the employment of vessels of differing capacities, and the most satisfactory conditions are obtained with 1-litre vessels. Results obtained by the author and by other workers are reviewed.

H. F. GILLBE.

Activation energy of adsorption processes. H. S. TAYLOR (J. Amer. Chem. Soc., 1930, 52, 5298—5299).—A preliminary discussion.

J. G. A. GRIFFITHS.

Specific adsorptive properties of active charcoals. I. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1930, 62, 1627—1633).—A theoretical consideration of the laws governing adsorption.

R. TRUSZKOWSKI.

Theory of gas adsorption. II. V. B. MECKLENBURG (J. Russ. Phys. Chem. Soc., 1930, 62, 1723—1747).—An exposition and experimental confirmation of Kubelka's theory (Z. Elektrochem., 1925, 31, 488) of the adsorption of gases by activated charcoal.

R. TRUSZKOWSKI.

Influence of subdivision of carbon on the adsorption of fatty acids. B. BRUNS (Kolloid-Z., 1931, 54, 33—35).—Extremely finely-divided non-activated carbon adsorbs relatively greater quantities of the higher members of the fatty acid series than of the lower members. Consequently, an adsorbent which normally shows an inversion of Traube's rule may be made to behave in accordance with the rule by fine subdivision. It is suggested that the inversion of Traube's rule is due to the opening up of small pores on subdivision, which are not accessible to the larger molecules.

E. S. HEDGES.

Poisoning effects of water vapour on the adsorption of carbon dioxide by manganese dioxide [at 25°]. H. W. FOOTE and J. K. DIXON (J. Amer. Chem. Soc., 1931, 53, 55—58; cf. A., 1930, 990).—The adsorption of carbon dioxide at pressures as high as 500 mm. by manganese dioxide, with and without adsorbed water, has been investigated. The adsorption is reversible and is diminished by 50% when about 35% of the surface of the manganese dioxide is covered with water. This indicates the presence of active adsorption patches. Similar experiments with carbon monoxide in place of carbon dioxide show that the adsorption of the former is highly irreversible, although results were obtained qualitatively similar to those for carbon dioxide.

J. G. A. GRIFFITHS.

Adsorption of electrolytes by crystalline surfaces. III. (Mlle.) L. DE BROUCKÈRE (J. Chim. phys., 1930, 27, 543—565; cf. A., 1928, 831; 1929, 757).—The previous work has been extended to the study of the adsorption of sodium and potassium iodide and bromide and of cadmium iodide on the microcrystalline surface of barium sulphate; the results indicate complete reversibility, the attainment of a definite equilibrium, and the formation of a unimolecular layer. The isotherms resemble in general those obtained with the chlorides, and when plotted logarithmically consist of two linear portions of which the first indicates that in sufficiently dilute solution the quantity adsorbed increases almost linearly with the concentration, whilst the second portion corresponds with saturation of the surface of the adsorbent. In the case of cadmium iodide the isotherms indicate that simple and complex molecules are adsorbed more readily than are simple ions. By comparison of the curves obtained with a series of salts having a common on it appears that the main factor in the

adsorption process is direct adsorption of the anions and that the equivalent number of cations are retained solely by electrostatic forces. The ease of adsorption of the alkali metal halides increases with increase of the at. wt. of the anion.

H. F. GILLBE.

Exchange of ions at the surface of colloidal platinum. S. W. PENNYCUICK (Kolloid-Z., 1931, 54, 21—32).—The hydrogen ions liberated from the surface of colloidal platinum when the colloid is coagulated by the addition of electrolytes have been determined by a conductometric method. Salts of univalent cations undergo little exchange adsorption and neither hydrochloric nor nitric acid is adsorbed at all by colloidal platinum. Barium, calcium, and aluminium chlorides undergo exchange adsorption, but hydrolytic adsorption occurs simultaneously. The effect of hydrolysis is most marked in the addition of potassium cyanide. A comparison of the amount of exchange of ions with the lowering of the electrokinetic potential shows a very close connexion and points to exchange adsorption as the cause of coagulation. Actually, no discontinuity occurs at the point of coagulation and ion-exchange is not then complete. The explanation is probably that the first coagulum consists of particles in loose contact, which still contain replaceable hydrogen ions, but that when these are replaced the particles adhere more firmly, or coalesce. With colloidal platinum ion-exchange does not appear to take place in stoichiometric ratio, but this observation is probably due to partial hydrolysis of the salts concerned.

E. S. HEDGES.

Adsorption of aluminium and thorium chlorides on clays and kaolins. N. A. HELD (J. Russ. Phys. Chem. Soc., 1930, 62, 1553—1570).—Aluminium and thorium can be determined electro-titrimetrically in the same solution, using a quinhydrone electrode. Adsorption of aluminium and thorium but not of chloride ions takes place on clay, which at the same time gives up calcium and magnesium ions; this process is accompanied by acidification of the solution, as a result of the reactions: $\text{AlCl}_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_2\text{Cl} + 2\text{HCl}$ and $\text{ThCl}_4 + 3\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_3\text{Cl} + 3\text{HCl}$.

R. TRUSZKOWSKI.

Influence of hydrogen ions on the adsorption of barium and aluminium ions by clays. N. A. HELD and M. N. SOKOLOVA (J. Russ. Phys. Chem. Soc., 1930, 62, 1571—1575).—The adsorption of barium and aluminium ions varies with the p_{H} of the solution; at a given p_{H} the adsorption series $\text{Ba} < \text{Al} < \text{Th}$ is obtained.

R. TRUSZKOWSKI.

Density, surface tension, and adsorption in the water-ammonia system at 20°. H. H. KING, J. L. HALL, and G. C. WARE (J. Amer. Chem. Soc., 1930, 52, 5128—5135; cf. Berthoud, A., 1918, ii, 310; Rice, A., 1928, 582).—A closed apparatus for the simultaneous determination of the density and surface tension of a liquid is described. The surface tension of liquid ammonia at 0°, 10°, and 20° is 26.43, 24.28, and 22.03, respectively. The Ramsay-Shields constant is 1.662, corresponding with an apparent mol. wt. of 24.5. The surface tension and density of 0—100% ammonia-water mixtures at 20° are recorded (cf. Mittasch and others, A., 1927, 104). The surface tension generally agrees with the mixture

law except in the middle region, where the values rise to a maximum deviation of 6 dynes per cm. If this deviation is due to adsorption of ammonia in the surface, the adsorption is 1–5% of the normal surface concentration. J. G. A. GRIFFITHS.

Unimolecular films on water and mercury.
II. Surface films on mercury. E. FAHR (J. Chim. phys., 1930, 27, 587–603).—Mercury, in an atmosphere of nitrogen, has been used for the study of surface films owing to the absence of disturbances due to the slight solubility of the second phase and on account of its high surface tension. Films of long-chain organic compounds on mercury exhibit the same phenomena as similar films on water. Observations with oleic and myristic acids and with cetyl alcohol films confirm Marcelin's views (A., 1929, 1001) and yield results for the chain length which accord well with those derived from X-ray measurements. The isotherm of the system oleic acid–mercury has been plotted from 15 to 59.5 dynes per cm.²; the latter is the saturation pressure and is approximately twice the value for oleic acid films on water. An attempt is made to interpret the behaviour of such films by regarding them as composed of dipoles oriented by the action of the electric field of the liquid. Calculation shows that the energy of a film of this type on mercury is roughly twice that of a similar film of water, in accordance with the relative saturation pressures of oleic acid films. H. F. GILLBE.

Adhesive forces in surface films. T. M. LOWRY (Nature, 1931, 127, 165).—The conception of the co-ordination of hydrogen can be used to account for the adhesion between contiguous molecules in a unimolecular film of a fatty acid on the surface of water. L. S. THEOBALD.

Ultramicroscopic structure of unimolecular soapy water films. C. SPIERER (Kolloid-Z., 1931, 54, 17–21).—The thinnest films obtainable with 5% sodium oleate solution have been examined in the ultramicroscope. They initially contain particles which are in Brownian movement, but later this ceases and formations resembling clouds appear. These are frequently striated like cirrus clouds, the period being a few μ . Finally, the whole surface becomes a gel. The appearance of the dark spot is described. The thinnest part of the film is about 4.5 μ . E. S. HEDGES.

Elliptical polarisation at the surface of liquids.
Application to study of unimolecular surface films. C. BOUCHET (Ann. Physique, 1931, [x], 15, 5–130).—The elliptical polarisation produced by reflexion at liquid surfaces, using the green mercury line 546, has been studied. Water gives the value $K = +0.00040$. The negative values previously reported are due to impurities in the surface. The values obtained for organic liquids are all positive and there is no distinction between aliphatic and aromatic compounds. The value $K(n-1)$, where n is the refractive index, varies inversely with the surface tension for a number of liquids. The thickness of the surface film calculated by the application of Drude's equation is of the order of molecular dimensions deduced from X-ray investigations; in the case

of pure fatty acids, the ellipticity varies little with the number of carbon atoms and thus depends on the diameter rather than on the length of the molecule. The value of elliptical polarisation for salt solutions is independent of the nature and concentration of the salt and is identical with that of pure water; this is apparently due to a film of adsorbed water at the surface. A study was made of the elliptical polarisation of unimolecular films of fatty acids. The values for the acids which are completely miscible with water are not proportional to the concentration; for butyric acid, K passes through a minimum. In the case of the higher fatty acids, K decreases as the concentration increases and tends towards a limiting minimum as saturation is reached. The value of the minimum is related to the length of the carbon chain as determined by X-ray methods. These results afford independent evidence of the existence of a single layer of molecules oriented vertically. The films adsorbed at the surface of solutions of soluble fatty acids are identical in structure with unimolecular films of insoluble fatty acids. E. S. HEDGES.

Surface potentials of unimolecular films of long-chain fatty acids. I. Experimental method.
 II. Evaluation of the resolved electric moments.
 III. Potentials of solid, liquid condensed, and double layer films. J. H. SCHULMAN and E. K. RIDEAL (Proc. Roy. Soc., 1931, A, 130, 259–270, 270–284, 284–294).—I. The work of Frumkin and Guyot is briefly reviewed. Using a modification of the apparatus employed by these workers, giving an accuracy in the potential measurements of ± 2 millivolts, measurements have been made of the potential rise at a 0.01N-hydrochloric acid–air interface by the surface solution of a crystal of myristic acid. It is found that the value of ΔV , the change of potential, which equals $4\pi n\mu$ (where n is the number of molecules per sq. cm. of the film-forming substance and μ is the effective vertical component of the average electric moment) shows an arrest for a period of 10–20 min. at 150–160 millivolts. This corresponds with the transition from vapour to liquid expanded film. Measurements were also made by spreading the film in the usual way from a solution in light petroleum. With certain precautions the values obtained for the potential could be repeated both on expansion and contraction of the film, but two critical regions where marked hysteresis occurred were observed—one over the region of area 88–100 Å.², and one from 40 to 30 Å.². The ΔV -area curves showed three well-defined arrest points at 39.5, 53.5, and 88 Å.², with one less defined between 26 and 30 Å.².

II. The value of μ (see above) was calculated from the Helmholtz equation to be 2.29×10^{-19} e.s.u. for a molecule of myristic acid in the expanded state. The value obtained from the $\Delta V-n$ curve gives for the true value of μ 2.5×10^{-19} e.s.u., the difference being due to a change in the zero potential after the deposition of an expanded film on the surface. On the surface of 0.01N-hydrochloric acid the value of μ for a molecule in the liquid condensed state at a pressure corresponding with equilibrium in the expanded state is 1.56×10^{-19} e.s.u., and has small values in the vaporous state. It rises for both the

solid condensed and the expanded state, and for the latter it has a constant value of 2.5×10^{-19} e.s.u. Identical results were obtained for palmitic and pentadecanoic acids in similar states of aggregation. The transition from the expanded or liquid state to the vaporous state occurs at constant potential, from which it can be deduced that an intermediary state exists between these two which has been designated the "pre-homalic" state and appears on expansion of a liquid phase beyond a critical area. Just previous to the disappearance of this phase the electric moment of the molecules in the highly expanded film reaches the large value $\mu = 3.7 \times 10^{-19}$ e.s.u., and experimental evidence is obtained which suggests that in the vaporous state the molecules are horizontally oriented. A comparison is made between the values of $\bar{\mu}$ obtained and those derived from measurements of refractive index and dielectric constant.

III. Measurements have been made of the surface potential of films of palmitic acid in various states of compression on a series of buffer solutions varying from p_H 2 to 7.3, and from the variation of ΔV with the nature of the substrate the contribution of the double layer to the interfacial potential can be calculated from the equation $\Delta V = 4\pi n\bar{\mu} + \Delta V_u$, where $4\pi n\bar{\mu}$ is the real contribution of the film-forming material, whilst ΔV_u is the contribution of the underlying double layer to the air-liquid *P.D.* observed. It is concluded that μ calculated from the apparent surface potential change $\Delta V = 4\pi n\bar{\mu}$ depends on the hydrogen-ion concentration of the underlying surface layer which differs from that of the bulk phase, on the character of the anion and its capillary activity, and also on the phase of the film. The value of $\bar{\mu}$, calculated from the increase in surface potential due to an increase in the number of mols. per cm^2 from $\Delta V = 4\pi n\bar{\mu} + \Delta V_u$, is independent of the p_H of the substrate, and depends only on the phase of the film. The vertical component of the electric moment of palmitic acid in the liquid condensed state is found to be 1.59×10^{-19} e.s.u., whatever the acidity of the substrate, but the apparent electric moment may vary from 2.06 to 1.7×10^{-19} e.s.u., owing to the effect of the underlying ionic layer. The borate and citrate ions, which are distinguished by different capillary activities, have a marked effect on the ionic double layer. Similar effects are observed for the molecule on compression of a film in the solid condensed state.

L. L. BIRCUMSHAW.

Relationships between phase boundary potential, adsorption, surface tension, and particle size. F. K. V. KOCH (Phil. Mag., 1931, 11, 585—592).—The Nernst formula for the variation of electrode potential with the concentration of ions is derived on the assumption that the ideal gas laws apply to the solution and that the charge at the interface is directly proportional to the number of ions or molecules adsorbed. Expressions for the adsorption isotherm and the surface tension isotherm are derived mathematically on the assumption of the Helmholtz double layer, but the adsorption isotherm has a different mathematical form from that of Freundlich. The following expression is derived for the variation of interfacial potential with particle

size: $\Delta e = (RT/nF) \log_e P_u/P = 2\sigma M/r\rho nF$, where Δe is the difference in potential between a spherical particle of radius r and the plane surface, P_u and P are the Nernst solution pressures, M is the mol. wt. of the liquid, σ the surface tension, and ρ the density.

E. S. HEDGES.

Relation between ballo-electric phenomena and *P.D.* at the interface gas/solution. A. FRUMKIN and A. OBRUTSCHEVA (Kolloid-Z., 1931, 54, 2—7).—The charge acquired by droplets of finely-dispersed water containing a surface-inactive electrolyte and a surface-active non-electrolyte depends on the concentration of the electrolyte and is qualitatively connected with the potential at the gas-solution boundary. When the positive end of the molecular dipole is oriented towards the gas phase the droplets assume a positive charge and when the negative end is towards the gas a negative charge is assumed. With increasing concentration of the capillary-active non-electrolyte the ratio of the ballo-electric effect to the interfacial potential is constant for ethyl acetate and trichloroacetic acid, but rises to a steady maximum for propionic acid. Although the concentration of the electrolyte has a large influence on the ballo-electric effect, it has little influence on the interfacial potential. The sign of the ballo-electric effect changes when a non-electrolyte is converted into an electrolyte, e.g., by the addition of an acid to aniline or the addition of alkali to a phenol.

E. S. HEDGES.

Surface tension of aqueous sucrose solutions. K. SMOLEŃSKI and W. KOZŁOWSKI (Rocz. Chem., 1931, 11, 29—34).—The surface tension of sucrose solutions is expressed by the equation $\sigma = 73.0 + 0.089c$, where c is the percentage sucrose content. The temperature coefficient of surface tension is 0.0018 for M solutions.

R. TRUSZKOWSKI.

Measurement of wetting tension and some results. W. HALLER (Kolloid-Z., 1931, 54, 7—13).—The method described for the measurement of wetting tension consists in determining the displacement of the liquid meniscus in a horizontal capillary tube under the application of varying pressures. The values for the wetting tension of isoamyl alcohol, *n*-heptyl acetate, petroleum, *n*-hexyl and benzyl alcohols, lactic acid, aniline, acetophenone, glycol water, and glycerol on a glass wall are tabulated. In many cases a marked hysteresis was observed. By slowly withdrawing the liquid the meniscus becomes semicircular and leaves a thin film on the glass wall, which is very stable for water, glycol, glycerol, and lactic acid. The wetting tension of water against ceresin, cellulose nitrate, cellulose acetate, and gelatin has been measured by coating the glass capillary with films of these substances. An ageing effect is shown by cellulose acetate, films obtained from freshly prepared solutions giving a higher value than those obtained from solutions which had been kept for a few days. Capillary-active substances form a layer at the solid-liquid interface; they may form (1) unstable films, which do not alter the wetting tension, but reduce the velocity of wetting, (2) metastable films, which reduce the wetting tension, (3) stable films, which increase the wetting tension.

Sugar solutions on glass give exceedingly thin films, which show interference colours. E. S. HEDGES.

Mechanical properties of surface energy. V. DUCCESCHI (Kolloid-Z., 1931, 54, 13—17).—Mechanical energy can be obtained from surface energy by the following method. A small and light turbine is lowered into a glass trough containing water, so that the vanes of the turbine cut the water surface. An aluminium plate, the surface of which is covered with a layer of camphor, menthol, or thymol, is then placed in the water a few cm. away from the turbine. As the film of camphor or other substance spreads over the water surface the turbine rotates and may continue for 10—15 min. The addition of capillary-active substances, such as ethyl ether and amyl alcohol, in the neighbourhood of the turbine stops the movement. E. S. HEDGES.

Kinetics in [metal] solid solutions. H. HANEMANN (Z. Metallk., 1930, 22, 404).—When a super-saturated solid-solution alloy is allowed to cool under certain conditions the new phase separates in layers the orientation of which depends on the orientation of the original mixed crystals; e.g., the ferrite in steels having a Widmanstätten structure is in layers parallel to the cube and octahedron surfaces of the γ -crystals. This behaviour is explained by assuming that the atoms move in a definite direction in the lattice during the decomposition of the unstable γ -phase. Since the carbon atoms in this phase are situated in the centre of the elementary cube they can move only in the (011) direction without coming into collision with an iron atom; hence if movement of the carbon atoms away from the nuclear point of the α -phase takes place along this direction the resulting iron layers must be parallel to the cube and octahedron surfaces of the original γ -crystals. The term "perfusion" is suggested for this type of movement of one kind of atom in a mixed crystal where no interchange of position with another atom takes place. A. R. POWELL.

Optical investigations on the passivity of iron and steel. L. TRONSTAD (Nature, 1931, 127, 127—128).—Mirrors of iron and steel show a change in reflected light as soon as they are rendered passive. The change corresponds with the formation of a surface film of refractive index approximately 3.0 and with an average thickness of approximately 30 Å. The mean refractive index agrees with that of ferric oxide. The optical properties of the mirrors are constant during continuous anodic treatment independently of the current densities used. Reactivation does not completely remove the oxide film, but its destruction on the ferrite grains is more pronounced than on the grains of cementite. L. S. THEOBALD.

Recovery of transmissivity of newly repassivated iron wires in nitric acid. R. S. LILLIE (J. Gen. Physiol., 1931, 14, 349—361).—Steel wire (No. 20 piano wire) activated in 70 vol.-% nitric acid was immersed in nitric acid of varying concentrations until recovery was complete, and finally in nitric acid of 70—100 vol.-%, in which it is re-activated by touching one end with zinc. The distance travelled by the activation wave was then measured. Auto-

matic repassivation requires a certain minimal concentration of nitric acid. The conditions governing the primary phase of recovery in irritable living tissue are analogous to those obtaining in newly repassivated iron wires, in which the agent responsible for such an effect is a layer of iron oxide. P. G. MARSHALL.

Microscopic and cinematographic study of Liesegang rings. (MME.) S. VEIL and L. BULL (Compt. rend., 1931, 192, 282—284).—A detailed illustrated account of the formation of these rings when a drop of silver nitrate solution is placed on a moist dichromated gelatin jelly. C. A. SILBERRAD.

Properties of protein-cellulose membranes. L. VELLUZ and J. LOISELEUR (Compt. rend., 1931, 192, 306—308).—In both artificial and natural protein-cellulose membranes each constituent exhibits its own characteristic properties, the membrane behaving as a solid solution. Cellulose renders the membrane insoluble in water and confers on it its typical mechanical properties, whilst the protein is responsible for the various colour reactions obtained. Thus such membranes give the xanthoprotein reaction when boiled with dilute nitric acid. A membrane containing 30% of casein is coloured mauve by the action of 1% potassium hydroxide solution after immersion in boiling 5% copper sulphate solution and subsequent washing; it also gives Axenfeld's reaction, due to the presence of the colloidal metal, when treated with gold chloride solution and subsequently reduced (reddish-brown colour by reflected, blue by transmitted light), the intensity of colour running parallel to the protein content. In a series of artificial gelatin membranes with 5% of this protein the properties of the membrane are exclusively those of cellulose, with 10% the Tyndall effect becomes apparent, with 75% the mechanical properties of cellulose are still apparent, but with 80%, gelatin properties predominate. J. W. BAKER.

Diffusion of electrolytes, non-electrolytes, and colloidal electrolytes. J. W. MCBAIN and T. H. LEE (J. Amer. Chem. Soc., 1931, 53, 59—74).—The method of Northrop and Anson (A., 1929, 587) yields accurate results which are independent of the porosity of the diaphragm. The Nernst and Einstein equations are combined to include all cases of diffusion. The diffusion coefficient, D , is then given by the relation $D = iRT/\Sigma(1/U_m)$, where $1/U_m$ is the resistance to movement of a particular species and i is the van't Hoff coefficient. When data for the diffusion of 0.025—0.5N-potassium laurate into more dilute solutions and into 0.0015N-potassium hydroxide at 25° are analysed on the basis of the above considerations, the results are found to accord with previous conclusions as to the nature of the solutions (McBain and Jenkins, J.C.S., 1922, 121, 2323). Data for sucrose and other solutions show that the viscosity attributable to the solute is not that which determines the rate of diffusion, and also that non-reacting solutes have a mutual influence on their individual rates of diffusion. J. G. A. GRIFFITHS.

Dependence of viscosity of cellulose ester solutions on temperature. II. E. KARRER, E. BERL, and H. UMSTÄTTER (Z. physikal. Chem., 1931, 152,

150—152).—An equation derived theoretically by one of the authors becomes when simplified $\log(1/\eta) = A - B/T$, where $1/\eta$ is the fluidity, A is proportional to the mean energy which must be acquired by a molecule before it can move past neighbouring molecules, and B is a function of the size, number, and weight of the mobile molecules. Since the experimental results obtained for cellulose ester solutions (A., 1930, 1115) conform to this equation at all temperatures between 20° and 48°, it follows that the ester molecules undergo no chemical change over this temperature interval.

H. F. GILLBE.

Viscosity-temperature relations of solutions of cellulose esters. III. E. BERL, H. UMSTÄTTER, and E. KARRER (Z. physikal. Chem., 1931, 152, 284—294; cf. A., 1930, 1115).—Viscosities of solutions of nitrates and acetates of celluloses of varying origin in tetrachloroethane, butyl acetate, and acetone have been determined. The formulae $\log \eta = kc$, and $\log \eta = B/T - A$ (where c denotes volume concentration and T the absolute temperature, k , A , and B being constants) express the results satisfactorily. Values of the viscosity are accurately reproducible provided no free acid is present in the solvent.

F. L. USHER.

Density of acid copper sulphate solutions. G. CHAPAS, C. CHARMETANT, and A. RAME (Chim. et Ind., 1930, 24, 794—796).—Diagrams are given showing lines of equal density in the ternary system $\text{CuO-SO}_3\text{-H}_2\text{O}$ (up to the limit of homogeneous solutions) and in the system $\text{H}_2\text{SO}_4\text{-CuSO}_4$. The saturated solution of copper sulphate in water at 15° has d 1.186. From solutions containing more than 47% SO_3 the sulphate crystallises as the monohydrate.

A. R. POWELL.

Viscosity of electrolytes. W. R. BOUSFIELD (Nature, 1931, 127, 129).—Certain general statements of Joy and Wolfenden (this vol., 164) are criticised.

L. S. THEOBALD.

Variations of colour of solutions of cobalt chloride. E. TOPORESCU (Compt. rend., 1931, 192, 280—282).—Solutions containing 0.717% of cobalt chloride in methyl, ethyl, *n*-propyl, *n*-butyl, and amyl alcohols change colour from blue to rose when cooled to +3°, -18°, -32°, -45°, and -65°, respectively. The dielectric constants of these solvents at these temperatures (with one doubtful exception) decrease in the same order. Addition to a red solution (e.g., in methyl alcohol or water) of a substance which diminishes the dielectric constant, e.g., ether, acetone, or hydrochloric acid, tends to turn the colour from red to blue; addition of one that raises the constant, e.g., carbamide or glycine, has the opposite effect. It would therefore seem that the change in colour depends on the dielectric constant of the solvent, and consequently on its state of polymerisation, rather than on any change in the cobalt chloride itself.

C. A. SILBERRAD.

Potassium chromate and potassium dichromate as light filters and the constitution of chromic acid from absorption measurement. W. V. BHAGWAT and N. R. DHAR (J. Indian Chem. Soc., 1930, 7, 913—921).—Absorption measurements have been made for potassium chromate and dichromate

solutions of various concentrations in different regions of the visible spectrum. The results are expressed as extinction coefficients and the percentage transmission has been determined. A saturated solution of potassium chromate transmits wave-lengths longer than 5150 Å., and a saturated solution of potassium dichromate can conveniently be used to cut off all the wave-lengths shorter than 5600 Å. Very dilute solutions of chromates and dichromates behave similarly and it appears that chromic acid in dilute solution exists mainly as H^+ , HCrO_4' , and CrO_4'' ions, and dichromates as HCrO_4' and CrO_4'' ions.

E. S. HEDGES.

Absorption of aqueous solutions of tartaric acid. R. LUCAS and M. SCHWOB (Compt. rend., 1931, 192, 225—227).—In view of the discrepant results of other investigators (cf. Bruhat and others, A., 1930, 10, 18, 1090, 1094, 1341) the absorption of ultra-violet light (λ 2654 and 2536) by solutions of tartaric acid has been determined, using silica vessels, and water distilled in a platinum vessel, and measuring the absorption photoelectrically (cf. Halban and Siedentopf, A., 1922, ii, 332). Differences of more than 100% are shown by the results for the two samples of tartaric acid used, and for both the absorption is smaller than the recorded values. The data also show clearly that Beer's law is not followed, the specific absorption for dilute solutions being more than three times that for concentrated solutions.

C. A. SILBERRAD.

Nomenclature of atmospheric disperse systems. H. GRIMM (Kolloid-Z., 1931, 54, 1—2).—A review of the literature relating to disperse systems in gases directs attention to the numerous terms in use for the same kind of system. A plea is made for a unified system of nomenclature.

E. S. HEDGES.

Method for measuring average particle size of emulsions. W. P. DAVEY (J. Physical Chem., 1931, 35, 115—117).—The particle size is obtained from measurements of the spreading of the emulsion on a clean surface of water. The volume of the droplets of the disperse phase is obtained independently by curdling a known volume of emulsion with one of a suitable electrolyte. The limitations of the method are discussed.

L. S. THEOBALD.

Photometric measurement of concentration and dispersity in colloidal solutions. II. T. TEORELL (Kolloid-Z., 1931, 54, 58—66; cf. this vol., 164).—The dispersity of a sol can be defined by the ratio of the absorption constants for light of short and of long wave-length (the "dispersity quotient"). This quotient has a higher value for highly-disperse than for coarsely-disperse systems, and for sols with particles of medium size the dispersity quotient is proportional to the size of particle. The light absorption method has also been applied to observations on the coagulation and ageing of mastic sols.

E. S. HEDGES.

Diffusivity of colloids. Determination of diffusion velocity of very slowly diffusing substances. H. R. BRUINS (Rec. trav. chim., 1931, 50, 121—128).—Measurements of the rate of diffusion of colloids are rendered invalid by the long duration of the experiments and an attempt has therefore

been made to develop a method by which the concentration differences occurring during the first rapid stages of diffusion can be measured. An optical interference method is described. Two parallel, interfering light beams from the same source pass vertically through the diffusion apparatus, one passing through the cell containing the sol and the other through pure water. They are then united by means of a lens and are examined by an optical device similar to the Zeiss water interferometer. The calculation of the diffusion coefficient from the optical data is described. Experiments with a sol of soluble starch indicate a diffusion coefficient of 0.026×10^{-5} , from which the mean particle radius is calculated to be 8×10^{-7} cm. The method yields results which are in accordance with the diffusion law, and the degree of reproducibility is 1–2%. E. S. HEDGES.

Ultrafiltration as a test for colloidal constituents in aqueous and non-aqueous systems. J. W. MCBAIN and S. S. KISTLER (*J. Physical Chem.*, 1931, 35, 130–136).—Cellophane provides a membrane which retains all but the smallest colloidal particles and allows simple molecules to pass through; the membranes can be thickened so as to retain the larger molecules and ions such as those of sucrose, and sodium or potassium chloride. The presence of colloidal constituents in non-aqueous solutions of electrolytes which show anomalous behaviour in electrical conductivity and osmotic measurements has been demonstrated. Such systems are silver bromate in diethylamine, silver nitrate in piperidine, ammonium iodide in aniline, barium perchlorate or cadmium iodide in amyl alcohol, potassium acetate or pyridine in acetic acid. Colloidal constituents also occur in aqueous solutions of potassium iodate. L. S. THEOBALD.

Preparation of colloids from molecular streams by the condensation method. N. TOMASCHEVSKI (*Kolloid-Z.*, 1931, 54, 79–81).—Colloid systems have been prepared by simultaneously distilling the disperse phase and the dispersion medium on to a surface cooled by liquid air, and then allowing the solid condensate to melt. Such systems are mercury in water, cadmium in ethyl ether, selenium in water, sodium in ethyl ether, benzene, xylene, and hexane, potassium in ethyl ether and xylene, rubidium and caesium in ethyl ether. The properties of these systems are described and their absorption spectra have been examined. The stability of the sols of alkali metals in ethyl ether is particularly high. E. S. HEDGES.

Preparation of colloidal gold by Zsigmondy's method. I. Influence of the nature of the distilled water. Action of traces of hydrogen sulphide. R. WERNICKE and R. B. LOSSEN (*Anal. Assoc. Quim. Argentina*, 1930, 18, 74–97).—The conditions under which red gold sols may be obtained consistently by Zsigmondy's method, viz., reduction of an alkaline auric chloride solution with formaldehyde, have been investigated. By employing water distilled twice from glass vessels satisfactory sols cannot be obtained, but if the water is allowed to remain in contact with vulcanised rubber for 24 hrs. or is boiled with a trace of rubber for 3–5 min. it acquires the property of yielding excellent sols,

although it becomes inert again on boiling. After repeated treatment the rubber becomes inactive, but reacquires its activity after about 24 hrs. Crude rubber produces the same effect, and although the water becomes opalescent it retains its activity on boiling. Contact with air also activates distilled water, but dissolved hydrogen sulphide is not the sole cause. Excellent sols, containing up to 0.33 part of gold per million parts, may be prepared by employing water containing sodium sulphide at a concentration of $1.23 \times 10^{-7} M$; at concentrations above $4.9 \times 10^{-6} M$ sol formation is inhibited. Zsigmondy's results are attributed to the action of atmospheric hydrogen sulphide and of the rubber tubing used.

H. F. GILLBE.

Colloidal platinum and its behaviour as a typical acidoid sol. S. W. PENNYCUICK (*J. Amer. Chem. Soc.*, 1930, 52, 4621–4635; cf. *A.*, 1929, 643, etc.).—In continuation of previous work, it is shown that the surface oxide layer is reduced on passing hydrogen through the sol and that the acidoid properties disappear, but are regenerated on passing oxygen. The charge on the colloidal particles is increased by hydrocyanic acid, and conductometric measurements indicate that this substance probably displaces from the surface the hexahydroxyplatinic acid which is combined, in the form of Werner compounds, with part of the surface oxide.

J. G. A. GRIFFITHS.

Chromic hydroxide. J. LISIECKI (*Rocz. Chem.*, 1930, 10, 736–742).—Stable chromic hydroxide sols are obtained by adding washed chromic hydroxide, prepared by the action of ammonia on chromic nitrate solution, to a solution of chromic chloride; such sols do not need to be dialysed. R. TRUSZKOWSKI.

Preparation of electrolytic-free sol of manganese dioxide. S. SARVOTTAM and T. S. NARAYAN (*J. Indian Chem. Soc.*, 1930, 7, 882–885).—The stability of sols of manganese dioxide prepared by different methods has been investigated. The most stable sols are obtained when potassium permanganate is reduced by concentrated ammonia solution, added drop by drop. The negatively-charged sol coagulated slowly on electro dialysis, the duration of its stability increasing with the negative potential applied. With an applied potential of 220 volts stable sols were obtained, in which no sensible amount of potassium hydroxide could be detected. The electrolyte-free sol was more sensitive to electrolytes. The sol can also be rendered electrolyte-free by dialysis of the hot solution. E. S. HEDGES.

Silicic acid hydrosol. I. Preparation from ethyl silicate by hydrolysis. II. Electrical properties. K. INABA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, 15, 1–15, 16–31).—I. Silicic acid hydrosol may be prepared by the hydrolysis of ethyl silicate in the presence of a small quantity of peptising agent in the form of a mineral acid or alkali. In acid solution the maximum concentration of silica giving a clear sol was 7–8%, coagulation taking place at higher concentrations; a higher concentration was obtained in alkaline solutions. The acid sol was particularly stable in the presence of 0.01–0.02N-acid and on electro dialysis it began to coagulate when the

concentration of acid was reduced to about 0.0002*N*. On the other hand, the alkaline sol could be electro-dialysed until completely free from alkali without coagulation, thus giving a neutral sol. The acid sol had a lower electrical conductivity and a higher viscosity than the neutral sol. On the addition of hydrochloric acid to the neutral sol, coagulation quickly occurred at concentrations between 0.0001 and 0.0002*N*, but at higher concentrations of acid the sols were stable.

II. The cataphoretic migration velocity of the particles of silicic acid sols prepared by different methods and in the presence of various electrolytes has been measured. The acid sols were found to have a relatively low degree of dispersion and a small charge ($\zeta = -0.003$ to -0.01 volt). Neutral or alkaline sols had a high degree of dispersion and a high charge ($\zeta = -0.02$ to -0.04 volt). On the addition of hydrochloric acid or the chlorides of potassium, barium, cerium, or thorium coagulation did not occur, but the migration velocity decreased to the isoelectric point, after which the direction of migration was reversed. Exceptions occurred in the addition of barium chloride or cerium chloride to alkaline sols, in which cases coagulation ensued. A viscosity minimum was observed in the neighbourhood of the isoelectric point. It is deduced that the charge of the acid sols is due to the chlorine ion or corresponding anion adsorbed from the dispersion medium, and that the charge of the neutral sol is due to silicate ions.

E. S. HEDGES.

Effect of multivalent hydroxy-compounds in the synthesis of hydrosols. IV. Sugars. A. DUMANSKI and L. G. KRAPIVINA (*Kolloid-Z.*, 1931, 54, 73—79, and *J. Russ. Phys. Chem. Soc.*, 1930, 62, 1713—1721).—The peptising effect of sugars in the formation of colloidal ferric hydroxide by the reaction of ferric chloride with sodium and ammonium hydroxides has been investigated and the results have been expressed in the form of triangular equilibrium diagrams. The sugars examined can be arranged in the following order of decreasing effectiveness: lactose > laevulose > maltose > galactose > dextrose > sucrose > raffinose. Sugars of the maltose type, containing a carbonyl group, are the best peptising agents. The stability of the sols produced by this method depends on both the charge and hydration of the particles.

E. S. HEDGES.

Influence of hydrolysis temperature on some properties of colloidal ferric oxide. IV. Variation of density and relative viscosity with sol concentration. G. H. AYRES and C. H. SORUM (*J. Physical Chem.*, 1931, 35, 412—416; cf. this vol., 164).—The density of the sols varies linearly with concentration and is not affected by the temperature of preparation. The densities of 17 different sols prepared between 100° and 140° and containing 2.0 g. Fe_2O_3 per litre gave a mean value at 25° of 0.9988 with a maximum variation of ± 0.0002 . No generalisation relating to the shape of the viscosity-concentration curve can be drawn even for concentrations up to 0.5%.

L. S. THEOBALD.

Unusual properties of colloidal dispersions. R. V. WILLIAMSON (*J. Physical Chem.*, 1931, 35,

354—359).—Experiments which show the marked changes in the plastic and elastic properties of dispersions produced by changes in temperature or in the magnitude and rate of application of stress are described. The flowing properties of paints, the behaviour of thixotropic dispersions of gas black in petroleum and of zinc oxide in gasoline, certain unusual properties of sodium silicate dispersions, and the liquefaction of viscose gels by a fall in temperature are described.

L. S. THEOBALD.

Complexity of the magnetic properties of elements in the colloidal state. S. S. BHATNAGAR (*J. Indian Chem. Soc.*, 1930, 7, 957—958).—The reported changes in magnetic susceptibility of metals when reduced to colloidal dimensions should be viewed with reserve. In the case of bismuth, the colloidal particles contain oxide, which can account for the differences observed.

E. S. HEDGES.

Action of electrolytes added to a colloidal solution in quantities insufficient to bring about coagulation. G. ROSSI and A. MARESCOTTI (*Gazzetta*, 1930, 60, 993—996).—Hydrochloric acid when added to a colloidal solution of arsenious sulphide in amounts which are insufficient to bring about coagulation may, according to the quantity added, exert either a stabilising or a destabilising influence on the sol in regard to the coagulating action of hydrochloric acid itself. These two effects are accompanied by an increase and a decrease, respectively, of the degree of dispersion of the sol.

O. J. WALKER.

Equilibrium phenomena in the coagulation of colloids. E. F. BURTON and M. ANNETTS (*J. Physical Chem.*, 1931, 35, 48—59).—Measurements of the light scattered and transmitted by sols of gum mastic and arsenious sulphide indicate that distinct changes occur in the sol on the addition of small traces of electrolytes even before coagulation sets in. On the addition of small amounts of aluminium nitrate, aluminium sulphate, or magnesium sulphate to sols of gum mastic the intensity of the scattered light decreases to a constant value until the particles settle visibly. The time required to reach this value depends on the amount of electrolyte added, and the curves obtained by plotting this time against the quantity of electrolyte show two maxima and minima in the case of aluminium, but only one maximum and minimum in the case of magnesium. With arsenious sulphide, no such zonal effects are obtained. The successive addition of small amounts of electrolyte to sols of gold, mastic, or arsenious sulphide shows the existence of stages of partial coagulation, some of the colloidal material being precipitated. The constitution of arsenious sulphide sol is discussed, and it is suggested that after being adsorbed by the colloidal particle hydrogen sulphide dissociates, leaving HS^- to provide the charge on the surface, whilst the hydrogen ion is associated with the diffuse outer region of the Helmholtz double layer.

L. S. THEOBALD.

Effect of hydrogen-ion concentration on flocculation values of ferric oxide sols. I. F. HAZEL and C. H. SORUM (*J. Amer. Chem. Soc.*, 1931, 53, 49—54).—The p_{H} of ferric oxide sols acidified (p_{H} 5.9—2.9) with hydrochloric acid and of the

coagulated media obtained by adding the critical concentration of electrolytes has been determined by means of the glass electrode. The stability of the sol towards potassium chloride, bromide, chromate, dihydrogen phosphate, ferricyanide, and ferrocyanide, ammonium and barium chlorides increases with increasing acidity, but the reverse is true of the sulphates of potassium, ammonium, and calcium. The stability towards ferric and aluminium chlorides is independent of the initial acidity, but depends on the constant value to which the p_H is altered by the hydrolysis of the salt. J. G. A. GRIFFITHS.

Coagulation of methylene-blue by means of mercuric chloride. N. N. ANDRONIKOVA (Kolloid-Z., 1931, 54, 82–84).—A certain minimal concentration of mercuric chloride is required to produce rapid coagulation of a methylene-blue solution. The coagulation is reversible in the sense that the precipitate is redissolved on heating or on the addition of a large volume of water. The character of the precipitate varies with the concentration of the mercuric chloride; low concentrations of the precipitant produce a coarse, blue precipitate, but higher concentrations give a violet precipitate. Mercuric chloride is adsorbed by the precipitate, the amount increasing with the concentration until the ratio is 2 mols. of mercuric chloride to 1 mol. of methylene-blue; at higher concentrations the composition of the precipitate falls to the ratio 3 mols. of mercuric chloride to 2 mols. of methylene-blue, after which the amount of mercuric chloride rises again. Similar effects were observed on the addition of potassium thiocyanate to methylene-blue solutions. E. S. HEDGES.

Acceleration produced by light in the flocculation of colloidal solutions in a fluorescent medium. A. BOUTARIC and J. BOUCHARD (Compt. rend., 1931, 192, 95–97).—Flocculation of colloids (mastic and other gums, arsenic sulphide, ferric hydroxide) by electrolytes (sulphuric acid and salts of alkali metals) in the presence of fluorescent substances (rhodamine, eosin, fluorescein, erythrosin) is accelerated by exposure to daylight and, to a much greater extent, to ultra-violet light. No acceleration occurs if the fluorescent material and/or electrolyte is absent. The quantity of electrolyte required for flocculation is also lowered in a fluorescent medium. Non-fluorescent dyes have no such influence, and (anti-oxygenic) substances, which inhibit fluorescence, repress the acceleration of flocculation. J. GRANT.

Dissolution of colloid particles on dilution of sols. A. J. RABINOVITSCH and V. A. KARGIN (Z. physikal. Chem., 1931, 152, 24–35).—The phenomena observed with silica sols (A., 1928, 835) have been found to occur in other cases. On dilution of a tungstic acid sol the p_H rises at first, then remains constant for a considerable range of dilution, and finally increases. The buffer effect is due to hydration of the colloidal particles and the consequent liberation of hydrogen ions from the nuclei, whilst at extreme dilutions (1:5000) the whole of the colloidal material enters into true solution; the velocity of the transition from the colloidal state is much greater than with silica sols. Potentiometric and spectrophotometric measurements with vanadium

pentoxide sols demonstrate the occurrence of a similar sequence of changes; a series of colourless complex polyvanadic acids is probably formed as an intermediate stage. The p_H changes which occur on dilution of arsenious sulphide sols indicate only slight hydrolysis at high dilutions, whilst with ferric hydroxide sols there is a small linear increase of the chloride-ion concentration; in neither case is there any evidence of true solution formation, and this phenomenon appears to be confined to acidic sols.

H. F. GILLBE.

Investigation of stream-double-refraction in very low concentrations. H. FREUNDLICH, J. V. TAMCHYNA, and H. ZOOHER (Z. wiss. Phot., Schaum-Festschr., 1930, 29, 102–109).—The limiting concentrations at which colloidal solutions of certain metallic oxides and dyes exhibit stream-double-refraction have been determined by macroscopic and microscopic methods. The effect is enhanced by ageing the sols, and with sols of vanadium pentoxide, ferric oxide, tungsten trioxide, cotton-yellow GX, benzopurpurin 4B and 6B, and aniline-blue can be detected at concentrations of 10^{-6} g. of substance per c.c. With aluminium oxide and titanium dioxide the limiting concentration is considerably higher.

J. W. GLASSETT.

Density of water adsorbed on silica gel. D. T. EWING and C. H. SPURWAY (J. Amer. Chem. Soc., 1930, 52, 4635–4641).—A gas dilatometer, with helium as the inactive gas, has been used to determine the density of water adsorbed on silica gel at 25.02°. With quantities of water up to 4.36 wt.-% of the gel, the vapour pressure of the liquid is very small. The density of the adsorbed water is about 1.027 and the pressure on the liquid is calculated to be about 750 atm. Quantities of adsorbed water greater than about 5% have a mean density less than that of free liquid water, suggesting the presence of the three phases—compressed, liquid, and gaseous water.

J. G. A. GRIFFITHS.

State of water in colloidal and living systems. R. A. GORTNER (Trans. Faraday Soc., 1930, 26, 678–686).—Emphasis is laid on the distinction between free and bound water in lyophilic colloidal systems and on the importance of this conception in relation to biological problems. W. O. KERMACK.

Optical properties of protein sols and the influence of neutral salts and p_H . N. JERMOLENKO (Kolloid-Z., 1931, 54, 66–78).—The refractive index of gelatin solutions does not vary with time and is independent of the treatment of the solution. Since the viscosity of the solution is affected considerably by the temperature at which the solution has been heated, by mechanical agitation, etc., whilst the refractive index is unchanged, it would seem that refractive index is not a function of the state of aggregation of the colloid. This point was also established in the case of gluten solutions. The refractive index is a linear function of the concentration for gelatin, gluten, and egg-albumin. The refractive index of gelatin scarcely changes with the hydrogen-ion concentration. The refractive index of gluten is constant for a given temperature and concentration, independently of whether the dispersion

medium is water or various salt solutions. No lyotropic effect is observed. E. S. HEDGES.

Changes in viscosity of gelatin sols in the process of gelation. S. N. BANERJI and S. GHOSH (J. Indian Chem. Soc., 1930, 7, 923–931).—An investigation of the hysteresis of the sol-gel transformation of gelatin has shown that the setting and melting temperatures are identical, provided that sufficient time is allowed for observation. The greater is the concentration of the gel, the shorter is the time at which the melting and setting temperatures become the same. Similar results were observed with soap gels in various alcohols and water. No firm gels of gelatin at any concentration can be obtained above 33°. Viscosity measurements show that there is a considerable difference according to whether the gelatin sol has been prepared at a temperature higher or lower than that at which the measurement is made. The sol prepared at a higher temperature has a higher viscosity than that prepared at a lower temperature. The viscosity increases with time when a gelatin sol prepared at a higher temperature is kept in a bath at a lower temperature, but the sol obtained by melting a gel shows a decrease in viscosity with time at a temperature higher than the m. p. of the gel. The ageing effect becomes appreciable within a short interval of time and is at a maximum in the region near the gelation temperature. It is supposed that a gelatin solution represents an equilibrium between simple molecules and aggregated molecules of gelatin and also that the aggregated molecules are in equilibrium with colloidal particles of gelatin. Gelation occurs when a sufficient quantity of aggregated molecules and colloidal particles is present, a view which explains the influence of concentration on the setting temperature.

E. S. HEDGES.

Hydrogels. Manganese dioxide hydrates. X. A. SIMON and F. FEHER (Kolloid-Z., 1931, 54, 49–58).—Manganese dioxide prepared in six different ways, after washing with water, alcohol, and acetone, gave on analysis a water content of 0.45–0.50 mol. of water to 1 mol. of manganese dioxide. In each case loss of water began at 70° and the vapour-pressure curves showed that the water is not bound by ordinary valency forces, but is colloid-chemically bound. The relatively small amount of water retained by the compound after treatment with alcohol and acetone is an indication of its lyophobic nature. It is deduced that no stable, stoichiometric, chemical compounds of manganese dioxide and water exist. Native manganese dioxide stores a certain amount of its water in the capillaries of its structure, but this part is removed by the treatment with acetone. The action of sulphuric, oxalic, acetic, and hydrochloric acids on freshly-precipitated manganese dioxide and on old preparations was examined. The freshly-prepared substance was peptised only by 2N-hydrochloric acid, and a precipitate which had been kept for 1½ years was not affected by any of these reagents. When kept, the preparations slowly lose water.

E. S. HEDGES.

Properties of starch with relation to time of formation of starch gels. O. W. CHAPMAN and

J. H. BUCHANAN (Iowa State Coll. J. Sci., 1930, 4, 441–450).—The viscosity at first increases with rise of temperature, thereafter decreasing; the maximum is reached in the order potato, wheat, maize, rice starch, i.e., in the order of decreasing grain size. Rapid heating increases, and addition of acid (0.0025N) decreases, the viscosity; addition of alkali causes an increase followed by a decrease in the viscosity. Sodium chloride (0.5M) has little effect. Sodium sulphate retards the attainment of maximum viscosity; sodium phosphate increases the maximum at a lower temperature. Acetates, sulphates, oxalates, and citrates hasten syneresis; other salts retard or prevent it.

CHEMICAL ABSTRACTS.

Distribution of ions in gels. E. J. BIGWOOD (Trans. Faraday Soc., 1930, 26, 704–719).—The rate of diffusion of sodium hydroxide from an aqueous solution of constant concentration into an agar gel as indicated by the alteration in the colour of an indicator present in the gel is approximately independent over a wide range of the concentration of agar, and the distance penetrated is approximately proportional to the square root of the time. In the case of gelatin gels these statements are true only for relatively high concentrations of sodium hydroxide and relatively low concentrations of gelatin. When the gelatin concentration is high and the sodium hydroxide concentration is low the rate of penetration decreases as the concentration of gelatin increases. The distance of penetration is not proportional to the square root of the time, but after a certain time a steady state may be reached in which equilibrium is apparently established. These results are probably related to the power of gelatin to neutralise small concentrations of sodium hydroxide.

W. O. KERMACK.

Behaviour of proteins towards colloids and towards electrolytes. W. PAULI (Trans. Faraday Soc., 1930, 26, 723–737).—The interaction of a highly-purified Congo-red sol with highly-purified protein is described (cf. Pauli and Weiss, A., 1929, 395). A theory of the phenomena is advanced in which emphasis is laid on the zwitterion constitution of proteins and this is applied generally to the mutual interaction and precipitation of lyophobic and lyophilic colloids, more particularly in the neighbourhood of their isoelectric points.

W. O. KERMACK.

Influence of volume on swelling. D. J. LLOYD (Kolloid-Z., 1931, 54, 46–49).—The observation that the degree of swelling of gelatin in sodium hydroxide solutions varies with the volume of solution is due to hydrolytic decomposition of the gelatin. When pure gelatin swells in sodium hydroxide solutions at a sufficiently low temperature (0°) to prevent hydrolysis, the amount of swelling is independent of the volume of liquid. The swelling of gelatin in solutions of inorganic salts is independent of the volume of the solution over a wide range of temperature and of concentration, whether the swelling reaches a maximum or leads to dissolution.

E. S. HEDGES.

Swelling power of thiocyanates and [formation of] compounds of cellulose and neutral salts. J. R. KATZ and J. C. DERKSEN (Rec. trav. chim., 1931, 50, 149–152).—When cellulose is immersed in

dilute solutions of thiocyanates no change occurs in the X-ray diagram, the salt being adsorbed at the surface or penetrating only a small way into the structure of the fibre. When cellulose swells in concentrated solutions of thiocyanates a definite X-ray spectrum is obtained, indicating the formation of a chemical compound between the cellulose and the salt. At extremely high concentrations of lithium thiocyanate a different X-ray spectrum is obtained, suggesting that in this case two different compounds can be formed. Mercerised and native cellulose give different X-ray spectra after swelling in concentrated lithium thiocyanate solution. E. S. HEDGES.

Adsorption and protection phenomena in complex colloidal media. C. MARIE and N. MARINESCO (Compt. rend., 1931, 192, 92—94).—The value of ϵ for aqueous solutions of gelatin, glycine, and *l*-leucine is greater than that for water, indicating permanent polarity of the solutes, whilst with aqueous suspensions of animal charcoal the similar difference is attributed to induced moments. Binary mixtures of these two types depress ϵ below that for water, indicating that the free dipoles are masked by the global polarisation of the system. Protection of colloids may thus be explained, the polarised protecting body surrounding the protected colloid and completely masking its properties. Permanently polarised gelatin added to a solution of amino-acid lowers ϵ owing to condensation of the dipoles of the latter by the former, although here simple association or molecular coupling results instead of pure protection. Dielectric analysis may therefore be used to determine the nature and amount of protective colloid required. J. GRANT.

Mitogenic radiation, and the effect of volatile substances from crushed onion root on colloidal phenomena. H. KOWARCZYK (Acta Biol. Exp., Warsaw, 1930, 6, 29—36).—The disturbing effect on the formation of Liesegang rings of placing crushed onion root in the vicinity of a gelatin surface on which rhythmic deposition of silver dichromate is proceeding is due to volatile products and not to mitogenic radiation. The formation of Liesegang rings is not affected by ultra-violet light. The above volatile substances enhance the rate of coagulation of gold sols.

R. TRUSZKOWSKI.

State of division of lichosan in the dissolved and solid state. H. PRINGSHEIM and C. LAMM (Kolloid-Z., 1931, 54, 36—42).—Lichosan precipitated by alcohol in the cold appears in daylight to be identical with that precipitated from a solution at 80° by the addition of boiling alcohol, but the fluorescence of the specimen prepared in the cold is considerably less. Mol. wt. determinations by the cryoscopic method gave a value of about 850 for the lichosan precipitated from hot solutions and a value of about 200 for the lichosan precipitated in the cold. The latter varies with time, however, increasing ultimately to about 850; simultaneously an increase in the viscosity of the solution is observed. The mol. wt. varies with the method of preparation. E. S. HEDGES.

Application of ternary co-ordinate systems to the graphical representation of the composition of colloidal systems. A. DUMANSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 1649—1663).—An exposition

of the application of triangular co-ordinates to the study of colloidal systems. R. TRUSZKOWSKI.

Thermodynamics of mixtures. V. FISCHER (Z. Physik, 1930, 66, 269—279).—For dilute solutions of gases in liquids it is shown that, neglecting the vapour pressure of the liquid and assuming a perfect gas, the osmotic pressure of the gas in solution is given by the ratio of the volume of the gas absorbed (at 760 mm. and the temperature at which dissolution is considered to take place) to the volume of the pure solvent in which the gas is dissolved. The ratio is identified with the absorption coefficient. Data for the following systems are used in illustration: acetylene-acetone, acetylene-acetone-water, acetylene-acetone-ethyl alcohol, acetylene-acetone-methyl alcohol. R. W. LUNT.

Calculation of entropy constants. I. Calculation of gas equilibria from spectroscopic data. J. M. BLJVOET (Chem. Weekblad, 1931, 28, 26—37).—Theoretical. It is shown that all the quantities necessary for the calculation of equilibria in gaseous systems can be derived from spectroscopic data.

H. F. GILLBE.

Oxidation of carbon monoxide by steam. R. NITZSCHMANN (Metallbörse, 1930, 20, 5—6, 118—120; Chem. Zentr., 1930, ii, 171).—The constants for the equilibrium $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 + 10,400 \text{ g.-cal.}$ between 327° and 2090° have been derived, and the composition of the products after 95—99% conversion at 327°, 427°, and 452° have been calculated.

A. A. ELDRIDGE.

Water-gas process with addition of oxygen. R. NITZSCHMANN (Metallbörse, 1930, 20, 285—286, 397—399, 510—511, 566—567, 678—679, 847—848, 903—904, 958—959; Chem. Zentr., 1930, ii, 171).—The equilibrium relations in the system $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ with the addition of oxygen in admixture with nitrogen have been examined, the results for varying conditions being tabulated.

A. A. ELDRIDGE.

Electrolytic dissociation of weak acids and bases. H. VON EULER and H. HELLSTRÖM (Svensk Kem. Tidskr., 1930, 42, 300—302).—The ionisation of weak electrolytes is discussed on the hypothesis that the separation of the constituent ions takes place in a series of stages which result in the formation of active, although not fully dissociated, molecules, in which the distance between the ions is relatively great. On the assumption that the ionisation energy of a molecule is employed in increasing the mean distance between the ions it becomes less difficult to assign a physical significance to extremely small ionisation constants. Methods of investigating the hypothesis experimentally are indicated.

H. F. GILLBE.

Relative strengths of bases in non-aqueous solutions. III. E. I. JOHNSON and J. R. PARTINGTON (J.C.S., 1931, 86—92; cf. A., 1929, 1011).—The esterification of phenylacetic acid in dry alcoholic solution in presence of hydrogen chloride is slightly accelerated by small amounts of benzil and furan, retarded by diphenylpyrone, phenylmethylpyrone, and unsubstituted γ -pyrone, and not affected by small quantities of di-*n*- and -*iso*-propyl ethers and glycerol.

The velocity data have been used to calculate the relative basic strengths of the pyrones as compared with water (cf. Lapworth, J.C.S., 1908, 93, 2187).

R. CUTHILL.

Recalculations of first dissociation constant of phosphoric acid in aqueous solution at 18°. Incidental determination of activity coefficients of undissociated acid molecules. J. W. H. LUGG (J. Amer. Chem. Soc., 1931, 53, 1—8).—From existing data (Abbott and Bray, A., 1909, ii, 660), and correcting for secondary dissociation, the equivalent conductivity at infinite dilution of $(\text{Na}^+ + \text{H}_2\text{PO}_4^-)$ and $(\text{H}^+ + \text{H}_2\text{PO}_4^-)$ is computed to be 70.1 and 340.5, respectively, at 18°. Values of the first stoichiometric dissociation constant of phosphoric acid are given by $pK_1 = 2.09 - \mu^{1/2}/(1 + 1.0\mu^{1/2}) - 1.8\mu$. The activity coefficient of the undissociated acid in dilute phosphoric acid solution is given by $p\gamma_{\text{H}_3\text{PO}_4} = -1.8\mu$.

J. G. A. GRIFFITHS.

Thermodynamic properties of weak acids and bases in salt solutions, and an exact determination of their dissociation constants. H. S. HARNED and B. B. OWEN (J. Amer. Chem. Soc., 1930, 52, 5079—5091; cf. Harned and Robinson, A., 1929, 140).—The *E.M.F.* data for cells without liquid junction are applied to acetic acid (*loc. cit.*) and formic acid in sodium chloride and potassium chloride solutions. The logarithm of the activity coefficient of the electrolyte, referred to unity at infinite dilution in water, varies linearly with the concentration of weak acid. This relation is valid at zero ionic strength and is believed to be very nearly true at all concentrations of salt. From the above data the dissociation constants of acetic and formic acids at 25° are computed to be 1.75×10^{-5} and 1.77×10^{-4} , respectively. The dissociation constants of ammonia, mono-, di-, and tri-methylamine are calculated to be 1.79, 43.8, 52.0, and 5.45×10^{-5} , respectively (*loc. cit.*).

J. G. A. GRIFFITHS.

Acid and base constants of glycine from cells without liquid junction. H. S. HARNED and B. B. OWEN (J. Amer. Chem. Soc., 1930, 52, 5091—5102; cf. preceding abstract).—An exact thermodynamic method, which eliminates the use of liquid junctions and takes into account certain previously neglected medium effects, is developed for the evaluation of the acid and base constants of an ampholyte. From determinations at 25° of the *E.M.F.* of the cells $\text{Pt}, \text{H}_2 | \text{NaOH}(0.1M) | \text{Na}(0.1\%) | \text{Hg} | \text{sodium glycine}(0.1M), \text{NaCl}(m) | \text{H}_2, \text{Pt}$; $\text{Pt}, \text{H}_2 | \text{sodium glycine}(0.1M), \text{NaCl}(m) | \text{AgCl}, \text{Ag}$; and $\text{Pt}, \text{H}_2 | \text{glycine hydrochloride}(0.1M), \text{NaCl}(m) | \text{AgCl}, \text{Ag}$, and existing *E.M.F.* data, the apparent dissociation constants of glycine at 25° are computed to be $K_A, 4.92 \times 10^{-3}$ and $K_B, 5.56 \times 10^{-5}$ (cf. Branch and Miyamoto, A., 1930, 542).

J. G. A. GRIFFITHS.

Strength of organic bases in glacial acetic acid solution. N. F. HALL (J. Amer. Chem. Soc., 1930, 52, 5115—5128; Conant and Werner, this vol., 40).—A large number of bases at 0.05M concentration in glacial acetic acid at 25° have been titrated electrometrically with perchloric acid (cf. Hall and Werner, A., 1928, 1188). The titration curves obtained with the weakest bases show an initial rapid rise of *E.M.F.*,

but no break; bases of intermediate strength give an initial rise and a break, whilst the strongest bases show a break only. There appears to be a close parallelism between the relative strengths of bases in glacial acetic acid and in water, and this affords a method for predicting the strength in water of bases which cannot be studied in the latter solvent. Data for the strengths of bases in water are collected and reviewed.

J. G. A. GRIFFITHS.

Temperature coefficient of dissociation of acetic acid in potassium and sodium chloride solutions. H. S. HARNED and G. M. MURPHY (J. Amer. Chem. Soc., 1931, 53, 8—17; cf. Harned and Owen, above).—The *E.M.F.* of the cells $\text{H}_2 | \text{HCl}(0.01M), \text{XCl}(0-3M) | \text{AgCl} | \text{Ag}$ and $\text{H}_2 | \text{acetic acid}(0.2M), \text{XCl}(0.05-3M) | \text{AgCl} | \text{Ag}$ has been determined at 20°, 25°, and 30°. The activity coefficients of hydrochloric acid decrease slightly with rise of temperature and the decrease becomes more pronounced with increasing concentration of salt. The relative partial heat contents of 0.01M-hydrochloric acid in the salt solutions have been computed (Harned, A., 1920, ii, 664), and the excess or electrical contribution to partial molal heat content of hydrochloric acid in these solutions is approximately proportional to the square root of the total molarity. The hydrogen-ion concentrations in the acetic acid solutions have been computed. The dissociation constant of the acid is 1.75×10^{-5} between 20° and 30°. The ionic activity coefficient of acetic acid in the salt solutions varies similarly to that of hydrochloric acid.

J. G. A. GRIFFITHS.

Hydrolysis equilibria of triphenylchloromethane and triphenylbromomethane. Free energy of reactions of triphenylchloromethane, triphenylbromomethane, and triphenylcarbinol. J. O. HALFORD (J. Amer. Chem. Soc., 1931, 53, 105—112).—Solubilities at 25° of triphenylchloromethane, triphenylbromomethane, and triphenylcarbinol in benzene have been determined and vapour-pressure data are recorded. By means of partition experiments between water and benzene, the free energies, ΔF_{298} , of the reactions are found to be $\text{CPh}_3\text{Cl}(\text{in benzene}) + \text{H}_2\text{O}(g) = \text{CPh}_3\text{OH}(\text{in benzene}) + \text{HCl}(g)$, 1755 g.-cal.; $\text{CPh}_3\text{Cl}(s) + \text{H}_2\text{O}(g) = \text{CPh}_3\text{OH}(s) + \text{HCl}(g)$, 900; $\text{CPh}_3\text{Br}(\text{in benzene}) + \text{H}_2\text{O}(g) = \text{CPh}_3\text{OH}(\text{in benzene}) + \text{HBr}(g)$, 4310. The results, together with existing data, afford information concerning the reactions of triphenylchloromethane with bromine, hydrogen bromide, and bromides. In benzene, the dissociation of triphenylbromomethane into neutral molecules is 10^6 times that of the chloro-compound, and of the two the bromo-compound has a slightly greater tendency to ionise.

J. G. A. GRIFFITHS.

Effect of light on the ferrocyanide-ferricyanide iodine-iodide equilibrium. R. G. DICKINSON and S. F. RAVITZ (J. Amer. Chem. Soc., 1930, 52, 4770—4778; cf. La Mer and Friedman, A., 1930, 542).—At 0°, where the thermal reaction is very slow, it is found that irradiation of the system $2\text{Fe}(\text{CN})_6^{4-} + 2\text{I}^- = 2\text{Fe}(\text{CN})_6^{3-} + \text{I}_2$ effects a shift of the equilibrium in the direction of increased free iodine. It is shown that the light absorbed by the I_3^- ion is

effective and that the quantum efficiency of the reaction is very nearly the same as that in the reaction $2\text{Fe}^{+++} + 2\text{I}^- = 2\text{Fe}^{++} + \text{I}_2$ (cf. Kistiakowsky, A., 1927, 528). Possible mechanisms for the reaction are discussed.

J. G. A. GRIFFITHS.

Vapour pressures and activities of volatile components in binary alloys at high temperatures. K. JELLINEK and G. A. ROSNER (Z. physikal. Chem., 1931, 152, 67–94).—The vapour pressure of cadmium at 567° is 48.2 mm. Vapour-pressure measurements have been made with binary alloys of cadmium with lead, tin, and copper at temperatures from 500° to 700° and over a fractional molar concentration range of 0.1–0.6, and with zinc-copper alloys between 600° and 800°. The activity coefficients α of cadmium and zinc in the alloys have been calculated; the α -concentration curves are very similar for the cadmium-lead and cadmium-tin alloys, but for the cadmium-copper alloys are of a different form owing to the limited solubility of copper in cadmium. The zinc-copper alloys are noteworthy in that α is almost independent of temperature, and the α -concentration curve intersects the theoretical curve at 52 mol.-% zinc. Since the $\log p-1/T$ curves for all the alloys are roughly parallel, the latent heats of evaporation of cadmium and zinc in the alloys can differ but little from their values in the pure state. The latent heats and the heats of mixing have been calculated, and the results, together with the calculated activity coefficients for the cadmium-lead and cadmium-zinc alloys, are compared with the results of Taylor's *E.M.F.* measurements (A., 1924, ii, 89).

H. F. GILLBE.

Activity coefficients of electrolytes. V. Principle of specific interaction in cadmium and magnesium sulphate and chloride solvents. H. B. FRIEDMAN and V. K. LA MER (J. Amer. Chem. Soc., 1931, 53, 103–105; cf. La Mer and Goldman, A., 1929, 1387).—The solubility data for thallium and lanthanum iodates in 0.1*N*-solutions of the chlorides and sulphates of magnesium and cadmium at 25° show that the principle of specific interaction does not apply when cadmium chloride is concerned.

J. G. A. GRIFFITHS.

Activity coefficient of copper iodate in aqueous salt solutions. B. H. PETERSON and E. L. MEYERS (J. Amer. Chem. Soc., 1930, 52, 4853–4857; cf. La Mer and Goldman, A., 1929, 1387).—The solubility of copper iodate in aqueous solutions of the chlorides and sulphates of potassium and magnesium has been determined at 25°. The activity coefficients of copper iodate approach values given by the Debye-Hückel limiting law with increasing dilution of the salts. Positive deviations from this law are observed when solutions of potassium sulphate are used as solvent.

J. G. A. GRIFFITHS.

Reduction of nitric acid by nitric oxide. I. Equilibrium. II. Electrochemical potential. H. BODE (Z. anorg. Chem., 1931, 195, 195–200, 201–206).—I. From observations of the decrease in pressure of nitric oxide when confined over nitric acid the equilibrium constant of the reaction $\text{H}^+ + \text{NO}_3^- + 2\text{NO} + \text{H}_2\text{O} = 3\text{HNO}_2$ is found to be 29.4 and 51 at

25° and 35°, respectively (cf. Klemenc and Hayek, A., 1930, 543).

II. From measurements of the *E.M.F.* of the cell $\text{Pt}[\text{NO}, \text{HNO}_2, \text{HNO}_3 \text{ (in equilibrium)}]|\text{HCl}|\text{H}_2(\text{Pt})$ the normal potentials of the reactions $\text{NO} + \text{NO}_3^- = 2\text{NO}_2 + \ominus$ and $\text{NO} + 2\text{H}_2\text{O} = \text{NO}_3^- + 4\text{H}^+ + 3\ominus$ have been found to be 0.517 ± 0.003 and 0.960 volt, respectively.

R. CUTHILL.

Thermodynamic properties of molten solutions of lead chloride in lead bromide. E. J. SALSTROM and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1930, 52, 4641–4650).—The density at 500° of lead bromide, lead chloride, and mixtures of the two have been determined. The molal volumes are additive. The *E.M.F.* of the cell $\text{Pb}(l)|\text{PbBr}_2(l) + \text{PbCl}_2(c_1)|\text{Br}_2(g), \text{graphite}$, where c_1 , the molal fraction of lead chloride, is 0.0–0.55, has been determined between 438° and 584°. If c_1 is 0.6, or larger, the reaction $\text{PbCl}_2(l) + \text{Br}_2 = \text{PbBr}_2(l) + \text{Cl}_2$ ($\Delta F_{773}, 11,090$ g.-cal.) interferes. The free energy of dilution of lead bromide with lead chloride and the activity coefficients are calculated. If both salts are assumed to be un-ionised, the results correspond with negative deviations from Raoult's law. The assumption of complete ionisation leads to results corresponding with positive deviations. It is desirable to attempt to take into account changes in interionic forces.

J. G. A. GRIFFITHS.

Thermodynamic properties of molten solutions of lithium bromide in silver bromide. E. J. SALSTROM and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1930, 52, 4650–4655).—Density data for the fused salts and mixtures are recorded. From the *E.M.F.* of the cell $\text{Ag}(s)|\text{AgBr}(l) + \text{LiBr}(0.0-0.89 \text{ mol. fraction})|\text{Br}_2(g), \text{graphite}$, between 440° and 615° the energy changes of molten silver bromide on dilution with lithium bromide have been calculated and the free energy of formation of molten silver bromide is given by $\Delta F = -21,510 + 6.7t$, where $t = 440-575^\circ$. The activity exhibits a large positive deviation from Raoult's law.

J. G. A. GRIFFITHS.

Thermodynamic properties of solutions of molten lead chloride and zinc chloride. A. WACHTER and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1930, 52, 4655–4661; cf. A., 1927, 418).—Density data for the fused chlorides are recorded. From the *E.M.F.* of the cell $\text{Pb}(l)|\text{PbCl}_2(l) + \text{ZnCl}_2(0.0-0.8 \text{ mol. fraction})|\text{Cl}_2$ between 493° and 602° the free energy of dilution and activity coefficients have been calculated. The values correspond with negative deviations from Raoult's law and the assumption of either no ionisation or complete ionisation of both salts does not account for the results, which moreover are only partly explained by assuming that the lead chloride is ionised and the zinc chloride is not. The *E.M.F.* of the cells $\text{Pb}(l)|\text{PbCl}_2(l)|\text{Cl}_2$ and $\text{Zn}(l)|\text{ZnCl}_2(l)|\text{Cl}_2$ is $1.2730-6.25 \times 10^{-4}(t-500)$ and $1.5725-6.95 \times 10^{-4}(t-500)$ volts, respectively (cf. Lorenz and Velde, A., 1929, 1241). The heats and free energies of formation of the molten chlorides are calculated.

J. G. A. GRIFFITHS.

Heats of dilution at 25° for certain uni-bivalent salts at high dilutions. I. Magnesium, calcium, strontium, and barium chlorides and

bromides. E. LANGE and H. STREECK (Z. physikal. Chem., 1931, 152, 1—23; cf. A., 1930, 997).—The molecular heats of dilution V_m of a number of alkaline-earth halides have been determined at concentrations from 0.1 to 0.0001M, and the results, together with the differential heats of dilution, are presented graphically. The $V_m - \sqrt{m}$ curves are linear at concentrations up to 0.01M, and the deviations from the linear law at higher concentrations become still greater if V_m is plotted against $m^{1/2}$. The extrapolated initial slope ($m=0$), which is in accordance with the Debye-Hückel limiting law, is 6.7 times that obtained for uni-univalent salts. For all the compounds investigated the values of V_m at high dilutions almost coincide. The results are discussed in relation to the Debye-Hückel theory and to activity and osmotic coefficients. The values of α between 0.1 and 0.0001M, derived from the V_m curves, vary in the same order as the radii of the non-hydrated ions, but this is not true of the values derived from the osmotic and activity coefficients. The individual behaviour of these salts in comparable concentration ranges cannot therefore be elucidated in terms of specific values of α . Certain discrepancies observed at concentrations above 0.01M cannot be explained on the assumption either of incomplete ionisation or of a change of dielectric constant. H. F. GILLBE.

Binary systems. III. J. H. KOERS and F. E. C. SCHEFFER (Rec. trav. chim., 1931, 50, 139—148).—A mathematical treatment of the crystallisation of a solid phase. E. S. HEDGES.

Phase equilibria in binary systems with continuous series of mixed crystals. E. KORDS (Z. physikal. Chem., 1931, 152, 161—196; cf. A., 1927, 1132).—Equations formally similar to the author's empirical equation connecting the vapour pressures of a binary mixture with the composition of the liquid phase (A., 1929, 994) are found to express the composition of the liquid or solid phase in binary systems where a continuous series of mixed crystals is formed, the m. p. of the pure components and the temperature at which fusion or solidification begins being known. Curves and tables are given to show the agreement between experimental values and those given by the formula. The same formula can also be applied to isotropic-anisotropic transformations in the liquid state, as shown in mixtures of *p*-azoxyanisole and *p*-azoxyphenetole. Application of the formula to the system albite-anorthite leads to the conclusion, which is supported by thermal considerations, that albite is polymerised in the liquid state. The usefulness of the method in dealing with geochemical problems, and in fractional crystallisation, is discussed. F. L. USHER.

Tensiometric stabilisation of crystalline hydrates. M. AUMÉRAS (Compt. rend., 1931, 192, 229—231).—Sodium sulphate decahydrate remains unchanged in a desiccator over sulphuric acid so dilute that the pressure of water vapour lies between the values for the vapour pressure of the saturated solution and the dissociation pressure of the decahydrate. C. A. SILBERRAD.

Hydrated calcium silicates. I. System $\text{CaO-SiO}_2\text{-H}_2\text{O}$. II. Hillebrandite and foshagite.

V. A. VIGFUSSON (Amer. J. Sci., 1931, [v], 21, 67—78).—I. Earlier work on the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ is discussed.

II. X-Ray investigations of hillebrandite and foshagite show that the two are practically identical. Probably both have the same formula $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$, differences in the analyses being explicable by partial hydrolysis and carbonation of foshagite.

C. W. GIBBY.

System $\text{MgO-FeO-Fe}_2\text{O}_3$ in air at one atm. [pressure]. H. S. ROBERTS and H. E. MERWIN (Amer. J. Sci., 1931, [v], 21, 145—157).—The ternary system has been investigated at temperatures above 1000° and at 0.2 atm. oxygen pressure. In the system $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$ the stable phase at temperatures above $1386 \pm 5^\circ$ is a hæmatite solid solution containing less oxygen than Fe_2O_3 , whilst at the higher temperatures the stable phase consists of magnetite solid solutions containing more oxygen than Fe_3O_4 . The only compound in the $\text{MgO-Fe}_2\text{O}_3$ system is $\text{MgO}\cdot\text{Fe}_2\text{O}_3$, which dissociates somewhat on heating; the resultant solid solution begins to melt in air at $1750 \pm 25^\circ$. In the ternary system there are two solid solution fields, of which the first begins at MgO below 1000° and with rising temperature extends towards $\text{MgO}\cdot\text{Fe}_2\text{O}_3$ and FeO ; a liquid phase appears at $1770 \pm 25^\circ$, when the solid phase contains iron oxide equivalent to 73% Fe_2O_3 . The second solid solution extends from $\text{MgO}\cdot\text{Fe}_2\text{O}_3$ to the iron oxide boundary ($1386 \pm 5^\circ$). There is probably little dissociation in either of the solid solutions up to 1770° . Solid solutions of about 1% MgO in $\text{MgO}\cdot\text{Fe}_2\text{O}_3$ may exist at temperatures from 1750° to 1000° or lower. Differential heating curves appear to support the conclusion derived from X-ray diagrams, viz., that magnesium ferrite and magnetite are isomorphous.

H. F. GILLBE.

System wollastonite-anorthite-pyroxene. L. KOCH (Neues Jahrb. Min., 1930, A, 61, 277—320; Chem. Zentr., 1930, ii, 1684).—The system $\text{CaSiO}_3\text{-anorthite-diopside}$ forms a ternary eutectic. A fourth substance corresponding with that present in slags from coal ash was not detected.

A. A. ELDRIDGE.

System water-potassium nitrate-calcium nitrate. M. A. HAMID and R. DAS (J. Indian Chem. Soc., 1930, 7, 881—882).—The equilibrium diagram for the system has been constructed.

E. S. HEDGES.

Polytherms of the ternary systems containing water, alkali sulphate, and a sulphate of the vitriol type. III. A. BENRATH (Z. anorg. Chem., 1931, 195, 247—254; cf. A., 1930, 702).—The isotherms for the systems manganous sulphate-thallos sulphate-water and manganous sulphate-rubidium sulphate-water between 0° and 100° are described. Data for the 100° isotherm and various points on the 12.5° and 40° isotherms of the system manganous sulphate-ammonium sulphate-water are also recorded.

R. CUTHILL.

Phase-rule studies on metallic thiocyanates. I. Systems $\text{Ba(CNS)}_2\text{-NaCNS-H}_2\text{O}$ and $\text{Ba(CNS)}_2\text{-KCNS-H}_2\text{O}$ at 25° . V. J. OCCLESIAW (J.C.S., 1931, 55—60).—The isotherms show the existence of the double salt $3\text{KCNS}\cdot 2\text{Ba(CNS)}_2\cdot 5\text{H}_2\text{O}$.

The solubilities of barium, sodium, and potassium thiocyanates are 62.61, 58.78, and 70.89 g. per 100 g. of solution, respectively. At 25° the stable form of sodium thiocyanate appears to be the dihydrate, and not the monohydrate as reported by Hughes and Mead (A., 1929, 1375). At about 30.3° the dihydrate passes into the anhydrous salt. R. CUTHILL.

Reaction between water vapour and sodium chloride at high temperature. S. BRETSZNAJDER (Rocz. Chem., 1930, 10, 729—735).—Sodium chloride undergoes hydrolysis with the production of sodium hydroxide and hydrogen chloride on heating with water at 750° in a crucible lined with sodium chloride. The equilibrium constant of the reaction is approximately 1.6×10^{-7} at 750°. The hydrolysis is accelerated by the addition of dried silica gel, which combines with the sodium hydroxide produced. The analogous reaction with calcium chloride begins at a lower temperature. R. TRUSZKOWSKI.

Reversibility of reactions between sulphur dioxide and calcium oxide and between calcium sulphide and sulphate. J. ZAWADZKI and Z. SYRZYŃSKI (Rocz. Chem., 1930, 10, 715—728).—Direct determination of the free sulphur liberated in the reaction between calcium sulphide and sulphate and between sulphur dioxide and calcium oxide is not possible, owing to the formation of a suspension of sulphur in the reaction gases. Measurements of the partial sulphur dioxide pressure in the reaction $\text{CaS} + 3\text{CaSO}_4 \rightleftharpoons 4\text{CaO} + 4\text{SO}_2$ give values in accordance with theory, in spite of the fact that the reaction is not strictly reversible, as a result of the side-reaction $\text{CaS} + 2\text{SO}_2 \rightleftharpoons \text{CaSO}_4 + \text{S}_2$. The thermal effect of the first reaction is -238.6 g.-cal., and that of the second +58.9 g.-cal. These values are in good agreement with those calculated from Nernst's theorem. R. TRUSZKOWSKI.

Equilibrium of the reciprocal system sodium chloride-magnesium sulphate in its application to natural salt waters. Conditions of formation of Glauber's salt at Karabugaz. N. S. KURNAKOV and S. F. SHEMTSCHUSHNI (Akad. Nauk, U.S.S.R., Material, 1930, 73, 339—409).—The equilibrium diagram is characterised at 0° by four and at 25° by seven surfaces or fields of crystallisation. The diagram is in accord with conditions observed at Karabugaz and other salt lakes in Aralo-Caspian territory. CHEMICAL ABSTRACTS.

Solid-phase rule in the system cellulose-cuprammonium hydroxide-sodium hydroxide. I. SAKURADA (Kolloid-Z., 1931, 54, 43—46).—The amount of cellulose dissolved by a mixture of cuprammonium hydroxide and sodium hydroxide increases at first with the concentration of the reagent, reaches a maximum, and falls at higher concentrations. This behaviour is in accordance with many other observations on the influence of the amount of solid phase on swelling and peptisation. E. S. HEDGES.

Heat of formation of cobaltous oxide. W. A. ROTH and H. HAVEKOS (Z. anorg. Chem., 1931, 195, 239—240).—By combustion of metallic cobalt the value of 57.5 ± 0.2 kg.-cal. has been obtained for the

heat of formation of cobaltous oxide under constant pressure at 20°. R. CUTHILL.

Conductivity of electrolytes in nitromethane. C. P. WRIGHT, D. M. MURRAY-RUST, and (Sir) H. HARTLEY (J.C.S., 1931, 199—214).—The conductivities of various electrolytes in nitromethane solution have been measured at 25° and at concentrations of 0.0001—0.002N. With tetraethylammonium nitrate, perchlorate, picrate, iodide, and thiocyanate the graph obtained by plotting Λ_c , the equivalent conductivity at concentration c , against \sqrt{c} is a straight line, the slope of which is in good agreement with the Debye-Hückel-Onsager equation. For lithium thiocyanate, perchlorate, and iodide, sodium thiocyanate and perchlorate, potassium thiocyanate and iodide, ammonium thiocyanate and perchlorate, thallium perchlorate, silver perchlorate, and perchloric acid, however, there are large deviations from the ideal behaviour, and it is found empirically that a straight line is obtained only by plotting Λ_c against $c^{2/3}$. Since these salts behave as strong electrolytes in methyl and ethyl alcohols, which have lower dielectric constants than nitromethane, it must be concluded that the association of ions is not determined solely by the electrical forces between them. It seems possible that hydroxylic solvents prevent association by forming sheaths round both anions and cations and that nitromethane, which has donor properties only, can attach itself by co-ordinate linkings only to the cation. This theory is supported by the observation that the increase in conductivity on addition of water to the solutions of the non-ideal electrolytes is far too great to be explained by change in dielectric constant. The mobility of the hydrogen ion in nitromethane is not abnormally high, as in hydroxylic solvents.

At 25° nitromethane has d 1.1312 and its viscosity is 0.00627; addition of water lowers the viscosity. The approximate mutual solubilities of nitromethane and water are: water in nitromethane, 2%; nitromethane in water, 10%. R. CUTHILL.

Conductivity of electrolytes in nitrobenzene. D. M. MURRAY-RUST, H. J. HADOW, and (Sir) H. HARTLEY (J.C.S., 1931, 215—219).—As an ionising solvent nitrobenzene is comparable with nitromethane, but there is a somewhat greater tendency to ionic association. At 25° and at concentrations of 0.0001—0.002N, tetraethylammonium picrate and perchlorate behave as strong electrolytes and obey the Debye-Hückel-Onsager equation, whereas silver perchlorate is only partly ionised, and perchloric acid occupies an intermediate position. Approximate measurements show that hydrogen chloride, benzenesulphonic acid, and trinitrobenzoic acid are only very slightly ionised at a concentration of about 0.01N. The mobility of the hydrogen ion in nitrobenzene is not abnormally high as it is in hydroxylic solvents.

R. CUTHILL.
Conductivity and viscosity of solutions of lithium nitrate in binary alcoholic systems [at 25°]. J. L. WHITMAN and D. M. HURT (J. Amer. Chem. Soc., 1930, 52, 4762—4770; cf. Whitman and Spencer, A., 1928, 957).—Viscosity and density data for the solvents water, ethyl, *n*-propyl, and isopropyl alcohols and their binary mixtures are recorded. The

conductivities of 0.0625–0.1*M* solutions of lithium nitrate in these solvents have been determined. The water–alcohol mixtures exhibit a maximum viscosity at some intermediate composition, but the conductivity–composition curves do not show minima. No maxima or minima occur in either the viscosity or conductivity curves for mixtures of two alcohols.

J. G. A. GRIFFITHS.

Relation between thermo-electric power, thermolysis, and ionic mobility in solid salts and mixed crystals. H. REINHOLD (Z. physikal. Chem., 1930, B, 11, 321–341; cf. A., 1928, 846).—A discussion of experimental results published elsewhere. The treatment follows the lines laid down by Wagner (A., 1930, 1341) and Eastman (A., 1928, 365, 370). Thermodynamic analysis of the total thermo-electric effect in the system $M|MX|M$ (where *M* denotes a metal and *MX* a conducting solid salt) enables the "homogeneous effect" due to the gradient of activity of the mobile ions along the temperature gradient to be calculated by difference. In the systems studied (halides of lead and silver, and silver sulphide, selenide, and telluride) the thermo-electric effect at the phase boundaries is small compared with the "homogeneous effect," except for salts with abnormally high conductivity. At present only a qualitative relation between "heat of transfer" and the temperature coefficient of mobility of the ions has been established. The former quantity is generally not identical with the heat of activation.

F. L. USHER.

Calculation of the electrical conductivity of the disperse phase of a suspension. A. SLAWINSKI (J. Chim. phys., 1930, 27, 604–610; cf. A., 1929, 1142).—Two glass tubes of the same size, fitted with metal end-plates, are filled with the suspension and placed one horizontally and the other vertically; a third tube is filled with the disperse medium. The ratios of the conductivities of the contents of the tubes and the height of the deposit are measured after settling, and from the results the conductivity of the disperse phase may be calculated by use of the formulæ and tables which are given. The method is applicable to all suspensions which give uniform deposits.

H. F. GILLBE.

Cadmium–lead chloride voltaic cell. R. T. PRIEPKE and W. C. VOSBURGH (J. Amer. Chem. Soc., 1930, 52, 4831–4837).—*E.M.F.* measurements between 17° and 40° are recorded. The *E.M.F.* of the cell $Cd(Hg)|CdCl_2 \cdot 2.5H_2O(sat.)|CdCl_2 \cdot 2.5H_2O(sat.)|PbCl_2|Pb(Hg)$ in presence of solid cadmium chloride hemipentahydrate agrees with values given by Obata (Proc. Phys. Math. Soc. Japan, 1921, [3] 3, 64, 136), but when cadmium chloride monohydrate is in true (above 34°) or metastable (below 34°) equilibrium with the electrolyte, the values of the *E.M.F.* agree with those recorded by Vosburgh (A., 1927, 1033). The *E.M.F.* of the cell $Cd(Hg)|CdCl_2 \cdot 2.5H_2O(sat.)|CdCl_2 \cdot 2.5H_2O(sat.)|Hg_2Cl_2|Hg$ is 0.2 millivolt lower than that recorded by Lipscomb and Hulett (A., 1916, ii, 213). The transition point is 34° and not 26° (cf. Vosburgh, *loc. cit.*). The *E.M.F.* of the cell $Pb(Hg)|PbCl_2(sat.)|PbCl_2(sat.)|Hg_2Cl_2|Hg$ agrees with values recorded by Gerke (A., 1922, ii, 682).

J. G. A. GRIFFITHS.

Temperature coefficients of certain reference electrodes. P. PUTZEYS (Bull. Soc. chim. Belg., 1930, 39, 454–457).—The temperature coefficients of the potentials of the deci- and centi-normal hydrogen electrodes have been determined from measurements with cells of the type $Pt|H_2|0.1N-HCl(25.2^\circ)|0.1N-HCl(T^\circ)|H_2|Pt$ at a series of temperatures between 14° and 41°. The *E.M.F.* of the 0.1*N*-electrode is given by $E_T - E_{25} = 0.334(T - 25) + 0.00279(T - 25)^2$, and of the 0.01*N*-electrode by $E_T - E_{25} = 0.391(T - 25) + 0.00335(T - 25)^2$.

H. F. GILLBE.

Electrode potential and solvent: solvation activity coefficient. F. K. V. KOCH (Phil. Mag., 1931, [vii], 11, 579–584).—Absolute normal potential may be regarded as the difference of two potentials, one dependent only on the solvent and the ion and the other dependent only on the element electrode and the ion. The Nernst electrolytic solution tension may be regarded as the distribution coefficient of the metal ion between the pure solvent and the element electrode and is thus equal to the ratio of two solvation activities. Values of the solvation potential have been calculated for a number of ions in water from the free energies of hydration. The solvation activity coefficient is defined as the factor by which the activity of solvated ions must be multiplied in order to give the electromotively equivalent activity of hydrated ions and is identical with the ionic distribution coefficient of the ion between two solvents when one solvent is water. The solvation activity coefficient is not only a function of the dielectric constant of the solvent, but depends also on specific intermolecular forces. The solvation of the electron is discussed.

E. S. HEDGES.

Potential of passive iron. A. TRAVERS and J. AUBERT (Compt. rend., 1931, 192, 161–163).—A measure of the degree of passivity of iron is said to be given by the potential set up by immersion of a polished electrode of electrolytic iron in different media. In 1% aqueous sodium sulphate the *P.D.* (–0.73 volt) decreases as the alkalinity of the solution is increased, the iron becoming quite passive at *p_H* 14. Immersion in a series of oxidising solutions of various types gives potentials equal to those obtained with platinum and these are therefore characteristic of the medium. On removing and washing the iron its activity is completely regained. It is difficult to harmonise this behaviour with the "oxide film" theory of Evans (A., 1929, 270), and attempts to render the metal passive by oxidation with air or oxygen failed when tested by this method.

H. A. PIGGOTT.

Reduction potential of ceric–cerous electrode. A. H. KUNZ (J. Amer. Chem. Soc., 1931, 53, 98–102).—From the *E.M.F.* data at 25°, for the cell $Pt, H_2 | H_2SO_4(c_3) | H_2SO_4(c_3), Ce_2(SO_4)_3(c_1), Ce(SO_4)_2(c_2) | Pt$, where $c_1 + c_2$ is 0.001–0.02*M*, c_2/c_1 is 0.1–18, and c_3 is 0.5 or 1.0 formal, the molal reduction potential of ceric and cerous sulphate in 1.0 formal sulphuric acid is found to be -1.44 ± 0.01 volt.

J. G. A. GRIFFITHS.

Potentiometric study of acid–base titration systems in the very strongly acid solvent formic acid. L. P. HAMMETT and N. DIETZ, jun. (J. Amer.

Chem. Soc., 1930, **52**, 4795—4807).—Potentiometric titrations at 25° in formic acid solution have been made with cells of the type Au|quinhydrone, sodium benzenesulphonate (sat.), 0.098*M*|sodium formate|sodium benzenesulphonate (sat.)|base (c), quinhydrone|Au, where the solvent in each cell compartment is anhydrous formic acid. Quinhydrone reacts slowly with formic acid in the presence of benzenesulphonic acid and hence titrations are commenced in basic solution. In formic acid, benzene sulphonic acid is a strong acid, water and ether are very feeble bases, whilst sodium formate, triphenylcarbinol, and carbamide are strong bases. The complete ionisation of the last two demonstrates the extremely high degree of acidity which is attainable in formic acid as compared with acetic acid (cf. Conant and Werner, this vol., 40) and water. Titration data are given and it is shown that the ion product constant of formic acid is about 10⁸ times that of water (cf. Schlesinger and others, *A.*, 1919, ii, 91, etc.) and thus formic acid does not differ from water as much in basicity as in acidity. Large salt effects are absent and in this respect formic acid resembles water rather than acetic acid as a solvent (*loc. cit.*). J. G. A. GRIFFITHS.

Potential differences at air-liquid interfaces. J. W. WILLIAMS and V. A. VIGFUSSEN (*J. Physical Chem.*, 1931, **35**, 345—353).—The uncertainties involved in the measurement of interfacial potential differences are discussed. Many experimental difficulties must be overcome before such data can be used to calculate the electric moments of molecules. The results of an unsuccessful attempt to reproduce the data of other workers by the air ionisation method of Guyot and of Frumkin are recorded and discussed. With this method, the potential varies with the distance of the radioactive electrode from the liquid surface. A temperature effect appears to exist.

L. S. THEOBALD.

Explanation of the electro-capillary Becquerel effect. H. FREUNDLICH and K. SÖLLNER (*Z. physikal. Chem.*, 1931, **152**, 313—314).—A correction of an error in an earlier paper (*A.*, 1929, 145). The only condition for the separation of metal is a positive value of the decomposition potential, and an impressed *E.M.F.* is not required. F. L. USHER.

Dependence of yield on temperature. E. N. GAPON (*Ukraine Chem. J.*, 1930, **5**, [Sci.], 165—168).—The following expressions are derived from the kinetic equations of velocity of reaction: $\log \log A/(A-x) = a_1 - b_1/T$ for unimolecular, and $\log x/(A-x) = a_2 - b_2/T$ for bimolecular reactions, in which x represents the yield of products per minute, A is the initial concentration of substrates, T the absolute temperature, and a and b are constants.

R. TRUSZKOWSKI.

Relation between energy of activation and the constant *S* of Arrhenius' equation. E. N. GAPON (*Ukraine Chem. J.*, 1930, **5**, [Sci.], 169—180).—The expressions $\log S = \log K_i + E/RT_i$, $\log K_i = \log \psi + \phi/RT_i$, and $K_i = \psi e^{-\phi/RT_i + E/RT_i - E/RT}$ are derived, in which S is Arrhenius' constant, T_i is the temperature at which the velocity coefficients K_i of a given group of reactions possess the same value, E is the energy of activation, and ψ and ϕ are characteristic

constants for all reactions. The above expressions apply to unimolecular reactions.

R. TRUSZKOWSKI.

Uniform propagation of flame. N. R. SEN and H. K. SEN (*Nature*, 1931, **127**, 125—126).—Mathematical analysis shows initial uniform flame propagation to be possible provided that pressure plays no part during the short interval concerned. The condition for uniform propagation is $0 = aQ/\rho C$, where 0 is the ignition temperature, ρ is the density of the inflammable mixture, C is the specific heat, and aQ is the fraction of the total heat of combustion which is utilised for conduction. The average flame temperature is twice that of ignition of the mixture, a relation which receives support from the experimental data of Dixon and McDavid. L. S. THEOBALD.

Propagation of flame in electric fields. I. Distortion of the flame surface. E. M. GUÉNAULT and R. V. WHEELER (*J.C.S.*, 1931, 195—199).—The influence of an electric field on the movement of the flame in mixtures of carbon monoxide and oxygen ignited at the centre of a glass vessel has been studied photographically. When the flame surface is between the plates of a charged condenser not only is there no evidence of movement of the flame caused by travel of the flame electrons towards the positive plate, but, on the contrary, there is a movement bodily towards the negative plate. The effect is probably mechanical and due to the positive ions carrying the flame with them rather than to an effect on the chemical reactions in the flame. H. F. GILLBE.

Radiation from the cyanogen-oxygen flame. K. TAWADA (*J. Soc. Chem. Ind. Japan*, 1930, **33**, 504—506B).—The total radiation from the explosion of cyanogen-oxygen mixtures was measured (cf. Garner and Tawada, *A.*, 1930, 263). The reduction in radiation caused by the addition of water or hydrogen is distinctly shown; the effect is about the same in amount for either, and increases with increase of initial pressure. Addition of hydrogen or water appears also to alter the reaction velocity, since explosion of wet mixtures is audible at pressures above 30 cm., whilst the explosion of dry mixture is inaudible. When more than 46% of cyanogen is present water seems to prevent liberation of carbon and consequently to reduce "black body" radiation; in the presence of excess of oxygen the reduced radiation is considered to be due partly to lowering of the flame temperature and partly to the analogous procedure occurring in the carbon monoxide flame. Only qualitative information was obtained by measuring the persistence of ionisation phenomena.

E. LEWKOWITSCH.

Kinetics of the acetylene-oxygen reaction. R. SPENCE and G. B. KISTAKOWSKY (*J. Amer. Chem. Soc.*, 1930, **52**, 4837—4847; cf. *A.*, 1930, 1528).—The intermediate compounds glyoxal, formaldehyde, and formic acid have been isolated by means of a circulating method. At 320°, the rate of reaction is accelerated or slightly retarded by oxygen according as acetylene or oxygen is in excess. When the concentration of oxygen is less than optimal, the rate of reaction is proportional to a power of the acetylene concentration less than two. Nitrogen has a very

slight retarding effect. From determinations of the temperature coefficient the energy of activation is computed to be 34,700 g.-cal. at 320°. The mechanism of the reaction is discussed.

J. G. A. GRIFFITHS.

Effect of intensive drying on the velocity of gaseous reactions. C. C. COFFIN and O. MAASS (Canad. J. Res., 1930, 3, 540—542).—Intensively dried gaseous ammonia and carbon dioxide do not react, but on liquefaction immediate combination takes place. This observation supports the view previously put forward, viz., that the liquid state is in itself a catalytic factor, and it is suggested that the effect of intensive drying is due to removal of all traces of the liquid phase rather than to the removal of water.

H. F. GILLBE.

Velocity of reaction of sodium with halogen hydrides. H. VON HARTEL (Z. physikal. Chem., 1930, B, 11, 316—320; cf. Schay, this vol., 282).—The velocities of the reaction of highly-diluted sodium vapour with hydrogen chloride, bromide, and iodide have been measured by determining, by means of a sodium resonance lamp, the distribution of sodium vapour in the reaction zone. With hydrogen iodide every collision is effective, with the bromide 1 in 6, and with the chloride 1 in 86. The respective heats of activation calculated from the Arrhenius-Trautz relationship are 200, 1900, and 4500 g.-cal. For the reaction with hydrogen chloride the heat of activation was also calculated, from the measured increase in velocity caused by raising the temperature of the reaction tube, to be 6200 g.-cal. Thus the heats of activation are nearly completely determined by the respective negative heats of reaction.

F. L. USHER.

Attempt to measure velocity of dissociation of nitrogen tetroxide by the method of sound waves. G. B. KISTIAKOWSKY and W. T. RICHARDS (J. Amer. Chem. Soc., 1930, 52, 4661—4671).—The velocity of sound at 25° in nitrogen tetroxide at pressures between 760 and 140 mm. is, within the experimental error of 0.5%, independent of frequencies between 10 and 80 kilocycles per sec. It is shown that these results indicate a minimum value (2.5×10^4) of the velocity coefficient of the dissociation of nitrogen tetroxide not greatly less than the maximum velocity coefficient deduced from the kinetic theory, assuming that the activation of a nitrogen tetroxide molecule involves a large number of degrees of freedom.

J. G. A. GRIFFITHS.

Kinetics of the polymerisation of vinyl acetate. H. W. STARKWEATHER and G. B. TAYLOR (J. Amer. Chem. Soc., 1930, 52, 4708—4714; cf. Whitby and others, A., 1928, 1186).—The velocity of polymerisation of vinyl acetate has been determined dilatometrically at 82°, 101°, and 111°. The polymerisation of vacuum-distilled vinyl acetate follows a unimolecular law and is probably a chain reaction. The temperature coefficient is 2.7 per 10° and the heat of activation is 25,000 g.-cal. The velocity coefficient falls rapidly during the reaction in toluene, but benzoyl peroxide catalyses the reaction and is destroyed in the process. Sulphur is a negative catalyst.

J. G. A. GRIFFITHS.

Permanganate decomposition in alkaline media. [Manganese dioxide gel.] R. H. FERGUSON, W. LERCH, and J. E. DAY (J. Amer. Chem. Soc., 1931, 53, 126—137).—The interaction at 50°, 75°, and 95° of sodium and potassium permanganates with the corresponding hydroxides at various concentrations, up to 6*N*, has been investigated, solutions of the pure substances being employed. No decrease of available oxygen (determined by titration in acid solution) seems to occur when the concentration of alkali is below certain limiting values, but greater concentrations lead to a diminution of the minimum towards which the available oxygen slowly approaches. Rise of temperature accelerates the reaction, and, in general, the final minimum of available oxygen in a solution of given alkalinity diminishes with rise of temperature. The products of the reaction are oxygen and the manganates of the metals. No precipitated or colloidal manganese dioxide could be detected, and the initial presence of this substance brings about a comparatively rapid decomposition of the permanganate to manganese dioxide. The reaction is probably bimolecular, and whilst at 50° and 75° it is accounted for by the equation $4\text{MnO}_4^{2-} + 4\text{OH}^- \rightarrow 4\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + \text{O}_2$, more available oxygen than is thus indicated is lost at 95°; the results are explained if the existence of a continuous series of soluble double salts or oxides of manganese and the alkali metal is assumed. Manganese dioxide gel is obtained by diluting 400 c.c. of the dark green alkali-permanganate reaction mixture with 100 c.c. of water and evaporating the product.

J. G. A. GRIFFITHS.

Kinetics of reaction between persulphate and thiosulphate ions in dilute aqueous solution. C. V. KING and O. F. STEINBACH (J. Amer. Chem. Soc., 1930, 52, 4779—4795; cf. Schwicker, A., 1928, 1107).—The velocity of the reaction $\text{S}_2\text{O}_8^{2-} + 2\text{S}_2\text{O}_3^{2-} = 2\text{SO}_4^{2-} + \text{S}_4\text{O}_6^{2-}$ in aqueous solution is very sensitive to impurities. The reaction is unimolecular with respect to persulphate and almost independent of concentration of thiosulphate. The salt effect is large and positive, and indicates that the velocity is determined by reaction between two negative ions. From determinations of the catalytic effect of iodide ions the bimolecular constant of the persulphate-iodide reaction is calculated (cf. Jette and King, A., 1929, 771; Kiss, *ibid.*, 772). Copper has a very large catalytic effect and the results are taken to indicate that oxidation of the negative cuprous ion-thiosulphate complex (produced from cupric ion by reduction with thiosulphate) to cupric ion by persulphate is bimolecular. As compared with copper, iron has a smaller and silver a very small catalytic effect. Sucrose catalyses the persulphate-thiosulphate and the persulphate-iodide reactions (cf. Kiss and Hatz, A., 1929, 271).

J. G. A. GRIFFITHS.

Velocity of decomposition of carbonatotetramminocobaltic ion and its dependence on hydrogen-ion concentration. K. J. PEDERSEN (J. Amer. Chem. Soc., 1931, 53, 18—30).—The kinetics of the reaction $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^{2+} + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + \text{CO}_2$ have been investigated at 25° in 0.01*M*-solutions at various hydrogen-

ion concentrations by means of the pressure of carbon dioxide developed. In glycolate buffers the decomposition proceeds almost to completion, whilst in some of the acetate buffers employed the reaction is balanced and appears to involve several consecutive reactions. There is a positive neutral salt effect, but no general acid catalysis. Provided that the pressure of carbon dioxide is low and the hydrogen-ion concentration is not too small, the velocity may be expressed as the sum of two terms, one being proportional to and the other independent of the hydrogen-ion concentration. J. G. A. GRIFFITHS.

Molecular attractive forces and the velocity of chemical reactions. C. C. COFFIN and O. MAASS (Canad. J. Res., 1930, 3, 526—539).—In the liquid state Δ^{γ} -butylene reacts readily with hydrogen chloride, the α -isomeride much more slowly, and the β -isomeride very slowly. The initial velocity is with the α - and β -compounds greater than with propylene, but as the hydrogen chloride concentration diminishes the velocity falls more rapidly; the reaction does not proceed to completion, on account of polymerisation of the hydrocarbon. In presence of an excess (2 mols.) of hydrogen chloride the reaction time is reduced to 0.07—0.1 of its normal value, and the acceleration is a linear function of the acid concentration. With Δ^{γ} -butylene the reaction is practically instantaneous at 0° and requires only 1 min. for completion at -78°. In the case of Δ^{β} -butylene an excess of the hydrocarbon also accelerates the reaction to a small extent. The products of the reaction, which is homogeneous, are from Δ^{α} -butylene *sec.*-butyl chloride with about 25% of a mixture of octyl chloride and octylene, from Δ^{β} -butylene about 65% of *sec.*-butyl chloride, and from the γ -isomeride almost pure *tert.*-butyl chloride, m.p. -26.5°. The f.p. curve of hydrogen chloride- Δ^{β} -butylene mixtures indicates the formation of an equimolecular compound. In the gaseous state only the γ -isomeride reacts with hydrogen chloride, the reaction being bimolecular and heterogeneous. The results, which are discussed from the point of view of the influence of molecular attraction on reaction velocity, support the view previously put forward, and suggest that in the liquid state there exists a catalytic factor due possibly to the state of molecular strain caused by the proximity of other molecules or to the existence of orientation resulting from the mutual attractions of polar molecules. H. F. GILLBE.

Effect of sulphur trioxide on decomposition of oxalic acid by sulphuric acid. E. O. WINE (J. Amer. Chem. Soc., 1930, 52, 4737—4741; cf. Lichty, A., 1907, ii, 445).—The rate of decomposition of oxalic acid in sulphuric acid containing 0—30% of free sulphur trioxide has been investigated at 15° and 25°. The rate of decomposition increases at first rapidly and then more slowly with increasing concentration of sulphur trioxide until a maximum is attained in acid containing approximately 14% of sulphur trioxide. The results, including the existence of a maximum velocity, when considered in conjunction with the equilibrium $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{O} + \text{SO}_3$, indicate that water is a powerful anticatalyst, whilst sulphur trioxide is relatively very weak. J. G. A. GRIFFITHS.

Decomposition of citric acid by sulphuric acid. E. O. WINE (J. Amer. Chem. Soc., 1930, 52, 4729—4737).—The velocity of decomposition of citric acid at 15°, 25°, and 35° by sulphuric acid containing 0—5% of water and 0—1.5% of sulphur trioxide has been measured by the rate of evolution of carbon monoxide. The reaction is quantitative, homogeneous, follows the unimolecular law, and is retarded very strongly by sulphur trioxide and by the products (acetonedicarboxylic acid and water). As the concentration of water is decreased, the rate of reaction rises to a maximum, varying with the temperature, and on further removal of water the rate decreases. The existence of a maximum is explained on the view that sulphur trioxide is a stronger inhibitor than water, taken in conjunction with the existence of the equilibrium $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{O} + \text{SO}_3$. The temperature coefficient per 10° ranges between 3.5 and 4.4 and increases as the water content of the sulphuric acid is increased. The reaction is considered to proceed by way of an unstable citric acid-sulphuric acid complex which is stabilised by water. J. G. A. GRIFFITHS.

Mechanism of the decomposition of chlorohydrin by alkali. L. SMITH [with N. T. HOLM and B. SVENONJUS] (Z. physikal. Chem., 1931, 152, 153—156).—The reaction between chlorohydrins and alkali is bimolecular; previous reports to the contrary are ascribed to the use of mixtures of isomerides having different decomposition velocities, and to the influence of atmospheric carbon dioxide, the volatility of the chlorohydrin, and the presence of non-hydrolysable impurities. The velocity coefficients of the hydrolysis of ethylene chlorohydrin (25°) and propylene chlorohydrin (18°) are 0.62—0.68 and 6.49—6.52, respectively. H. F. GILLBE.

Kinetics of the formation of malonamide from ethyl malonate and ammonia in homogeneous solution. Reaction of the third order. K. C. BAILEY (Proc. Roy. Irish Acad., 1930, 39B, 567—573).—In homogeneous solution in ethyl alcohol-water mixtures at temperatures between 0° and 33.8° the reaction between ethyl malonate and ammonia is homogeneous and termolecular, and when the solvent medium contains 44.5% of alcohol has a velocity coefficient of 0.0311 at 0°; the temperature coefficient of the velocity is 1.68—1.70. By increasing the alcohol content of the solvent to 73% the velocity coefficient falls to less than one sixth of its previous value, but the reaction is still termolecular; this effect is probably due to the formation of a molecular compound. Although ethyl alcohol is one of the products of the reaction the velocity rises during the later stages of the reaction; the reason is obscure. H. F. GILLBE.

Chemical kinetics in mixed solvents. VIII. Velocity of formation of tetra-substituted ammonium salts in mixtures of acetone and chloroform. G. E. MUCHIN and R. B. GINSBURG (Ukraine Chem. J., 1930, 5, [Sci.], 147—158).—The values of the velocity coefficient of reactions between allyl bromide and pyridine or dimethylaniline are higher in mixtures of acetone and chloroform than those calculated for each solvent separately. The deviation of *K* may

amount to 50%, and is greater at higher than at lower temperatures.

R. TRUSZKOWSKI.

Chemical kinetics in mixed solvents. IX. G. E. MUCHIN and R. I. BARANOVA (Ukraine Chem. J., 1930, 5, [Sci.], 159–163).—The velocity of reaction at 35° and 45° of pyridine and allyl bromide dissolved in various esters varies inversely with the mol. wt. of the solvent for esters of the same homologous series. K is greatest in methyl salicylate, in which both the benzene nucleus and the hydroxyl group appear to activate the reaction.

R. TRUSZKOWSKI.

Velocity measurements on the opening of the furan ring in hydroxymethylfurfuraldehyde. II. H. P. TEUNISSEN (Rec. trav. chim., 1931, 50, 1–20).—The velocity of hydrolysis of hydroxymethylfurfuraldehyde into formic and lævulic acids has been determined by methods similar to those previously employed (A., 1930, 1256) in various mixtures of water and ethyl or methyl alcohol in the presence of 0.5*N*-hydrochloric acid at 100° (sealed tubes) and at the b. p. of the mixtures. The value of the pseudo-unimolecular coefficient $k \times 10^3$ in 10, 15, 25, 35, 50, and 75% alcohol at 100° is 1.39, 1.31, 0.90, 0.55, 0.22, and ± 0 , respectively, and in 10, 20, 30, and 40% methyl alcohol it is 1.11, 0.63, 0.20, and ± 0 , respectively. The amount of humin produced decreases as the concentration of alcohol is increased. In aqueous ethyl alcohol the temperature coefficient of the reaction between 90° and 100° is 2.0. Although hydrolysis no longer occurs in 40% methyl alcohol, evidence of alcoholysis is found in the increasing amounts of iodoform obtained by the action of iodine and potassium hydroxide as the heating is continued. An unidentified *p*-nitrophenylhydrazone, m. p. 125–130°, was obtained from the reaction product. Hydrolysis of a 1% solution of furfuryl alcohol into lævulic acid in the presence of 0.1, 0.05, and 0.02*N*-hydrochloric acid and 0.4 and 0.02*N*-oxalic acid was similarly investigated, but in all cases large amounts of resinous products are obtained and hence the unimolecular coefficient decreases rapidly as the reaction proceeds, whilst the yield of lævulic acid never exceeds 40–50%. Furfuryl alcohol is hydrolysed by water alone at 100°.

J. W. BAKER.

Denaturation of proteins. VII. Denaturation in the presence of alcohol. N. BOOTH (Biochem. J., 1930, 24, 1699–1705).—The unimolecular velocity coefficients of the denaturation of hæmoglobin increase with increasing alcohol content under otherwise similar conditions. The minimum point of the p_H -velocity curve is shifted considerably from the neutrality point of water to the acid side by addition of alcohol, and becomes more abrupt on the side of lower than on that of greater p_H values. The critical increment of activation increases appreciably with the amount of alcohol present. The magnitude of the critical increment is inversely proportional both to the dielectric constant of the medium and to the percentage of water present.

S. S. ZILVA.

Electromotive activation of oxygen. [Oxidation of ferrous sulphate.] A. B. LAMB and L. W. ELDER, jun. (J. Amer. Chem. Soc., 1931, 53, 137–163).—The kinetics of the oxidation of ferrous

sulphate (chiefly 0.15*M*) solutions at 30° by air have been investigated in relation to the catalytic effects of various substances. The progress of oxidation in the solution is determined from the potential of a bright platinum electrode which is calibrated empirically. The velocity of oxidation is independent of the rate of stirring (1250 r.p.m.) if the oxygen is absorbed at a rate less than 0.01 equivalent per litre per hr. The reaction is approximately unimolecular with respect to oxygen and bimolecular with respect to ferrous sulphate; the velocity is almost independent of concentration of sulphuric acid between 3*M* and 0.1*M*, but increases rapidly with further progressive decrease of acidity. Of the metallic ions investigated, chromic has a slight retarding action and cupric a catalytic effect which increases greatly with progressive increase of acidity. 0.023*M*-Sodium pyrophosphate increases the rate of oxidation by about 1000 times, but the actual velocity is markedly dependent on the rate of stirring (cf. Smith and Spoehr, A., 1926, 249). The oxidation potential of this solution is low. Equally large catalytic effects are produced by sufficient ground steam-activated coconut charcoal and by platinum-black; silica gel is inactive in comparison. The effect of charcoal is approximately proportional to the weight added and is maximal in solutions 0.5–1*M* with respect to sulphuric acid; in these liquids copper sulphate has little effect. Potassium ferrocyanide in neutral solution is oxidised by air about half as rapidly as corresponding solutions of ferrous sulphate in 0.01–3.0*M*-sulphuric acid; copper salts have negligible catalytic action.

In confirmation of the view that the catalysis is due to the formation of specific peroxides, minute quantities of such a substance have been extracted from aerated charcoal by means of sulphuric acid—the greatest activity being manifest in *M*-acid; further, the catalysis by copper sulphate or charcoal is depressed by traces of amyl alcohol etc.

From direct measurements of the depolarising action of the acid solutions of ferrous sulphate containing charcoal, it is found that electrodes utilising these solutions possess great advantages as compared with the oxygen electrodes previously investigated at the ordinary temperature (cf. Hofmann, A., 1919, ii, 8; von Náray-Szabó, A., 1927, 208).

J. G. A. GRIFFITHS.

Kinetics of heterogeneous formation of formate. G. BIRSTEIN and N. LOBANOV (Z. anorg. Chem., 1931, 195, 173–194; cf. A., 1927, 319).—In the reaction between formaldehyde and sodium hydroxide in aqueous solution in presence of cupric oxide the primary reaction is $\text{H}\cdot\text{CHO} + \text{NaOH} = \text{H}\cdot\text{CO}_2\text{Na} + 2\text{H}$, half the hydrogen being used up in reducing the copper oxide to copper and the remainder being liberated as gas. The reaction exhibits a period of induction due to the autocatalytic effect of the copper formed. When the reactants are present in equivalent amounts the rate of the reaction may be represented by the equation $dx'/dt = ka^{4/3}x'(1-x')^{4/3}$, where x' is the quotient of the amount which has reacted in time t by a , the initial concentration, and the temperature coefficient is comparable with that of a normal chemical reaction. If, however, either reactant is present in excess, the velocity equation is

$dx'/dt = kax'(1-x')$, the velocity coefficient, k , diminishing with increase in the concentration of the reactant present in excess. The former equation can be deduced by combining the usual equation for the velocity of a homogeneous bimolecular equation with the adsorption isotherm, and it is believed that the seat of reaction is the surface of the solid phase. When formaldehyde and sodium hydroxide react in presence of copper prepared by reducing cupric oxide with formaldehyde and alkali, the reaction is $2\text{H}\cdot\text{CHO} + \text{NaOH} = \text{H}\cdot\text{CO}_2\text{Na} + \text{MeOH}$, but is kinetically bimolecular, probably because adsorption processes still play an important part.

R. CUTHILL.

Photography of waves and vortices produced by the discharge of an explosive. D. B. GAWTHROP, W. C. F. SHEPHERD, and G. ST. J. PERROTT (J. Franklin Inst., 1931, 211, 67—86).—Photographic records have been made, by the Schlieren method, of the shock waves and other disturbances sent out by the detonation of small charges of explosive fired in the open and at one end of cellophane tubes. The "wave-speed" camera of Payman and Shepherd (Safety in Mines Res. Bd., Paper 29, 1926) was used. The spherical shock wave has a high initial speed, which, however, falls rapidly, so that the wave is soon overtaken by solid particles scattered by the explosion. The plane shock wave sent along a tube, when the explosive is confined at one end, maintains its high initial speed for some time. On emerging from the tube the plane wave changes to a spherical wave and gives rise to a vortex ring, which travels more slowly.

J. LEWKOWITSCH.

Theory of combustion of colloidal powders in a closed vessel. H. MURAOUR (Compt. rend., 1931, 192, 227—229).—The theory supposes that the powder burns because its temperature is raised to that of its decomposition by the shock of the gaseous molecules already given off, and that the temperature of the layer immediately in contact with the powder, and in which combustion is incomplete, is lower than that of explosion. The temperature rises with the more complete combustion at increased distance from the surface of the powder. At high pressures layers of gas parallel to such surface do not intermix, owing to their high density, but do so at lower pressures, thus increasing in this case the temperature of the layer at the surface of the powder. Hence the increased velocity of combustion at low densities of loading. Other deductions are drawn, and shown to be in accord with the author's experimental results (cf. A., 1930, 1530; B., 1930, 442).

C. A. SILBERRAD.

Evaluating results of corrosion tests of ferrous metals. K. PITSCHNER.—See B., 1931, 160.

Initial corrosion rate of steels. H. O. FORREST, B. E. ROETHELI and R. H. BROWN.—See B., 1931, 116.

Adsorption and promoter action in catalysis. A. C. ROBERTSON (J. Amer. Chem. Soc., 1931, 53, 382—383; cf. Elissaffoff, A., 1915, ii, 681).—Investigations of the decomposition in quartz vessels of hydrogen peroxide in the presence of copper sulphate and glass wool indicate that a tenfold increase of glass wool increases the rate very little, and a filtered

extract of the glass wool is as catalytically active as the solid material. It is considered that the reaction is probably homogeneous in the absence of glass wool and that the mechanism is different under "promotion" conditions. The reaction cannot be regarded as an example of the effect of adsorption on catalytic reaction rates (cf. Rudel and Haring, B., 1931, 110).

J. G. A. GRIFFITHS.

Catalytic decomposition of hydrogen peroxide by acetates. M. O. CHARMANDARIAN and E. A. ALEXEEVA (J. Russ. Phys. Chem. Soc., 1930, 62, 1677—1683).—Nickel sulphate and acetate do not catalyse the decomposition of hydrogen peroxide, chromic sulphate and acetate and manganese and copper sulphates have a feeble effect, cobaltous sulphate and manganous and lead acetates a slightly greater effect, and cupric and cobaltous acetates exert a powerful catalytic influence which appears in the case of copper salts to depend on the presence of ionic copper.

R. TRUSZKOWSKI.

Inhibition in decomposition of organic acids by sulphuric acid. E. O. WÜIG (J. Amer. Chem. Soc., 1930, 52, 4742—4751).—Available data of the reactions of sulphuric acid with oxalic (Bredig and Lichty, A., 1906, ii, 602; Wüig, this vol., 315), formic (Schierz, A., 1923, ii, 230), malic (Whitford, A., 1925, ii, 559; Dittmar, A., 1930, 1131), *o*-benzoylbenzoic (Gleason and Dougherty, A., 1929, 318), triphenylacetic (Dittmar, A., 1929, 656), and citric acid (Wüig, *loc. cit.*) are considered. In all cases the inhibiting effect of water is an exponential function of the concentration of the inhibitor. In the three cases fully examined, maximal velocities are obtained when the sulphuric acid contains specific concentrations of water or sulphur trioxide, the latter also being an inhibitor. In general, the addition of an inhibitor increases the temperature coefficient, which is increased by increasing concentrations of the inhibitor. The mechanisms of the decompositions are discussed in relation to Taylor's theory (A., 1923, ii, 399).

J. G. A. GRIFFITHS.

Effect of copper and lead ions on the rate of decomposition of hydrogen peroxide at various acidities. H. W. RUDEL and M. M. HARING.—See B., 1931, 110.

Catalytic oxidation of carbon monoxide. J. C. W. FRAZER (J. Physical Chem., 1931, 35, 405—411).—A *résumé* of previous results on the catalytic oxidation of carbon monoxide by means of oxides specially prepared to be free from impurities which poison the surface. The high catalytic activity of these purified oxides is attributed to their indefinite composition and to the ease with which oxygen can be taken up or released according to conditions.

L. S. THEOBALD.

Photo-electric properties of ammonia catalysts. A. K. BREWER (J. Amer. Chem. Soc., 1931, 53, 74—83; cf. Kunsman, A., 1927, 603).—The photo-electric properties of reduced magnetite, alone and promoted by aluminium and potassium oxides, have been investigated in a vacuum, and in the presence of nitrogen, hydrogen, and traces of oxygen, at temperatures up to 700°. The unpromoted iron catalyst has the same photo-electric threshold as electrolytic iron;

neither has a temperature coefficient. The presence of gases had only small effects. The catalyst promoted with 1.3% of aluminium oxide has similar properties, thus indicating that the surface contains a very low concentration of aluminium oxide and no metallic aluminium. The photo-electric emissivity of the catalyst containing 0.2% of potassium oxide, alone or in addition to alumina, increases to a maximum at about 300°, followed by a minimum at about 450°, and thereafter increases rapidly with rise of temperature. When the temperature is lowered, the minimum at 450° almost disappears. Nitrogen and hydrogen increase the emissivity; oxygen has a pronounced depressing action. When the temperature is raised, the photo-electric thresholds extend towards the red, and the results point to the dissociation of potassium oxide at elevated temperatures and the sparse distribution of metallic potassium over the surface, the ratio of free to total potassium being greatly diminished by the presence of alumina. It is suggested that whilst the photo-electric properties of the doubly-promoted catalyst are due to the potassium oxide which remains uncombined with the alumina, the catalytic properties are due to $K_2Al_2O_4$, which more than offsets the anti-catalytic effects of potassium oxide alone. J. G. A. GRIFFITHS.

Dissociation of gypsum in presence of catalysts. J. E. ADADUROV D. E. DERIBAS, and P. Y. KRAINI (J. Appl. Chem., Russia, 1930, 3, 509—531).—By proper choice of catalyst the yield of sulphur trioxide at 600° can be raised from 0.18 to 25.85%, whilst that of sulphur dioxide is reduced to 0.54% (with manganese dioxide as catalyst). Numerous catalysts were employed. The results are in accord with the resonance theory of catalysis. When the wave-length of an element is identical with that of the catalysed substance the element is a catalyst. The catalytic activity diminishes with increase in the wave-length. There is a minimum temperature for activity at each wave-length. CHEMICAL ABSTRACTS.

Reaction between metallic magnesium and aqueous chloride solutions. I. IITAKA (Proc. Imp. Acad. Tokyo, 1930, 6, 363—366).—Magnesium is attacked rapidly by 0.01*M*-sodium chloride solutions at $p_H < 4$; at higher p_H values the reaction is very slow. F. J. WILKINS.

Catalysis of reactions between solids. II. Reaction mechanism of the catalytic formation of stannate. S. TAMARU and N. ANDÔ (Z. anorg. Chem., 1931, 195, 309—320; cf. A., 1930, 171).—The equilibrium constants of the following reactions have been determined at 900°: $CaSnO_2 + CaO + H_2O = Ca_2SnO_4 + H_2$, p_H/p_{H_2O} , 1.98; $CaSnO_2 + H_2 = CaO + Sn + H_2O$, p_H/p_{H_2O} , 1.98; $Ca_2SnO_4 + CO = CaSnO_2 + CaO + CO_2$, p_{CO}/p_{CO_2} , 5, approximately. It is considered that the action of hydrogen in catalysing the formation of stannate from stannic oxide and lime is to be attributed to the consecutive reactions $SnO_2 + H_2 = SnO + H_2O$, $SnO + CaO = CaSnO_2$, and $CaSnO_2 + H_2O + CaO = Ca_2SnO_4 + H_2$, the further reaction $CaSnO_2 + H_2 = CaO + Sn + H_2O$ finally setting in when the formation of stannate is complete. A convenient method of opening up cassiterite consists in convert-

ing it into stannate by heating with excess of lime in a reducing atmosphere. R. CUTHILL.

Adsorption catalysis. M. BORN and J. FRANCK (Nachr. Ges. Wiss. Göttingen, 1930, 77—89; Chem. Zentr., 1930, ii, 1654).—A discussion of the part played in adsorption catalysis by the fact that a protracted association between the reaction partners is established, with particular reference to the reaction $2H_2 + N_2 = N_2H_4$. A. A. ELDRIDGE.

Catalytic researches with a high-pressure circulating apparatus. E. BERL and R. BERMANN (Z. angew. Chem., 1931, 44, 34—39).—An apparatus for carrying out catalytic reactions with gas mixtures at high temperatures and pressures is described; the gas can be continuously circulated through the hot catalyst and the liquid products of the reaction continuously condensed and removed under a constant high pressure. Treatment of water-gas in the apparatus, using a zinc oxide catalyst free from alkali, results in the production of methyl alcohol of high quality, whereas when a catalyst containing alkali is used a complex mixture of higher alcohols, acids, aldehydes, and other compounds is obtained. These results are obtained only when the gas mixture is circulated rapidly through the catalyst; slow circulation induces the reaction to proceed more nearly towards completion, and methane and carbon dioxide are the chief products. The presence of sulphur in the gas mixture reduces the activity of the catalyst and promotes the more rapid formation of the end products of the reaction. A. R. POWELL.

Electrodeposition of chromium. J. W. CUTHBERTSON.—See B., 1931, 162.

Heat-treatment of chromium deposits to increase their resistance to corrosion. R. J. WIRSHING.—See B., 1931, 162.

Electrodeposition of chromium-iron alloy. G. FUSEYA and K. SASAKI.—See B., 1931, 118.

Electrodeposition of lead-thallium alloys. C. G. FINK and C. K. CONARD, jun.—See B., 1931, 162.

Electrodeposition of iron-nickel alloys from cyanide solutions. L. E. STOUT and J. CAROL.—See B., 1931, 161.

[Electro]deposition of nickel-cobalt alloys. C. G. FINK and K. H. LAH.—See B., 1931, 161.

[Electro]deposition of nickel at a low p_H . W. M. PHILLIPS.—See B., 1931, 161.

Preparation of metal powders by electrolysis of fused salts. II. Thorium. F. H. DRIGGS and W. C. LILLIENDAHL.—See B., 1931, 118.

Spectroscopic study of decomposition and synthesis of organic compounds by electrical discharges. I. Electrodeless discharge. W. D. HARKINS and D. M. GANS (J. Amer. Chem. Soc., 1930, 52, 5165—5175; cf. A., 1930, 1171; Austin, *ibid.*, 1268).—The spectra of the decomposition products in the electrodeless discharge of benzene, acetylene, naphthalene, *n*-heptane, aniline, nitrobenzene, phenol, and chlorobenzene are reproduced. The colours of the initial ring discharge and of the glow discharge are listed. In all cases, insoluble brown solid pro-

ducts are obtained, but only in minute yield from *n*-hexane. In addition to the gaseous products C_2 , CH , C^+ , and H , given by benzene, acetylene, and naphthalene, aniline yields CN , NH , N_2 , and N_2^+ , nitrobenzene yields CN , N_2 , N_2^+ , CO , and OH , phenol yields CO and OH , and chlorobenzene yields Cl . J. G. A. GUFFEITHS.

Relationship of photochemical reaction velocity to the intensity of illumination. E. GAVIOLA (Anal. Asoc. Quim. Argentina, 1930, 18, 133—136).—An expression has been derived for the relationship between the number N_0 of excited molecules present in an irradiated gas and the intensity I of the illumination. By consideration of the average life of an excited molecule it is shown that $N_0 = [(a^2 + 4ckI)^{1/2} - a]/2$, where c is the probability of removal of the excited molecule by collision, a the probability of its removal by other causes, such as collision with the containing walls, absorption or emission of radiation, etc., and k is a constant. The equation is of general application to photochemical systems.

H. F. GILLBE.

Photochemical kinetics of mixtures of hydrogen and chlorine. Oxygen-free gases. M. BODENSTEIN and W. UNGER (Z. physikal. Chem., 1930, B, 11, 253—278; cf. Cremer, A., 1927, 947).—In the mechanism previously suggested for the photochemical combination of hydrogen and chlorine, the reaction chain was assumed to be broken only in the gas phase by union of chlorine and of hydrogen atoms with oxygen. Chapman and Grigg (A., 1929, 154) and Trifonov (*ibid.*, 776) showed that a retarding process occurred also at the walls of the reaction vessel. The problem has now been further attacked by studying the reaction in gases from which oxygen had been very thoroughly removed, with the object of eliminating the retardation in the gas phase. In these circumstances only the chlorine atoms are destroyed, and the process has been shown to take place, not by re-combination at the walls, but by their reaction in the gas phase with a compound of silicon produced by the attack of the glass or silica walls by activated chlorine. In oxygen-free gas the reaction conforms to the simple law $d[HCl]/dt = kI_{abs}[H_2]$, I_{abs} denoting the intensity of the absorbed light. Apparent discrepancies in earlier work are explained by taking into account the conditions under which each of the two mechanisms predominates.

F. L. USHER.

Influence of radiation on the coloration of glasses. P. GILARD and A. LECRENIER.—See B., 1931, 158.

Latent photographic image. F. C. TOY and G. B. HARRISON (Nature, 1931, 127, 129).—A reply to Trivelli (A., 1930, 1534). The authors' experiments show that illumination produces little, if any, increase in the electrolytic conductivity of silver bromide. Trivelli's theory also requires the temperature coefficient of photographic sensitivity to be comparable to some extent with that of electrolytic conductance; this is not so.

L. S. THEOBALD.

Relation between photographic reversal and the sensitivity of the silver halide grain. F. E. E.

GERMANN and D. K. SHEN (J. Physical Chem., 1931, 35, 93—99; cf. A., 1929, 893).—Development in the case of silver iodide grains in a one-grain layer emulsion is shown to be a slow process; certain grains in a developer containing no soluble halide were still incompletely developed after 15 min. Maximum developability is reached with an exposure of 64 sec. and only 17% of the iodide grains are developable. The developability-exposure curves for large- and small-grained fractions separated by centrifuging coincide with that of the uncentrifuged emulsion, indicating that the undevelopability of 83% of the grains is not due to depletion of a material in the solution which promotes sensitivity. No appreciable difference in sensitivity appears between large and small grains of the same emulsion. Treatment of the grains before exposure with quinol or pyrogallol results in increased developability with time of treatment up to 100%, and after thorough washing with water the plate does not return to its initial state of low developability. Silver iodide plates are also sensitised by solutions of acetonesemicarbazone, sodium nitrite, sodium sulphite, and sodium hydrogen sulphite. The sensitisers only increase the developability of the grains and have no effect on their speed. The terms sensitisers and desensitisers should be restricted to substances which increase or decrease developability of the grains; substances which increase or decrease the speeds should be termed accelerators or retarders, respectively. The rôle of sensitisers appears to be one of preventing or delaying reversal in an emulsion possessing a wide range of speeds of the various grains. The insensitivity of pure silver iodide emulsions is due probably to the existence of this wide range of speeds combined with quick reversal. Reversal is discussed and a case of rapid photo-retrogression of a silver iodide plate pointed out.

L. S. THEOBALD.

New photographic effect. F. E. POINDEXTER (J. Opt. Soc. Amer., 1931, 21, 59—69).—Various mechanisms of the formation of latent images about sensitivity centres as nuclei in the silver halide grain are discussed. An apparatus for the measurement of the relative reduction in photographic density on parts of an emulsion subjected to mechanical pressure is described. The formation of a latent image was largely prevented by the application of pressure. Consideration is given to the difficulty of accounting for the pressure effect on the basis of existing assumptions as to matter and radiation, since the compression of the film and silver bromide crystals is unlikely to hinder the passage of electrons or photo-conduction currents.

N. M. BLIGH.

Effect of light and salts on gelatin. A. GALINSKY (Biochem. J., 1930, 24, 1706—1715).—When gelatin is made insoluble by treatment with potassium dichromate and exposure to light a change in the protein allied to denaturation, which does not involve a change in the Hausmann numbers or in the digestibility of the protein, takes place first. The chromium is then fixed in the form of the sesquioxide without forming a definite compound with the gelatin. The reaction does not proceed to completion and is probably reversible, equilibrium being attained when

90% of the gelatin has become insoluble. The reaction is catalysed by the insoluble gelatin.

S. S. ZILVA.

Irradiated ergosterol. A. WINDAUS (Nachr. Ges. Wiss. Göttingen, 1930, 36—57; Chem. Zentr., 1930, ii, 1391).—Irradiation of ergosterol leads to the formation of at least five or six products which are not precipitable by digitonin. The nature of these products is discussed.

A. A. ELDRIDGE.

Conversion and action of ergosterol. W. HIRSCH (Med. Welt, 1930, 4, 655—658; Chem. Zentr., 1930, ii, 83).—It appears probable that by the use of monochromatic radiation the proportion of the antirachitic substance could be increased and that of the three by-products diminished.

A. A. ELDRIDGE.

Chemical effects of cathode rays. I. Decomposition of ammonia. G. R. GEDYE and T. E. ALLIBONE (Proc. Roy. Soc., 1931, A, 130, 346—366).—An apparatus is described in which measurements were made of the decomposition of gaseous ammonia at pressures between 71.4 and 0.02 cm. by high-velocity cathode rays of maximum voltage 240 kilovolts. Over the pressure range the rate of formation of permanent gas (nitrogen and hydrogen) is approximately proportional to the pressure and independent of the nature of the surface. Hydrazine is also formed, the relative yield for the same relative amount of decomposition being greater at low pressures. If hydrazine is an intermediate product it must be decomposed much faster than ammonia, and two possible hypotheses, both of which agree with the experimental results, are advanced to explain this. Most of the chemical reaction is considered to be due to simple ionisation. Two possibilities are discussed: (a) the combination of a positive ion and an electron, and (b) the combination of a positive and a negative ion. The latter is preferred and a possible mechanism, which permits a maximum efficiency of two molecules of ammonia

decomposed per ion pair, is $\text{NH}_3^+ + \text{NH}_3 = 2\text{NH} + 2\text{H}_2$, $2(\text{NH} + \text{NH}_3 = \text{N}_2\text{H}_4)$, $2\text{N}_2\text{H}_4 = 2\text{NH}_3 + \text{N}_2 + \text{H}_2$. It is calculated that 1.2 molecules are decomposed for each ion pair formed. The results are compared with those obtained by the decomposition of ammonia by α -rays and other radiations. No confirmation is obtained of McLennan and Greenwood's conclusion that at 4 mm. pressure equilibrium is entirely on the side of formation and that the initial rate of decomposition is independent of pressure. The advantages of the cathode-ray method are indicated.

L. L. BIRCUMSHAW.

Thermal hydrogen-oxygen combination. Formation of hydrogen peroxide, and influence of surface nature. R. N. PEASE (J. Amer. Chem. Soc., 1930, 52, 5106—5110).—The reaction between hydrogen and oxygen at total pressures between 5 and 760 mm. has been investigated in pyrex vessels by a flow method at temperatures between 510° and 650°. At 760 mm., quantities of hydrogen peroxide which can be determined are formed together with water which is produced autocatalytically. The results indicate that the peroxide is a primary product of the reaction which is favoured by a high hydrogen:oxy-

gen ratio and by high temperature. The initial presence of traces of water vapour is not essential for the reaction. At low total pressures there is immediate, but not complete, reaction up to a limiting pressure and then a rapid decrease in velocity with progressively higher pressures (cf. Thompson and Hinshelwood, A., 1929, 403). Hydrogen peroxide could not be detected in the products of the rapid reaction. The previous treatment of the pyrex glass surface has a very marked effect on the velocity of the reaction. A very pronounced retarding effect is produced by covering the surface with potassium chloride, potassium hydroxide, and other substances.

J. G. A. GRIFFITHS.

Separation as carbonates of the constituents of sylvine. E. URBAIN (Compt. rend., 1931, 192, 232—233).—Sylvine is dissolved to saturation in water, sodium hydrogen carbonate and excess of magnesium carbonate are added, and the mixture is agitated in an atmosphere of carbon dioxide. The potassium is almost completely precipitated as $\text{KHMg}(\text{CO}_3)_2$, whence it is extracted as carbonate with regeneration of magnesium carbonate. The great excess of sodium chloride has no appreciable effect on the solid phase; $\text{MgCO}_3 + \text{NaHCO}_3 + \text{KCl} = \text{MgKH}(\text{CO}_3)_2 + \text{NaCl}$. The solution is treated by the ammonia-soda process to regenerate sodium hydrogen carbonate, the residual solution of ammonium chloride being advantageously cooled to -10° , and the residual liquid used to dissolve fresh sylvine, as in this way a considerable quantity of sodium hydrogen carbonate usually lost is recovered.

C. A. SILBERRAD.

Everitt's salt. III. Reaction of formaldehyde with potassium ferrocyanide solution. T. KIRI-GAKUBO (J. Soc. Chem. Ind. Japan, 1930, 33, 513—515B).—The micro-crystalline (rhombohedral) greenish-white precipitate obtained by the reaction between potassium ferrocyanide and formaldehyde is identical in crystallographic and chemical properties and composition with the crystalline component of Everitt's salt prepared by the method of Hofmann, Heine, and Höchtlen (A., 1905, i, 38), but is obtained in a purer form. The minutely granular impurity accompanying the crystals in Everitt's salt may be isomeric, and is analogous to the pale yellow precipitate from the ferrocyanide-formaldehyde reaction (cf. A., 1930, 454, and J. Soc. Chem. Ind. Japan, 1929, 32, 1123).

E. LEWKOWITSCH.

Preparation of basic cupric acetate from the neutral salt. Z. A. IOFA, S. M. KOBRIN, and L. L. KLYACHKO.—See B., 1931, 156.

Reaction of calcium carbonate with magnesium salts in solution under pressure. E. SAUER and J. HUTER (Z. anorg. Chem., 1931, 195, 241—246).—When a dilute solution of magnesium chloride or sulphate is heated under pressures of up to 15 atm. in an autoclave there is no detectable amount of hydroxide formed, but in presence of calcium hydrogen carbonate or the solid carbonate the magnesium salt is largely converted into hydroxide.

R. CUTHILL.

Calcium, strontium, and barium stannites. S. TAMARU and H. SAKURAI (Z. anorg. Chem., 1931, 195, 24—34).—By condensing the vapour of stannous

oxide on the carbonate of calcium, barium, or strontium heated in a vacuum at about 900°, the *stannites*, CaSnO_2 , BaSnO_2 , and SrSnO_2 , respectively, are formed. When calcium stannite is subjected to the action of steam at 800° in presence of stannous oxide the product is the metastannate, CaSnO_3 , whereas in absence of stannous oxide the orthostannate, Ca_2SnO_4 , results.

R. CUTHILL.

Calcium, barium, and strontium thioxy-stannites. S. TAMARU and Y. TANAKA (Z. anorg. Chem., 1931, 195, 35—40).—The *thioxy-stannites* of calcium, barium, and strontium, SnS_2CaO , SnS_2BaO , and SnS_2SrO , may be prepared by heating the corresponding carbonates or oxides with excess of stannous sulphide; they have d^{25} 3.683, 4.464, and 3.880, respectively. They react with water according to the equation $\text{SnS}_2\text{MO} + 2\text{H}_2\text{O} = \text{SnS} + 2\text{M}(\text{OH})_2$.

R. CUTHILL.

Contamination of mercury by gold. W. SWIENTOSŁAWSKI and S. ZAGRODZKI (Rocz. Chem., 1931, 11, 19—28).—An apparatus for the repeated submission to a high-tension current of a sample of mercury is described. The gold content of mercury so treated is the same at the end as at the beginning of the experiment when iron parts are used in the apparatus, but increases when platinum parts are employed. By dissolving mercury in nitric acid and examining the residue microscopically 0.001 mg. of gold can be detected. Gold-free mercury cannot be prepared by redistillation, or by electrolysis or reduction of mercuric nitrate; the purest samples prepared contained about 10^{-8} g. of gold per 100 g.

R. TRUSZKOWSKI.

Preparation of luminescent substances. N. F. ZHIROV (J. Appl. Chem., Russia, 1930, 3, 675—680).—Phosphorescence of boric acid with fluorescein (1 in 10^4) as activator can be used to detect 0.02 mg. of boric acid. Triphenylmethane gives a weak yellow luminescence. Complete luminophores possess no advantage. The boric acid was purified by crystallisation from concentrated nitric acid containing hydrogen peroxide.

CHEMICAL ABSTRACTS.

Neodymium selenates. J. MEYER and (FRL.) C. KITTELMANN (Z. anorg. Chem., 1931, 195, 121—126).—From a mixed solution of neodymium sulphate octahydrate and potassium sulphate *potassium neodymium sulphate*, $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, separates, and the corresponding *rubidium salt*, $\text{RbNd}(\text{SO}_4)_2$ or $\text{RbNd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, may be obtained in a similar way, the anhydrous salt crystallising from a hot solution and the dihydrate in the cold. By the action of selenic acid on neodymium oxide or nitrate, *neodymium selenate*, $\text{Nd}_2(\text{SeO}_4)_3 \cdot 8\text{H}_2\text{O}$, may be prepared; the *pentahydrate*, $\text{Nd}_2(\text{SeO}_4)_3 \cdot 5\text{H}_2\text{O}$, is formed by evaporating a solution of the octahydrate on a water-bath. Neodymium selenate forms double *selenates* with the alkali selenates: $\text{KNd}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{RbNd}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$, and $\text{NaNd}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$. All the above salts are red in colour. Approximate solubility determinations at 0° and 20° have been made.

R. CUTHILL.

Mechanism of the combustion of carbon at low pressures. A. EUOKEN (Z. angew. Chem., 1930, 43, 986—993).—The mechanism of the production of

2 mols. of carbon monoxide and 1 mol. of carbon dioxide in the primary reaction between graphitic carbon and oxygen at low pressures, and of the influence of the two oxides on the course of the reaction, is discussed in the light of Sihvonen's results (A., 1930, 1379). The conclusions reached do not accord fully with those of Sihvonen, but this may be due in part to the experimental difficulties of the work.

H. F. GILLBE.

Oxidation of carbon monoxide by dissociated water vapour. G. I. LAVIN and W. F. JACKSON (J. Amer. Chem. Soc., 1931, 53, 383—384; cf. Taylor and Lavin, A., 1930, 870).—The 5% oxidation of carbon monoxide by oxygen in the discharge tube (Harteck and Kopsch, A., 1930, 1388) is attributed to the presence of small quantities of water; this is a source of hydroxyl which reacts thus: $\text{OH} + \text{CO} = \text{CO}_2 + \text{H}$ (cf. Bonhoeffer and Haber, A., 1929, 11). Under the conditions water vapour oxidises carbon monoxide, and the oxidation in oxygen is progressively increased by increasing concentrations of water vapour.

J. G. A. GRIFFITHS.

Variation of hydrogen-ion concentration with carbon dioxide pressure above 1 atm. I. Colorimetric measurement. M. B. MOORE and J. H. BUCHANAN (Iowa State Coll. J. Sci., 1930, 4, 431—439).—The p_{H} was determined (± 0.1) by the use of bromophenol-blue. The value at 25° is minimal at about 6 atm., not decreasing appreciably with further increase of pressure to 33.3 atm. At 0° the p_{H} is 0.1—0.2 lower than at 25° up to 23.4 atm. The limiting value is not affected by the addition of citric acid until this alone would account for the low value. Hence the power of carbon dioxide to inhibit the growth of organisms in carbonated beverages is due to a cause other than high hydrogen-ion concentration.

CHEMICAL ABSTRACTS.

Formation of carbon tetrachloride from its elements. A. STOCK, H. LUX, and W. WUSTROW (Z. anorg. Chem., 1931, 195, 149—157).—At 400—600° activated carbon combines very slowly with chlorine to form carbon tetrachloride.

R. CUTHILL.

Thermal decomposition of carbonyl chloride. II. A. STOCK, W. WUSTROW, H. LUX, and H. RAMSER (Z. anorg. Chem., 1931, 195, 140—148; cf. A., 1925, ii, 987).—At 400° neither the reaction $2\text{COCl}_2 = \text{CO}_2 + \text{CCl}_4$ nor the reverse change occurs to any measurable extent, even in presence of activated carbon, silica, or aluminium chloride.

R. CUTHILL.

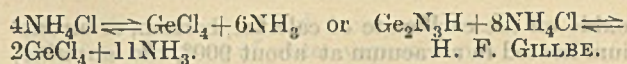
Behaviour of the various modifications and varieties of silica when mixed with carbon and heated in a current of chlorine. E. GRUNER and J. ELÖD (Z. anorg. Chem., 1931, 195, 269—287).—The conditions under which the various forms of silica yield silicon tetrachloride when mixed with carbon and heated in chlorine have been studied. Amorphous silica prepared by precipitating sodium silicate or hydrolysing silicon tetrafluoride and dehydrated by heating at dull redness starts to react appreciably at 740°, tridymite at 1060—1070°, cristobalite at 1060—1070°, and quartz at 1220°. With naturally-occurring forms of silica gel, such as

flint, opal, and chalcedony, the reaction temperature varies from 800° to 1100°, according to the age of the mineral; the reactivity of the more recent minerals is comparable with that of the artificial amorphous silica. Quartz glass is attacked at 1130—1140°. The relative reactivities seem to depend chiefly on the density; the higher is the density the smaller is the reactivity. By a process of differential chlorination the amounts of the various modifications in a mixture may be approximately determined. The temperature is first so adjusted that only the amorphous silica reacts, then when reaction is complete the temperature is raised until the cristobalite and tridymite react, and finally the quartz is caused to react. The tetrachloride given off at each stage is absorbed in alkali, from which the silica is precipitated by addition of acid and weighed. This method of separation is not, however, applicable to mixtures containing aged silicic acid gels. It seems most probable that in the reaction of silica with chlorine and carbon the first step is the reaction $\text{SiO}_2 + 2\text{Cl}_2 = \text{SiCl}_4 + \text{O}_2$, followed by $2\text{C} + \text{O}_2 = 2\text{CO}$ (cf. Spitzin, A., 1930, 874).

Pneumatolytic synthesis of silicates. I. C. J. VAN NIEUWENBURG and H. B. BLUMENDAL (Rec. trav. chim., 1931, 50, 129—138).—Silica volatilises in superheated steam (365—410°, 200—350 atm.). When silica and certain metallic oxides in separate crucibles are simultaneously treated with superheated steam reaction takes place through the volatilisation, and in this way the syntheses of β -wollastonite, strontium metasilicate, alamosite, willemite, tephroite, antigonite, and diopside have been effected. The mineralogical significance of these results is discussed. Similar results were obtained when ferrosilicon was used in place of silica, but whether these were due to oxidation to silica by the steam or occurred through the intermediary of silicon hydride has not been established.

E. S. HEDGES.

Germanium. VIII. Action of ammonia on germanium tetrachloride: germanium imide. J. S. THOMAS and W. PUGH (J.C.S., 1931, 60—71).—It is suggested that the substance $\text{GeCl}_4 \cdot 6\text{NH}_3$ is merely a mixture of ammonium chloride and germanium imide. The solution obtained on washing the substance with liquid ammonia in an apparatus designed to prevent the ingress of water yields on evaporation crystals of ammonium chloride practically free from germanium, whilst the insoluble residue consists of germanium imide of 97.2% purity. The imide forms a light, white powder which is immediately decomposed by water; it reacts rapidly with 2 mols. of hydrogen chloride and the resulting salt reacts further with formation of the tetrachloride. No evidence has been obtained of the formation of germanium amide at temperatures above -20° during the action of ammonia on the tetrachloride. On heating the mixture of imide and ammonium chloride at various temperatures between 130° and 300° a constant amount of ammonia is evolved, but no definite equilibrium pressure is attained. The reactions which occur are probably: $2\text{Ge}(\text{NH})_2 \rightleftharpoons \text{Ge}_2\text{N}_3\text{H} + \text{NH}_3$ and $\text{Ge}_2\text{N}_3\text{H} + 2\text{NH}_4\text{Cl} \rightleftharpoons \text{Ge}_2\text{N}_3\text{H} \cdot 2\text{HCl} + 2\text{NH}_3$, together with either $\text{Ge}(\text{NH})_2 +$



H. F. GILLBE.

Nitrogen compounds of germanium. I. Preparation and properties of germanic nitride. W. C. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 5160—5165).—Germanium nitride, Ge_3N_4 , is prepared by the action of ammonia on the metal at 650—700° or on the oxide at 700—750°. The nitride is stable towards air, water at 100°, and boiling sodium hydroxide, and is only slowly attacked by strong acids, but at 600—700° hydrogen effects reduction to ammonia and the metal, whilst oxidation occurs in oxygen at 800—900°. At 600—1000° germanium nitride is decomposed into its elements and a brown volatile substance, possibly *germanous nitride*, Ge_3N_2 . The brown colour of germanium nitride (cf. Schwarz and Schenk, A., 1930, 437) is not entirely due to finely-divided metal, since chlorine does not react below 575°; between 600° and 700° the reaction is probably $\text{Ge}_3\text{N}_4 + 6\text{Cl}_2 = 3\text{GeCl}_4 + 2\text{N}_2$.

J. G. A. GRIFFITHS.

Heteropoly-acids of germanium. I. Germanomolybdic acid. C. G. GROSSCUP (J. Amer. Chem. Soc., 1930, 52, 5154—5160).—*Germanomolybdic acid* is prepared by the gradual addition of 70 g. of molybdic oxide to a boiling solution of 5 g. of germanic oxide and 7 g. of sodium hydroxide in 200 c.c. of water. Yellow efflorescent crystals of the acid, $\text{H}_8[\text{Ge}(\text{Mo}_2\text{O}_7)_6] \cdot 24\text{H}_2\text{O}$, m. p. 65° (approx.), are obtained by extraction by Drechsel's method (A., 1887, 703). The acid is analysed by distillation with 9*N*-hydrobromic acid. The following reaction occurs with alkali: $\text{GeO}_2 \cdot 12\text{MoO}_3 \cdot \text{aq.} + 24\text{NaOH} = \text{GeO}_2 \cdot \text{aq.} + 12\text{Na}_2\text{MoO}_4 + \text{aq.}$, and titration may be effected with chlorophenol-red as the indicator (cf. Scroggie, A., 1929, 779). The acid yields sparingly soluble compounds with salts of metals, guanidine, and the alkaloids, and 0.00183 g. of the free acid ($\equiv 0.082$ mg. of germanic oxide) imparts a yellow colour to 5 c.c. of water, thus indicating a possible method for the colorimetric determination of germanium.

J. G. A. GRIFFITHS.

Germanochlorides of alkaloids, caesium [and rubidium]. A. TCHAKIRIAN (Compt. rend., 1931, 192, 233—234).—Germanochlorides of quinine, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot \text{HCl} \cdot \text{GeCl}_2$, and of pilocarpine, $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2 \cdot \text{HCl} \cdot \text{GeCl}_2$, are precipitated on mixing 10% solutions of the two chlorides. Both compounds are very hygroscopic, and are hydrolysed by water. The quinine compound is insoluble in alcohol or chloroform, but soluble in a warm mixture of the two. On mixing hydrochloric acid solutions of germanous and caesium or rubidium chlorides, the double salt CsGeCl_3 or RbGeCl_3 is precipitated. The caesium salt melts without decomposition and is unaffected by gaseous hydrogen chloride at 100°; it is concluded therefore that its constitution is $\text{Cs}[\text{GeCl}_3]$.

C. A. SILBERRAD.

Zirconium and hafnium sulphates. G. VON HEVESY and E. CREMER (Z. anorg. Chem., 1931, 195, 339—344).—The behaviour of zirconium and hafnium sulphates on heating shows that whether prepared from the tetrahalides or from the oxides there is always present an excess of sulphate radical; it is

for this reason that at. wt. determinations based on analysis of the sulphates are always low. The excess of sulphuric acid is removed only by heating at temperatures at which decomposition commences. The temperature-dissociation pressure curves give no indication of the formation of a definite basic sulphate. Zirconium sulphate has the higher decomposition pressure. The heat of decomposition of the hafnium salt is about 95–100 kg.-cal. and of the zirconium salt about 60–70 kg.-cal. Both compounds yield on thermal decomposition the monoclinic-tetragonal form of the oxide. Debye-Scherrer diagrams of the two sulphates after heating at 500° indicate that the lattice dimensions do not differ by more than 1%.

H. F. GILLBE.

Stannic ethoxide and the stannic acids. P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1931, 195, 83–104).—Electrolyte-free stannic ethoxide with the composition $\text{Sn}(\text{OEt})_4 \cdot 2\text{EtOH}$ is obtained by interaction of stannic chloride and sodium ethoxide in absolute alcohol solution. By slow hydrolysis of alcoholic solutions of this compound there are formed gels of hydrated stannic oxide in which the pores are large enough not to hold water by capillary condensation and the smallest particles are of such size that their vapour pressure does not depend on their dimensions. The isothermal dehydration curves of such preparations show "steps" corresponding with the hydrates $2\text{SnO}_2 \cdot 5\text{H}_2\text{O}$, $\text{SnO}_2 \cdot 2\text{H}_2\text{O}$, $4\text{SnO}_2 \cdot 7\text{H}_2\text{O}$, $2\text{SnO}_2 \cdot 3\text{H}_2\text{O}$, $\text{SnO}_2 \cdot \text{H}_2\text{O}$, and $2\text{SnO}_2 \cdot \text{H}_2\text{O}$, of which only the last two are stable in dry air. By controlled dehydration the various hydrates have been obtained in the pure state, and subjected to X-ray examination, the results indicating that in detecting crystalline compounds in solids with very fine grains X-ray methods are sometimes less useful than isothermal dehydration.

From a solution of stannic chloride in absolute alcohol a compound $\text{SnCl}_4 \cdot 2\text{EtOH}$ crystallises.

R. CUTHILL.

Ceric selenate. J. MEYER and F. SCHULZ (Z. anorg. Chem., 1931, 195, 127–128).—By the action of a 50% solution of selenic acid on ceric hydroxide yellow ceric selenate, $\text{Ce}(\text{SeO}_4)_2$, is obtained.

R. CUTHILL.

Mechanism of precipitation processes. II. Reaction between sulphuric acid and lead bromide. Z. KARAOGLANOV and B. SAGORTSCHEV. III. Reaction between sulphuric acid and lead bromide. Z. KARAOGLANOV [with B. SAGORTSCHEV] (Z. anorg. Chem., 1931, 195, 105–112, 113–120; cf. this vol., 182).—II. When lead bromide reacts with sulphuric acid in aqueous solution the precipitate always contains bromine, apparently in the form of a secondary product of reaction, possibly $(\text{PbBr})_2\text{SO}_4$. The amount of this substance in the precipitate is at its highest immediately after the reactants are mixed, and at once starts to fall owing to conversion into the pure sulphate, which has a smaller solubility product. This process takes place at the interface secondary product/solution and leads to the deposition of a layer of sulphate on the surface of the solid phase. As a result, the reaction is progressively retarded, and ultimately practically ceases before reaction is complete. The rate of

reaction probably also depends on the temperature, stirring, the composition of the liquid phase, the surface area of the solid phase, and the rates of diffusion. If equal amounts of sulphuric acid are precipitated with equivalent amounts of lead chloride and bromide under the same conditions, equivalent amounts of the secondary products are formed.

III. The behaviour of the above system can be explained satisfactorily by supposing that the secondary product of reaction, the estimated solubility product of which is 10^{-4} – 10^{-5} , is formed by the reaction $2\text{PbBr}^+ + \text{SO}_4^{2-} = (\text{PbBr})_2\text{SO}_4$, and decomposes according to the equation $(\text{PbBr})_2\text{SO}_4 = \text{PbSO}_4 + \text{PbBr}_2$. This latter process seems to proceed in the main in accordance with Nernst's theory of heterogeneous reactions, although the deposition of one of the products of reaction at the interface complicates it somewhat.

R. CUTHILL.

Reduction of nitrates by ferrous hydroxide. C. SANDONNINI and S. BEZZI (Gazzetta, 1930, 60, 693–700).—The oxidation of ferrous hydroxide by sodium nitrate in neutral and alkaline solutions has been followed by determination of the ammonia evolved on boiling. At 100° and in neutral solutions the hydroxide is oxidised to black ferrosiferrous oxide, according to the equation $12\text{Fe}(\text{OH})_2 + \text{NaNO}_3 \rightarrow 4\text{Fe}_3\text{O}_4 + \text{NH}_3 + \text{NaOH} + 10\text{H}_2\text{O}$. Prolonged boiling does not cause further oxidation. The rate of oxidation is retarded in faintly alkaline solution, by reason of the rapid agglomeration of the ferrous hydroxide. Oxidation becomes much more rapid in strongly alkaline solution and proceeds to a higher stage: $8\text{Fe}(\text{OH})_2 + \text{NaNO}_3 \rightarrow 4\text{Fe}_2\text{O}_3 + \text{NH}_3 + \text{NaOH} + 6\text{H}_2\text{O}$.

F. G. TRYHORN.

Structure of PCl_4Br . J. H. KOLITOWSKA (Rocz. Chem., 1930, 10, 743–750).—Phosphorus tetrachlorobromide reacts with phenol to yield chlorobromophosphorus triphenoxide, $(\text{OPh})_3\text{PClBr}$, indicating that the bromine atom and one chlorine atom differ in their mode of combination from the remaining three chlorine atoms.

R. TRUSZKOWSKI.

Preparation of arsenic tri-iodide by the wet method. P. G. PATERNOSTO (Rev. fac. cien. quim. La Plata, 1930, 7, 43–46).—Arsenious oxide (2 g.) is treated with hydrochloric acid (*d* 1.19, 30 c.c.); a hot solution of potassium iodide (10 g.) in water (10 c.c.) is added, the precipitate being collected on asbestos after 4–5 min. and dried in a vacuum. Arsenic tri-iodide (yield, 94%; purity, 99.8%) is extracted from the mixture by means of carbon disulphide.

CHEMICAL ABSTRACTS.

Non-existence of the sub-iodides of bismuth, BiI_2 and BiI . V. CAGLIOTI (Gazzetta, 1930, 60, 933–935).—An X-ray examination of the system bismuth-iodine shows that only the tri-iodide BiI_3 exists.

O. J. WALKER.

Preparation of sulphuryl chloride. J. MEYER (Z. angew. Chem., 1931, 44, 41–42).—The gases are bubbled through sulphuric acid, then passed downwards through a six-bulb condenser, each bulb of which is half filled with glass wool which supports a thin layer of granular activated charcoal. At the beginning of the preparation the uppermost charcoal layer is

moistened with a little sulphuryl chloride and the gas stream is passed at the rate of 3–4 bubbles a second; after 20 min. liquid sulphuryl chloride collects in the receiver at the rate of 150 g. per hr.

A. R. POWELL.

Interaction between iodine pentoxide and nitric oxide. M. S. SHAH and T. M. OZA (J.C.S., 1931, 32–36).—The reaction between iodine pentoxide and nitric oxide commences at 80° and is rapid at 120°; the time required for completion varies with the quantity of nitric oxide used. Iodine is liberated and in presence of moist sodium hydroxide all the gas evolved is converted into nitrate and nitrite. The mechanism of the reaction is discussed. The initial product may be nitrogen peroxide, formed according to the equation $10\text{NO} + 2\text{I}_2\text{O}_5 = 2\text{I}_2 + 5\text{N}_2\text{O}_4$, and subsequently oxidation takes place to pentoxide: $5\text{N}_2\text{O}_4 + \text{I}_2\text{O}_5 = \text{I}_2 + 5\text{N}_2\text{O}_5$; or nitrogen pentoxide may be the primary product: $10\text{NO} + 3\text{I}_2\text{O}_5 = 3\text{I}_2 + 5\text{N}_2\text{O}_5$, and nitrogen peroxide may be formed by the further action of nitric oxide.

H. F. GILLBE.

Preparation of iodine trichloride. E. C. TRUESDALE and F. C. BEYER (J. Amer. Chem. Soc., 1931, 53, 164–165).—Details of a rapid and economical method for the preparation of definite (large) quantities of iodine trichloride are given. When the iodine in a bulb-tube has been converted into the monochloride by a current of chlorine, the temperature is raised to just below 100°, chlorine is then passed more rapidly, and the iodine trichloride carried over is solidified in a bulb immersed in ice.

J. G. A. GRIFFITHS.

Reactions involving hydrogen peroxide, iodine, and iodate ion. I. Introduction. W. C. BRAY and H. A. LIEBHAFSKY. **II. Preparation of iodic acid. Preliminary rate measurements.** W. C. BRAY and A. L. CAULKINS (J. Amer. Chem. Soc., 1931, 53, 38–44, 44–48; cf. A., 1921, ii, 629; Abel, A., 1928, 1194; Auger, A., 1912, ii, 40).—I. The effects of variation of concentration of reactants and of hydrogen ions on the reactions of hydrogen peroxide with iodine and iodate or iodide are discussed in relation to the mechanisms.

II. The above considerations afford a method for the preparation of iodic acid. 10 G. of finely-divided iodine, 10 c.c. of concentrated nitric acid, and 50 c.c. of 3% hydrogen peroxide are heated at 70°. Whenever the colour, which decreases when the reaction starts, becomes deeper, more hydrogen peroxide, to a total of 300 c.c., is added as required. The product is evaporated to dryness.

The unimolecular velocity coefficient (k , 0.6 ± 0.1) at 25° of the homogeneous reaction in the system potassium iodate 0.0069–0.042M, sulphuric acid 0.015–0.3N, hydrogen peroxide 0.006–0.21M, and iodine $0.5\text{--}8 \times 10^{-4}\text{M}$ is independent of the first three, but decreases rapidly with decrease of concentration of iodine below 3×10^{-4} . The first-order reaction is interpreted as the rate of hydrolysis of iodine, $\text{I}_2 + \text{H}_2\text{O} \rightarrow \text{HIO} + \text{H}^+ + \text{I}^-$, and the diminution of k is due to the effect of the reverse reaction as equilibrium is approached.

J. G. A. GRIFFITHS.

Formation of a ferromagnetic iron sesquioxide by decomposition of van Bemmelen's hydrated

sesquioxide. G. CHAUDRON and A. GIRARD (Compt. rend., 1931, 192, 97–99).—Thermal analysis shows that the compound $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ prepared by hydrolysis of sodium ferrite is less stable than the natural hydrates and loses water at 100° (e.g., after 48 hrs. in boiling water) to 140°, forming a strongly ferromagnetic oxide which above 675° is converted rapidly into oligist or ordinary iron sesquioxide (cf. Huggett, A., 1929, 1369). The Curie point varies according to the thermal history of the oxide or ferrite (cf. Huggett, A., 1927, 207; 1928, 841). The ferrite, hydrate, and oxide all form birefringent hexagonal tablets, whilst slow oxidation of magnetite (Malaguti) yields a cubic form.

J. GRANT.

Production and properties of pure metals. M. L. V. GAYLER (Metall.-Wirt., 1930, 9, 677–679; Chem. Zentr., 1930, ii, 2179).—Crucibles of the corresponding oxides are used, but for iron, manganese, and chromium alumina crucibles are employed. The production of electrolytic iron is described. Chromium, prepared electrolytically with a rotating cathode, contains only hydrogen (removed at 600°) and oxide (removed by treatment with hydrogen at 1500–1600°); with removal of hydrogen the metal becomes soft and ductile. The properties of pure manganese and beryllium are described.

A. A. ELDRIDGE.

Ferrous ferrites. I. Ferrites from ortho- and meta-ferric hydroxides. A. KRAUSE and J. TULECKI (Z. anorg. Chem., 1931, 195, 228–238).—Ferrous ferrites of various compositions have been prepared from metaferric hydroxide by addition of ammonia to a mixed solution of ferric chloride peptised with hydrochloric acid and ferrous chloride and from orthoferric hydroxide by addition of ammonia to a mixed solution of ferrous and ferric chlorides. By heating the reacting mixture at the b. p. the proportion of ferrous iron in the product is increased, the maximum having been observed in a ferrite prepared from the meta-hydroxide, the composition of which when air-dry was $\text{FeO} \cdot 1.13\text{Fe}_2\text{O}_3 \cdot 0.54\text{H}_2\text{O}$. The ferrites obtained from the meta-hydroxide are much more resistant to atmospheric oxidation than those prepared from the ortho-hydroxide, and in the air-dry state they also contain more ferrous iron and less water. This difference in properties is ascribed to the difference between the isoelectric points of the two hydroxides, the ortho-hydroxide having acid properties only in an alkaline solution. All the ferrites obtained were ferromagnetic.

R. CUTHILL.

Higher oxides of group VIII elements. III. Nickel peroxides. D. K. GORALEVITSCH (J. Russ. Phys. Chem. Soc., 1930, 62, 1577–1625).—A number of oxides, Ni_6O_{11} , Ni_5O_7 , Ni_3O_4 , Ni_3O_{13} , Ni_2O_5 , Ni_9O_{17} , Ni_2O_3 , Ni_3O_{12} , Ni_3O_{15} , $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$, Ni_5O_8 , $\text{Ni}_{11}\text{O}_{17}$, and Ni_9O_{16} are obtained by the oxidation of powdered nickel or of nickelic salts. These oxides evolve oxygen (6–15%) on treatment with sulphuric acid. Certain of these oxides represent mixtures in various proportions of the oxides NiO , Ni_2O_3 , Ni_3O_4 , and NiO_2 , whilst others are nickelic salts of pernickelic acid, H_4NiO_4 , such as Ni_3O_4 ($=\text{Ni}_2\text{NiO}_4$), or of the condensation products of this acid. The struc-

tural formulæ of the fifteen peroxides prepared are given. R. TRUSZKOWSKI.

Photo-electric microanalysis. M. MATSUI and T. NODA (*J. Soc. Chem. Ind., Japan*, 1930, 33, 517—518B).—The concentration of a dilute solution may be determined from its quantitative relation to $\log I_0/I$, where I_0 and I are the photo-electric currents corresponding with the light transmitted through a cell containing water and the test solution, respectively. A caesium cell filled with argon was used as photo-electric cell and an incandescence lamp as light source: the determination is accurate to 5% or less.

E. LEWKOWITSCH.

Determination of small amounts of hydrogen and oxygen in activated carbons. A. STOCK, H. LUX, and J. W. R. RAYNER (*Z. anorg. Chem.*, 1931, 195, 158—163).—The carbon is rendered gas-free and then burnt in a known amount of oxygen. From the weight of water formed the amount of hydrogen in the carbon may be calculated and the amount of oxygen can be obtained from the amount of carbon dioxide formed and the amount of oxygen remaining uncombined. R. CUTHILL.

Tödt's "spot apparatus" for the colorimetric determination of p_H . I. M. KOLTHOFF (*Chem. Weekblad.*, 1931, 28, 78—79).—A criticism of the apparatus and of the claims made for it. Since colorimetric methods yield satisfactory results for unbuffered solutions only when the indicator solution has the same p_H as the solution tested, and the indicators supplied are not neutralised, determinations made with the apparatus are valueless.

H. F. GILLBE.

Determination of small amounts and traces of water and carbonic acid in silicates. I. E. DITTLER and H. HUEBER (*Z. anorg. Chem.*, 1931, 195, 41—59).—Lindner's method for the determination of water by liberation of hydrogen chloride from α -naphthyloxychlorophosphine (A., 1925, ii, 901) has been applied to the determination of the water expelled from silicates by heating. In the analysis of micas and epidotes this method is capable of much greater precision than the usual gravimetric methods, but its applicability is restricted to such minerals of low water content. R. CUTHILL.

Drop method for detection of bromides. A. V. PAVLINOVA (*Ukraine Chem. J.*, 1930, 5, [Sci.], 231—232).—Filter-paper is soaked in feebly alkaline fluorescein solution and dried; a drop of a solution of sodium nitrite (10%) and hydrogen peroxide (3%) and of dilute sulphuric acid are placed side by side on the paper, and a drop of the solution under examination at the confluence of the two drops, when a red stain, due to the formation of eosin, indicates the presence of bromide (minimum concentration 1 in 12,500). The coloration obtained can be intensified by exposure to ammonia vapour. Should iodine be present, the stain should first be treated with thio-sulphate solution. R. TRUSZKOWSKI.

Bromo-iodometric investigations. V. J. H. VAN DER MEULEN (*Chem. Weekblad*, 1931, 28, 82—86).—In a solution half saturated with sodium chloride

bromide is completely oxidised to bromate by an excess (2.5 times the theoretical quantity) of hypochlorite in presence of a weak acid such as carbonic or boric; for quantitative work the temperature should be 80—90°. The excess of hypochlorous acid is destroyed by addition of hydrogen peroxide and the excess of peroxide is removed by boiling the solution; the bromate may then be determined by addition of potassium iodide to the acidified solution and titration with thiosulphate. The method may be applied to the determination of bromide in admixture with iodide, iodate, and bromate after determination of the other anions by the method previously described (this vol., 55); it is necessary to add the potassium hydrogen carbonate before addition of the bromine employed to oxidise the iodide. H. F. GILLBE.

Determination of iodide in presence of chloride and bromide. F. L. HAHN (*Z. anorg. Chem.*, 1931, 195, 75—82; cf. A., 1927, 124).—In confirmation of the observations of Gorbatshev and Kasatkina (A., 1930, 1143) it is found that in the potentiometric titration of iodide with permanganate in presence of chloride and bromide the first inflexion on the titration curve occurs when 1 equivalent of permanganate per mol. of iodide has been added and the second when the amount of permanganate is double this. If the mol. ratio of bromide to iodide does not exceed 10:1, the first inflexion gives the more exact result.

R. CUTHILL.

Analysis of dilute iodine solutions. H. A. LIEBHAFSKY (*J. Amer. Chem. Soc.*, 1931, 53, 165—166; cf. Bray and Caulkins, this vol., 324).—Sufficient of the aqueous iodine solution is extracted with 25 c.c. of carbon tetrachloride to supply iodine equivalent to 1—5 c.c. of 0.004*N*-sodium thiosulphate. The carbon tetrachloride is added to 50 c.c. of 1% potassium iodide made 0.001*N* with respect to acid. Starch solution is added when titration with thiosulphate is almost complete. Conditions at the carbon tetrachloride-aqueous layer interface favour the formation of the blue starch-iodide compound.

J. G. A. GRIFFITHS.

Quantitative precipitation of sulphides in buffered solutions. I. Cobalt sulphide. M. M. HARING and M. LEATHERMAN. II. Nickel sulphide. M. M. HARING and B. B. WESTFALL (*J. Amer. Chem. Soc.*, 1930, 52, 5135—5141, 5141—5145).—I. Hydrogen sulphide precipitates cobalt sulphide quantitatively from a boiling solution of the chloride containing about 0.2 g. of the metal, if the solution has been treated with 25 c.c. of 0.4*N*-ammonium acetate, 4.5 c.c. of 6.8*N*-acetic acid, and 70 c.c. of water to make the p_H 3.93. The precautions to be observed during the precipitation and the subsequent conversion of the precipitate into the metal are enumerated. The precipitation of the sulphide is quantitative when the initial p_H of the solution is greater than 3.93.

II. To 10—15 c.c. of solution containing 0.2 g. of nickel are added 34 c.c. of 0.4*N*-ammonium acetate, 2.8 c.c. of 6.8*N*-acetic acid, and about 40 c.c. of water. The liquid (p_H 4.4) is heated at 90° before the hydrogen sulphide is passed. Precautions to be observed during the precipitation and subsequent conversion of the sulphide into the oxide are given. Complete

precipitation of the sulphide occurs when the initial p_H of the solution is greater than 4.4.

J. G. A. GRIFFITHS.

Determination of sulphite ions in the presence of thiosulphate ions, using fuchsin. V. E. MALINOVSKI (Ukraine Chem. J., 1930, 5, [Sci.], 181—186).—0.3 Mg. of sulphite ion in 0.001*M* solution decolorises 1 drop of 0.001*M*-fuchsin reagent containing 0.0002*M*-sulphuric acid. The presence of thiosulphate at concentrations less than 0.1*M* does not interfere with this reaction. This reaction cannot be applied to the determination of sulphite.

R. TRUSZKOWSKI.

Volumetric determination of sulphate in water. R. SCHMIDT.—See B., 1931, 180.

Volumetric determination of Caro's acid, persulphuric acid, and hydrogen peroxide in presence of each other. K. GLEU (Z. anorg. Chem., 1931, 195, 61—74).—The method described depends on the observation that in a solution containing sulphuric acid hydrogen bromide reduces Caro's acid completely long before it reacts appreciably with persulphuric acid and hydrogen peroxide and that arsenious acid reacts immediately with the bromine liberated, but only slowly with the hydrogen peroxide and persulphuric acid. The solution for analysis is slightly acidified with sulphuric acid and then 5 c.c. of *N*-potassium bromide and a known excess of 0.1*N*-arsenious acid are added. After 1—2 min. 0.1*N*-potassium bromate is added gradually until there is permanent slight yellow coloration due to free bromine, which is removed by titrating with arsenious acid until the solution is colourless. After the addition of 5 c.c. of 2*M*-manganous sulphate the hydrogen peroxide is titrated with 0.1*N*-permanganate, the endpoint being indicated by the appearance of the yellow colour of bromine. Finally a known excess of arsenious acid and 10 c.c. of 10*M*-sulphuric acid are added and the mixture is boiled for 10 min. to reduce the persulphuric acid, after which the excess of arsenious acid is titrated back with bromate. R. CUTHILL.

Detection of tellurium in bismuth. H. TÖPELMANN.—See B., 1931, 161.

Determination of nitrate by Grandval and Lajoux' method. B. A. SKOPINTZEV (J. Appl. Chem., Russia, 1930, 3, 747—758).—Loss of nitrate during evaporation owing to the presence of sulphur compounds in the gas is avoided by addition of 0.1*N*-sodium hydroxide (0.5—1.0 c.c.). The volume of the standard sample should be 1—3 c.c., and the burette must be read to 0.01 c.c. The presence of ammonium compounds is objectionable only if the content is greater than the equivalent amount of alkalis.

CHEMICAL ABSTRACTS.

Determination of hypophosphites and arsenites by the mercurimetric method. A. IONESCO-MATIU and (MME.) A. POPESCU (J. Pharm. Chim., 1931, [viii], 13, 12—19).—Hypophosphites and arsenites are determined volumetrically by reaction with mercuric chloride, the metallic mercury so formed being transformed into sulphate, which is determined as previously described (B., 1929, 698).

E. H. SHARPLES.

Permanence of standardised arsenious acid solutions. I. TANANAEV (Ukraine Chem. J., 1930, 5, [Sci.], 217—226).—The diminution in titre of arsenious acid solutions is due to oxidation to arsenic acid; the velocity of this process is proportional to the alkali content, the daily oxidation of a 0.1*N* solution in *N*-sodium hydroxide amounting to 0.176%. Feebly alkaline solutions (p_H 7—9) do not change their titre during 18 months. Arsenious acid solutions are best prepared by dissolving arsenious oxide in carbonate-free sodium hydrogen carbonate solution. Micro-organisms do not develop in such solutions, nor do the latter evolve arsine. R. TRUSZKOWSKI.

Quantitative study of the boric acid-alcohol flame reaction. W. STAHL (Latvij. Univ. Raksti, 1930, 1, 369—400).—The flame reaction of boric acid with methyl or ethyl alcohol can be observed when the temperature of the liquid is 100° below the b. p. of the alcohol, but is most marked near the b. p., and with a mixture of 1 vol. of sulphuric acid to 5 vols. of alcohol. A modification of Rosenblatt's apparatus, by means of which it is possible to detect 0.005 mg. of boric acid with methyl alcohol, or 0.02 mg. with ethyl alcohol, is described. The flame colour with methyl alcohol is less influenced by water than is the case with ethyl alcohol. F. L. USHER.

Rapid determination of small quantities of boric acid by intensity of flame coloration. W. STAHL (Latvij. Univ. Raksti, 1930, 1, 401—407; cf. preceding abstract).—Boric acid, in quantities of 0.3 mg. and upwards, may be roughly estimated by comparing the colour intensity of a Bunsen flame fed with the vapour of the methyl ester with that given by a series of standard solutions. Preliminary separation of the ester by distillation is unnecessary.

F. L. USHER.

Analysis of products of [thermal] decomposition of carbonyl chloride. A. STOCK and W. WUSTROW [with H. LUX, H. RAMSER, and A. SCHEIDER] (Z. anorg. Chem., 1931, 195, 129—139).—The separation and analysis of mixtures of carbonyl chloride, carbon monoxide, carbon dioxide, chlorine, carbon tetrachloride, and hydrogen chloride by fractional condensation and the use of mercury vapour, alkali, aniline, and sodium amalgam as absorbents are described (cf. A., 1925, ii, 987).

R. CUTHILL.

Drop method of detection of thiocyanate and ferrocyanide ions together. A. V. PAVLINOVA and T. N. BACH (Ukraine Chem. J., 1930, 5, [Sci.], 233—234).—A drop of ferric chloride solution is placed on a filter-paper, then a drop of dilute sulphuric acid, and finally a drop of the solution under examination, when a blue stain enclosed in a red ring indicates the presence of ferrocyanide and thiocyanate ions.

R. TRUSZKOWSKI.

Quality of filter-paper and sensitivity of the drop method. A. V. PAVLINOVA and T. N. BACH (Ukraine Chem. J., 1930, 5, [Sci.], 235—236).—Potassium ferrocyanide can be detected by the drop method at a dilution of *N*/8445 using ash-free filter-paper, and of *N*/5000 using ordinary filter-paper.

R. TRUSZKOWSKI.

Helium. VIII. Determination of minute quantities of helium. IX. Helium content of iron, of the accessory components of ferrous meteorites, and of terrestrial metals. F. PANETH and W. D. URRY (Z. physikal. Chem., 1931, 152, 110—126, 127—149).—VIII. By employing a heated wire manometer in a manner similar to that previously described (A., 1930, 1543) quantities of helium of from 7×10^{-9} to 1×10^{-4} c.c. may be determined with an error which falls from 50% to 1% as the quantity increases within the limits stated. The variation of the galvanometer deflexion with the gas pressure is described, and details are given of the precautions which are necessary to obtain accurate results.

IX. An apparatus whereby metals and other materials may be dissolved in acid without admission of air or of radioactive impurities is described; the helium and radium contents may thus be determined in one specimen. By employing this apparatus in conjunction with the heated wire manometer the helium content of iron derived from 38 meteorites has been found to lie between 0.23 and 36×10^{-6} c.c. per g.; the non-ferrous constituents appear to contain only slightly smaller quantities of helium. In certain stony meteorites the helium content of the ferrous constituent is only about one sixth of that of the stony part, and the distribution in the latter is irregular. Two specimens of commercial copper contained no helium of radioactive origin, whereas one specimen of iron contained 10^{-6} c.c. per g. Investigation of the liberation of helium from ferrous meteorites on heating shows that only about 2—6% of the total helium is evolved on heating at 1000° for many hours; the age of such meteorites, therefore, cannot be determined by this method (cf. A., 1930, 1398).

H. F. GILLBE.

Spectro-analytical investigations. IX. Spectro-analytical determination of strontium in calcium. K. RUTHARDT (Z. anorg. Chem., 1931, 195, 15—23).—The determination of strontium in concentrations of the order of 0.1—0.4 at.-% in calcium salts by the comparative spectroscopic method (Gerlach and Schweitzer, "Die chemische quantitative Emissionsspektralanalyse," Leipzig, 1930, p. 60) is described. Amounts of strontium too small to be detected by ordinary chemical methods may be determined.

R. CUTHILL.

Detection of magnesium by means of dyes. J. V. DUBSKÝ and A. OKÁČ (Chem. Listy, 1930, 24, 492—493).—2 : 4 - Dihydroxyphenylazo - *p* - nitro - benzene gives a blue adsorption compound with magnesium salts in alkaline solution; 0.0002 mg. of magnesium can be detected in this way. An identical coloration is given by nickel, and a similar one by cobalt.

R. TRUSZKOWSKI.

Indirect determination of magnesium carbonate in the presence of calcium carbonate. G. A. PANTSCHENKO (Ukraine Chem. J., 1930, 5, [Sci.], 187—196).—The mixture of carbonates is dissolved in a known volume of standardised acid, and excess of acid is titrated back using borax solution, whence the total alkaline-earth alkalinity is calculated. Calcium is precipitated as oxalate from the solution, and the oxalate is titrated, using permanganate,

Magnesium is calculated as the difference between total and calcium alkalinity. R. TRUSZKOWSKI.

Determination of magnesium as pyrophosphate. S. S. MIHOLIĆ (Bull. Soc. Chim. Yougoslav., 1930, 1, 24—16).—Traces of carbon present in the precipitate can be effectually destroyed by heating for 2 hrs. at 480°. This operation can be satisfactorily carried out in a Gooch crucible of Jena glass having pore diameter 20—30 μ .

F. L. USHER.

Determination of magnesium with 8-hydroxyquinoline gravimetrically, volumetrically, and colorimetrically. W. A. HOUGH and J. B. FICKLEN (J. Amer. Chem. Soc., 1930, 52, 4752—4755; cf. Strebinger and Reif, A., 1929, 1258).—1—10 Mg. of magnesium in 50—150 c.c. of solution is precipitated as described (*loc. cit.*) and the precipitate, after being washed with dilute ammonia, is ignited and weighed as magnesium oxide; 0.0001—0.0025 g. of magnesium is best determined volumetrically. The washed precipitate obtained as above is dissolved in 100 c.c. of hot *N*-sulphuric acid and the solution is titrated with potassium permanganate (4.17 g. per litre, 1 c.c. \equiv 0.0001 g. of magnesium) until, on the addition of 0.5 c.c., the pink colour persists for 2 min. 0.5—5.0 Mg. of magnesium in 70 c.c. of ammoniacal solution may be rapidly determined colorimetrically by addition of 60 c.c. of reagent (0.5 g. of 8-hydroxyquinoline in 100 c.c. of alcohol diluted to 1 litre). The filtrate and ammoniacal washings from the precipitate are made up to 150 c.c. The depth of colour, due to uncombined 8-hydroxyquinoline, is inversely proportional to the weight of magnesium. Of the other metals commonly found in natural waters, calcium alone interferes.

J. G. A. GRIFFITHS.

Cyanide method of separating zinc from cadmium. N. A. TANANAEV and N. S. FEDULOV (Ukraine Chem. J., 1930, 5, [Sci.], 213—216).—Potassium cyanide is added to the solution under examination, containing cobalt, copper, zinc, and cadmium, until the coloration disappears or changes, when sodium sulphide is added in excess, the solution is boiled, and the precipitate of zinc and cadmium sulphides is collected, washed, and extracted with boiling potassium cyanide solution, which dissolves zinc but not cadmium sulphide. Zinc is detected by acidifying the filtrate with acetic acid, when it is precipitated as sulphide. In this way 1 part of cadmium can be detected in the presence of 100 parts of zinc, or of the above other metals. Conversely, 1 part of zinc can be detected in the presence of 100 parts of cadmium, or of 50 parts of copper. Manganese if present should previously be eliminated as dioxide by oxidation with hydrogen peroxide.

R. TRUSZKOWSKI.

Rapid determination of zinc in brass alloys. THEWS and HARBISON.—See B., 1931, 117.

Detection of zinc, copper, and silver. A. SERGEEV (Ukraine Chem. J., 1930, 5, [Sci.], 227—230).—Sodium hydroxide solution and powdered aluminium are added; the presence of zinc is indicated by a swelling of the grains of metal. Silver is detected by feebly acidifying the solution with nitric acid, and adding a drop of mercury, when grey or silvery needles

separate. Copper is detected by dipping a heated glass rod into a drop of solution and heating in a reducing flame, when an orange coloration appears on the glass; 0.0003 mg. of copper can be detected by this method. R. TRUSZKOWSKI.

Distinction between neutral and basic lead acetate. W. A. MUNDT (Ann. Farm. Biochim., 1930, 1, 119—120).—Basic lead acetate (1 in 3000), but not the neutral salt, forms yellow lead peroxide with hydrogen peroxide. CHEMICAL ABSTRACTS.

Iodometric determination of thallium in presence of ferric iron. Determination in cadavers. R. FRIDL (Deut. Z. ges. gerichtl. Med., 1930, 15, 478—488; Chem. Zentr., 1930, ii, 1583).—A procedure is described in detail. In a case of fatal poisoning by thallium acetate solution (100 g., 2.5%) the liver contained 3.3 mg., the kidneys 1.6 mg., and the urine 5.0 mg. of thallium per 100 g. (cf. this vol., 56).

A. A. ELDRIDGE.

Microchemical detection of certain heavy metals by drop reactions with diphenylthiocarbazine. H. FISCHER (Mikrochem., 1930, 8, 319—329).—The colour reaction between a carbon tetrachloride solution of diphenylthiocarbazine and aqueous solutions of various heavy metal salts is well adapted to microchemical drop reactions on porcelain or on filter-paper. Copper salts give a yellowish-brown coloration, and in presence of 2% ammonia 0.02 microg. in 0.05 c.c. may be detected; the limit in presence of a 246,000-fold excess of lead or a 144,000-fold excess of cadmium is 0.05 microg. Lead (0.1 microg. in 0.05 c.c.) in presence of 5% potassium cyanide solution yields a completely specific brick-red coloration and the sensitivity is not lowered in presence of 9000—18,000 times the quantity of antimony, zinc, copper, cadmium, or nickel, and is reduced only by one half by a 58,000-fold excess of silver. Silver (0.05 microg. in 0.05 c.c.) in neutral solution yields a violet precipitate which on shaking becomes dispersed throughout the carbon tetrachloride; acids interfere and ammonia greatly reduces the sensitivity. In faintly alkaline solution containing sodium potassium tartrate 0.5 microg. of silver in presence of 4570 microg. of lead, 1000 microg. of zinc, or 900 microg. of antimony may be detected. Although the reaction with zinc is very sensitive, other metals interfere to such an extent as to render the method of little value. An alkaline aqueous solution of diphenylthiocarbazine will detect 0.03 microg. of cobalt; 1.0 microg. may be detected in presence of 1050 microg. of nickel. H. F. GILLBE.

Thio-salts. V. L. MASALSKI (Ukraine Chem. J., 1930, 5, [Sci.], 129—134).—For the qualitative analysis of mixtures containing copper, silver, mercury, arsenic, antimony, and tin the metals are as usual precipitated as sulphides, which are treated with 20% sodium hydroxide solution. The insoluble residue contains copper, silver, and mercury, which are detected in the usual way. The alkaline solution is acidified, and the reprecipitated sulphides are treated with ammonium carbonate, which dissolves arsenious sulphide, and the antimony is separated from the tin by the action of hydrochloric acid and hydrogen peroxide. R. TRUSZKOWSKI.

Cathode-ray tube in X-ray spectroscopy and quantitative analysis. G. R. FONDA and G. B. COLLINS (J. Amer. Chem. Soc., 1931, 53, 113—125).—The X-ray spectrum of the substance is excited directly by allowing electrons from a cathode-ray tube to impinge on the material as a target. An ionisation chamber and vacuum-tube amplifier for registering and determining the intensity of the spectral lines are described. Data of the relation between composition and the intensity of the $K\alpha$ radiations from copper-zinc, copper-nickel, iron-nickel, iron-molybdenum, silver-cadmium, and tin-antimony alloys are recorded. 0.5% of an element can be detected, and more than 3% can be determined. J. G. A. GRIFFITHS.

Spectro-analytical determinations in micro-analysis. X. Excitation of spectral lines by high-frequency sparks, and determination of traces of mercury. W. GERLACH and E. SCHWEITZER (Z. anorg. Chem., 1931, 195, 255—268).—The spectro-analytical determination of mercury by means of the spectrum produced by high-frequency sparks is described. By adding a little copper sulphate to the solution for analysis, then passing hydrogen sulphide and sparking the precipitated mixture of sulphides, amounts of mercury even less than 4 γ can be determined with a maximum uncertainty of $\pm 25\%$. If the mercury is deposited electrolytically on tinfoil before being sparked quantities less than 0.07 γ may be determined. Suitable apparatus for the production of high-frequency sparks and for the sparking of solids and liquids is described. R. CUTHILL.

Analytical chemistry of rhenium. II. Determination of rhenium as nitron perrhenate after precipitation as sulphide. W. GEILMANN and F. WEIBKE (Z. anorg. Chem., 1931, 195, 289—308; cf. A., 1930, 1547).—Rhenium sulphide is precipitated quantitatively from a solution containing 30—35 c.c. of hydrochloric acid (d 1.19) per 100 c.c. by heating at 90—95° and then passing in hydrogen sulphide as the solution cools, the current of gas being continued for 2—2.5 hrs. The precipitate is collected on an asbestos filter and the filtrate again boiled and saturated with hydrogen sulphide. After washing the united precipitates with hydrogen sulphide water containing 5% of hydrochloric acid they are suspended in 5% sodium hydroxide solution and oxidised to sodium perrhenate with hydrogen peroxide. The excess of peroxide is then destroyed by boiling and the rhenium is precipitated from the acid solution as nitron perrhenate and determined as such. The maximum error in the above determination is 0.1—0.2 mg. of rhenium and as little as 0.075 mg. of rhenium in 100 c.c. of solution can be detected by precipitation as sulphide. Any molybdenum present in the solution is precipitated by nitron at the same time as the rhenium. Insoluble rhenium compounds should be oxidised to perrhenate by fusion with a mixture of equal parts of sodium peroxide and sodium carbonate. R. CUTHILL.

Diphenylamine as indicator in determination of iron in silicates. C. J. SCHOLLENBERGER (J. Amer. Chem. Soc., 1931, 53, 88—98; cf. Szebellédy, A., 1930, 1149; Sarver, B., 1927, 557).—The effect of

sulphuric, hydrochloric, phosphoric, hydrofluoric, and fluoroboric acids, and salts, on the electrometric titration curves of ferrous salts with dichromate has been investigated and correlated with the effects of these substances on the sharpness of the diphenylamine end-point and the thiocyanate end-point of the back titration of the ferric iron with titanous chloride. The sharpness of the former end-point in the presence of sulphuric acid with either hydrofluoric or phosphoric acid is related to the lowering of the oxidation potential by the last two acids, which, unlike fluoroboric acid, cause serious errors in the thiocyanate end-point. The ferrous and total iron in silicates is determined by adding to the silicate in a platinum crucible (cf. Sarver, *loc. cit.*) 6 c.c. of water, 6 c.c. of 1:1 sulphuric acid, and, after boiling, 6 c.c. of hydrofluoric acid. The cooled liquid is diluted to 25 c.c. and titrated with dichromate, diphenylamine being used as indicator. 4 G. of boric acid are added and the liquid is titrated with titanous chloride, thiocyanate being used as indicator. Organic matter may interfere; manganese does not.

J. G. A. GRIFFITHS.

Detection of cobalt as caesium cobaltinitrite. H. YAGODA and H. M. PARTRIDGE (J. Amer. Chem. Soc., 1930, 52, 4857—4858).—The residue obtained by evaporating to dryness the solution of cobalt sulphide in aqua regia is dissolved in 1—2 c.c. of 6*M*-acetic acid, and then 2 c.c. of 6*M*-potassium nitrite and 0.5 c.c. of 0.5*M*-caesium nitrate are added. 0.01 Mg. of cobaltous ion per c.c. yields a yellow precipitate in about 3 min. Iron, manganese, and nickel do not interfere.

J. G. A. GRIFFITHS.

Rapid determination of nickel in plating baths. A. WOGRINZ.—See B., 1931, 162.

Sensitive test for molybdenum. J. V. TAMCHYNA (Chem. Listy, 1930, 24, 465—466).—Molybdic acid gives a violet coloration with potassium ethylxanthate in dilutions not exceeding 1:4,000,000. The presence of excess of tungsten does not interfere with this reaction, which cannot, however, be applied in the presence of copper, iron, nickel, or bismuth.

R. TRUSZKOWSKI.

Detection of zirconium. F. PAVELKA (Mikrochem., 1930, 8, 345—351).—The limiting concentration for the detection of zirconium by the colour reaction with carminic acid is 1 in 10⁵; titanium, phosphate, sulphate, and fluoride interfere, but thorium, cerium, and aluminium are without influence on the reaction if 20% of hydrochloric acid be added to the solution. For the galloxyaniline reaction the limiting concentration is 2 in 10⁶, and the sensitivity is not greatly reduced by the presence of aluminium, thorium, beryllium, or cerium if 10% of hydrochloric acid be added. The zirconium-galloxyaniline complex may be precipitated by addition of 4% sodium arsenate solution to the hot acidified mixture, addition of alcohol to dissolve any excess of galloxyaniline, and filtration of the complex arsenate through a filter pencil; 2—3 microg. of zirconium yield a definite blue deposit. The *m*-nitrophenylarsinate may be precipitated by a similar method, and the reaction is then especially useful when large quantities of cerium are present. In all the reactions employing gallo-

xyaniline nitrate must be absent, and the reagent should be added in the solid form, as its solutions become less sensitive when kept. When employed as a drop reaction the limiting concentration is about 1 in 2000, and the reaction is applicable in presence of 500 times the quantity of thorium.

H. F. GILLBE.

Determination of platinum in platinum ore. W. R. SCHOELLER.—See B., 1931, 117.

Ultra-violet spectrophotometry. G. E. DAVIS and C. SHEARD (J. Opt. Soc. Amer., 1931, 21, 47—58).—A simple type of container for the under-water spark, with suitable electrical circuits, and a new type of quartz cell to contain liquids under examination are described. Experimental technique, modifications of apparatus, and methods of obtaining data with the quartz spectrograph and Hilger rotating-sector photometer are considered.

N. M. BLIGH.

Cathode sputtering. C. H. CARTWRIGHT (Rev. Sci. Instr., 1930, [ii], 1, 758—763).—The practical technique of sputtering, and a suitable apparatus, are described and discussed with special reference to the deposition of gold and platinum.

N. M. BLIGH.

"Star trail" method for spectrographic determination of elements. A. C. SHEAD and G. F. SMITH (J. Amer. Chem. Soc., 1930, 52, 5295).—The image of a bright line from the spectrum falls on a film moving rapidly at constant speed so that the trace of the line is spread out into a band of uniform density. The density depends on the concentration of the given element in the solution employed. The concentration of the element can be determined by comparison with the bands obtained when solutions of known concentration are used.

J. G. A. GRIFFITHS.

Low-vacuum pressure control apparatus. L. A. RICHARDS (Rev. Sci. Instr., 1931, [ii], 2, 49—52).—An apparatus is described for maintaining any constant vacuum, independent of atmospheric changes, in any number of vacuum tanks, the pressure in each being independently variable. A control vacuum is employed, and is preserved by a pump started automatically by an electrical make and break actuated by variations of external pressure.

N. M. BLIGH.

Determination of the reflectivity of metals and reflectors for ultra-violet rays by means of a cadmium cell and electrometer. A. RÜTTENAUER (Licht u. Lampe, 1928, 17, 2 pp.; Chem. Zentr., 1930, ii, 1664).

Effect of various factors in the output of Leclanché cells. V. A. KOSTJEJEV.—See B., 1931, 166.

Filter flasks with interchangeable side-tubes. F. FRIEDRICHS (Chem.-Ztg., 1931, 55, 31).—The ordinary conical flask for vacuum filtration is provided with a side tubulure into which any type of tube may be fitted by means of rubber or glass stoppers.

A. R. POWELL.

Filter-paper containing iodine. K. SCHERINGA (Pharm. Weekblad, 1930, 67, 1362).—Filter-papers several years old were found to contain 0.5 mg. of combined iodine.

S. I. LEVY.

Electrode containers for rapid p_H measurement. W. KORDATZKI (Chem. Fabr., 1931, 25—

27).—Three electrode containers for the hydrogen or quinhydrone electrode are described. The first consists essentially of a crucible of porcelain, glazed except for its lower extremity. When it is immersed in potassium chloride solution for *E.M.F.* measurement against a calomel electrode the unglazed tip acts as a diaphragm. Several crucibles are used alternately and are kept in saturated potassium chloride solution when not in use. Another design consists of a glass tube narrowed at the bottom and closed by a rod of porous porcelain with rubber connexion. A half-cell suitable for continuous *p_H* measurement is similarly fitted to a porcelain rod. The tube above this is packed with solid potassium chloride and charged with potassium chloride solution. A side tube communicating with an upper tube in which the solution to be examined is contained enables this to be held in contact with the potassium chloride solution, and, if necessary, run through the apparatus at any desired rate. A series of comparative determinations is given.

C. IRWIN.

Luther's calcium electrode of the third order. J. VELIŠEK and K. SVENCON (Chem. Listy, 1930, 24, 467—471).—The results obtained for the concentration of calcium ions, using the above electrode, are neither accurate nor reproducible.

R. TRUSZKOWSKI.

Vacuum evaporation and distillation. H. N. NAUMANN (Chem. Fabr., 1931, 4—7).—Most vacuum distillation apparatus involves a relatively enormous gas velocity. With liquids which foam the contamination of the distillate can be avoided only by greatly reducing the throughput. A swan-neck connexion between the flask and the condenser minimises this effect as far as possible. When evaporation is to be carried to dryness a flask in two halves is of service. The lower half, of copper, has a central pocket in which the last traces of liquid collect and into which the boiling capillary extends. An apparatus capable of distilling up to 10 litres per hr. at 10—20° is described. This is recommended for the preparation of sera and other sensitive biochemical products.

C. IRWIN.

Vacuum fractionation of phlegmatic liquids. K. HICKMAN and W. WEYERTS (J. Amer. Chem. Soc., 1930, 52, 4714—4728; cf. A., 1930, 567).—Still heads, with special manometric devices, for fractionating liquids under accurately known low pressures are described. In order to obtain correct data, the thermometer should be situated in an expansion of the column where the vapour has a relatively small velocity, and the manometer should operate directly from the wall of this expansion. The methods have been applied to the purification of 1-chloronaphthalene and *n*-butyl benzoate, and the separation of the latter from ethyl phthalate. J. G. A. GRIFFITHS.

Separatory funnel for washing heavy, volatile liquids. H. S. KING (Proc. Nova Scotian Inst. Sci., 1930, 17, 240—241).—The apparatus is constructed from two separatory funnels, the stem of the first ending in the bulb of the second and the top of the second being joined to the bulb of the first. A heavy liquid in the first funnel can be delivered into the second out of contact with the atmosphere, and after

any supernatant liquid has been discarded, is returned for further washing by inverting the apparatus.

H. BURTON.

Gas analysis. E. VOSSIECK and A. SCHMITZ (Chem. Fabr., 1930, 529—531).—In the modified apparatus described the combustion and absorption of the gases are conducted in two independent systems so that two analyses can be made side by side. The absorption pipette has the wide part (30 c.c.) at the top and the narrow calibrated part (20 c.c.) at the bottom, whereas in the combustion pipette these positions are reversed. Various minor modifications in the absorption and cooling apparatus are described.

A. R. POWELL.

Slow-combustion pipette for gas analysis. H. R. AMBLER (J. Sci. Instr., 1931, 8, 18—19).—In the apparatus described the slow combustion of gases is ensured without risk of explosion by controlling the rate of supply of oxygen, which is led through a capillary tube under a surface of mercury. The apparatus may also be used as an explosion pipette and for the absorption of gas in liquid reagents.

E. S. HEDGES.

Evaporation of large quantities of liquids in the laboratory. C. BLACHER (Chem. Fabr., 1930, 534).—The apparatus previously described by Fuchs (A., 1930, 1549) is modified by inverting the reservoir flask in a beaker from which the liquid is continuously siphoned into the evaporating vessel as the level sinks therein. In this way the reservoir can be repeatedly refilled without disturbing the evaporation.

A. R. POWELL.

Physical methods in chemical laboratories. XVI. Action of electrical discharges on gaseous elements and compounds. H. GEHLEN (Z. angew. Chem., 1931, 44, 30—34).—The preparation, properties, and reactions of active nitrogen and hydrogen are reviewed and a brief account is given of the action of a glow discharge on various organic gases and vapours.

A. R. POWELL.

Autographic apparatus for determining inflexion points in magnetic susceptibility curves. J. L. HOUGHTON (J. Sci. Instr., 1931, 8, 7—14).—The apparatus described enables automatic records of the variation of magnetic susceptibility with temperature to be taken. An alternating current from a valve oscillator is supplied to the magnetising coil of the apparatus and the output from the search coil, amplified and rectified by triode valves and a Westinghouse rectifier, is registered on a thread recorder, together with the temperature of the specimen under examination.

E. S. HEDGES.

Adjustable drop-control for burettes. F. HOLLANDER (Science, 1931, 73, 45—46).—A mechanical drop-control for micro-titrations is described.

L. S. THEOBALD.

Simple burette without faucet. P. S. TOLCHKOV (J. Chem. Ind., Russia, 1929, 6, 207—208).—Simple arrangements for filling burettes without admittance of air are described.

CHEMICAL ABSTRACTS.

Inorganic lubricants. IV. Lubricants for temperatures above and below normal. W. A. BOUGHTON (J. Amer. Chem. Soc., 1930, 52, 4858—4860).—High b.p. aqueous solutions of meta- and

ortho-phosphoric acids, sodium metaphosphate alone and mixed with borax, and orthophosphoric acid afford lubricants which may be used within ranges of temperature between 25° and 160°. Fused salts mixed with graphite or kaolin afford lubricants effective within ranges of temperature between 45° and 360°. Solutions of metaphosphoric acid may be used at temperatures between -75° and 0°.

J. G. A. GRIFFITHS.

Manometer for small pressure differentials at high pressures. J. H. BOYD, jun. (J. Amer. Chem. Soc., 1930, 52, 5102—5106).—The instrument is suitably enclosed to permit the use of high pressures and consists of a mercury reservoir of diameter 8.9 cm.; beneath the surface of the mercury projects the lower end of a riser well of 8 mm. bore in which can be moved a screw which permits an electrical circuit through the mercury to be completed or broken. The level of the mercury in the well is measured in terms of the position of the top of the screw when, on slowly raising the screw, the circuit is

just broken. Pressure differentials of 1 in. of mercury at a total pressure of 3000 lb. per sq. in. can be determined to within 0.001 in.

J. G. A. GRIFFITHS.

Content of iron soluble in hydrochloric acid of asbestos used for Gooch crucibles. E. CATTELAIN (Bull. Soc. chim., 1930, [iv], 47, 1404—1406).—The iron content of a number of samples of white asbestos fibre "for Gooch crucibles," determined by extraction with hydrochloric acid, varied from 1.187 to 8.553%. Other specimens, e.g., of cord and powder, contained from 0.067 to 12.873%. In all cases traces of manganese also were present. H. F. GILLBE.

Dropping-flask for boiling liquids. E. KRÜGER (Chem.-Ztg., 1930, 54, 987).—An Erlenmeyer flask with the side-tube drawn out at the end and slightly bent over is convenient for delivering drops of boiling water, e.g., to precipitates. The neck drawn out a little and bent in the opposite direction will deliver large quantities. L. J. HOOLEY.

Geochemistry.

Iodine content of Latvian waters in relation to the distribution of goitre. J. KUPZIS (Latvij. Univ. Raksti, 1930, 1, 425—453).—Systematic analysis of the water in different parts of Latvia reveals a correlation between iodine deficiency and the incidence of goitre. No effect can be traced to an abnormally large content of calcium, magnesium, iron, or humic substances. Determination of iodine excreted with the urine affords a more satisfactory indication of the adequacy or otherwise of the iodine supply of a district than analysis of the water supply only. The causes of iodine deficiency are discussed.

F. L. USHER.

Radioactivity of Stone Mountain springs. J. A. HOOTMAN and W. S. NELMS (Amer. J. Sci., 1931, [v], 21, 37—38).—The radioactive content of springs at Stone Mountain, Georgia, is due mainly to radium emanation originally dissolved in the water. The values obtained range from 15.60 to 0.12 millimicrocuries per litre.

C. W. GIBBY.

Radioactivity of the mineral springs of South Poland. L. WERTENSTEIN, W. BARTNICKA, and J. BICZYK (Spraw. Proc. państ. Inst. farm., 1926; Chem. Zentr., 1930, ii, 29).—The radioactivity of 49 springs did not exceed a few Mache units.

L. S. THEOBALD.

Application of thermo-magnetic analysis to the study of iron minerals and oxides. J. HUGGET and G. CHAUDRON (Korrosion u. Metallschutz, 1930, 6, 79—82; Chem. Zentr., 1930, ii, 1347).—The Curie point of magnetite is near 570°; heating at 330° in air affords an unstable, strongly magnetic compound of composition between Fe_2O_3 and Fe_3O_4 . Martite and oligist show instability at 570° and 675°. Goethite, paramagnetic, becomes ferromagnetic when heated in air at 360°. The magnetisability increases in a vacuum owing to removal of water, and at 570° diminishes further. Goethite dehydrated at 600°

in a vacuum behaves like magnetite. Lepidocrocite behaves similarly. Pyrite and markasite, at first non-magnetic, undergo oxidation at 400°. Pyrrhotite when heated in air above 250° exhibits at first an increase and then an irregular decrease in magnetisation up to 340°. Rust behaves like goethite or lepidocrocite.

A. A. ELDRIDGE.

Mineral collection of the Kongsberg silver works as basis for the study of the origin of the silver deposits. R. STØREN (Tidsskr. Kjemi Berg., 1931, 11, 16—21).—The different forms and modes of occurrence of native silver and argentite in the Kongsberg mining field are described, and the probable modes of formation of the silver minerals are discussed. The mossy variety of native silver invariably contains mercury, in some cases up to 7%, whilst this element is absent from the wire silver; the former kind of silver is also always accompanied by small amounts of nickel and cobalt minerals, thus resembling the occurrence at Temiskaming in Canada. It is suggested that a part of the native silver may have been formed from the reduction of argentite by hydrocarbons; support is afforded to this view by the frequent occurrence of small quantities of anthracite in the lodes. Little attention has hitherto been paid to the presence of mercury in the silver; this element is more abundant than was formerly supposed, although no definite mercury ores occur, and the investigation of the source of this mercury is regarded as being important for determining the mechanism of the origin of the silver deposits. H. F. HARWOOD.

Formation of talc. E. ENK (Kolloid-Z., 1931, 54, 84—86).—The geological formation of talc is further discussed from a colloid-chemical point of view (cf. A., 1930, 732).

E. S. HEDGES.

Boleite, pseudoboleite, and cumengeite. G. FRIEDEL (Z. Krist., 1930, 73, 147—158; Chem. Zentr., 1930, ii, 1355).—Boleite, tetragonal, is not

identical with pseudoboleite (cf. Gossner and Arm, A., 1930, 1352). A. A. ELDRIDGE.

Pegmatites of sodalitic syenite from Ruma Island (Los Archipelago, French Guinea). Serandite, a new mineral. A. LACROIX (Compt. rend., 1931, 192, 189—194).—These pegmatites consist primarily of micropertthite, between the plates of which are found (the groups are in approximate order of crystallisation): (1) sodalite, clæolite, and eucolite, with occasionally astrophyllite and arfvedsonite, also leucophanite, fluorspar, serandite, ægyrine, blende, and molybdenite; (2) analcite and mesolite; (3) villiaumite in fine carmine crystals. Eucolite is occasionally replaced by catapleiite, or converted into eudialite. Serandite, leucophanite, and catapleiite are confined to the pegmatites, lavenite being the only silicozirconate in the syenite, which also contains pyrochlore and galena, but no blende or molybdenite. The sodalite fluoresces intensely (orange-yellow) in ultra-violet light, as also do the catapleiite (green), leucophanite (peach), and fluorspar (violet). Serandite is a new mineral, crystallising in monoclinic, peach-coloured crystals sometimes 5 cm. long. d 3.215; optically positive, γ 1.688, β 1.660 (approx.), $\gamma-\alpha$ 0.035. Its composition is SiO_2 48.72, Al_2O_3 0.29, Fe_2O_3 0.03, FeO 1.33, MnO 28.99, MgO 0.06, CaO 10.42, Na_2O 7.38, K_2O 0.26, $\text{H}_2\text{O}+$ 2.67, $\text{H}_2\text{O}-$ 0.11, total 100.46%; corresponding with that of an acid manganous sodium calcium metasilicate, $(\text{Mn,Ca})_{7.5}(\text{Na,K})_3\text{H}_2(\text{SiO}_3)_{10}$. C. A. SILBERRAD.

Gneisses in Manitoba and Saskatchewan. E. L. BRUCE and A. F. MATHESON (Trans. Roy. Soc. Canada, 1930, [iii], 24, IV, 119—132).—The Kisseye-new gneiss near the ore-body in the Sheritt Gordon mine in northern Manitoba is described. It consists of andesine, amphibole, and garnet, with some magnetite and quartz, and has been derived by the recrystallisation of a sedimentary rock. Chemical analyses are given of the rock and of the contained garnets. Similar gneisses also occur in northern Saskatchewan. L. J. SPENCER.

Hydrargillite and sulphidic bauxite in Istria. T. KORMOS [with GEDEON] (Bán. Kohász. Lapok, 1903, 63, 269—277; Chem. Zentr., 1930, ii, 1851).—Analyses are recorded. The mud of the medicinal spring at Santo Stefano contains: Al_2O_3 28.79, SiO_2 41.72, TiO_2 0.40, Fe_2O_3 2.25, Mn_2O_3 trace, CaO 5.16, P_2O_5 0.22, FeS_2 1.18, loss on ignition 20.687%. A. A. ELDRIDGE.

Meliphanite and leucophanite. W. H. ZACHARIASEN (Z. Krist., 1930, 74, 226—229; Chem. Zentr.,

1930, ii, 1964).—Meliphanite has the formula $(\text{Ca,Na})_2\text{Be}(\text{Si,Al})_2(\text{O,F})_7$; leucophanite has the formula $(\text{Ca,Na})_2\text{BeSi}_2(\text{O,OH,F})_7$. A. A. ELDRIDGE.

Origin of desert varnish. J. D. LAUDERMILK (Amer. J. Sci., 1931, [v], 21, 51—66). A sample of "desert varnish," the properties of which are described, contained SiO_2 90.00, Al_2O_3 1.20, Fe_2O_3 2.40, CaO 0.60, MgO trace, MnO 4.46, loss on ignition 1.40%. C. W. GIBBY.

Radium in rocks. II. Granites of Eastern North America from Georgia to Greenland. C. S. PIGGOT (Amer. J. Sci., 1931, [v], 21, 28—36).—Figures given for the radium contents of rocks are revised (cf. A, 1929, 1035). Eleven other rocks have been examined. Granite from Stone Mountain, Georgia, and from North Jay, Maine, contain, respectively, 3.81 and 3.39×10^{-12} g. Ra per g. The radium content of the others varies from 2.79 to 0.26×10^{-12} g. per g., with an average value of about 0.9×10^{-12} . C. W. GIBBY.

Chemical reactions of colloidal clay. R. BRADFELD (J. Physical Chem., 1931, 35, 360—373).—A general review in which the characteristics of hydrogen clays, the titrable acidity of electro-dialysed clays, the distribution of a base between an electro-dialysed bentonite and organic acids, and the effect of the exchangeable cations on the physical properties of clays are discussed. L. S. THEOBALD.

Composition of New York soils. J. A. BIZZELL (Cornell Univ. Agric. Exp. Sta. Bull., 1930, No. 513, 25 pp.).—Among numerous soils examined the total calcium content alone is characteristic of soil type. The total contents of nitrogen, phosphorus, sulphur, potassium, and magnesium, whilst in no way associated with type, tended to be higher in more finely textured soils. The nitrogen and sulphur contents were higher and the potassium and magnesium contents lower in surface soils than in subsoils. A. G. POLLARD.

Nature and fate of the meteor crater bolide. H. L. FAIRCHILD (Science, 1930, 72, 463—467).—Speculative. The nature of the meteor which produced the Meteor Cradle, Arizona, is discussed. L. S. THEOBALD.

Barringer meteorite. D. M. BARRINGER, jun. (Science, 1931, 73, 66—67).—Polemical (cf. preceding abstract). L. S. THEOBALD.

Chemical aspects of the origin of petroleum. S. C. LIND (Science, 1931, 73, 19—22).—A presidential address. L. S. THEOBALD.

Organic Chemistry.

Thermal chlorination of methane by a flow method. R. N. PEASE and G. F. WALZ (J. Amer. Chem. Soc., 1931, 53, 382).—Chlorination (non-catalytic) of methane occurs in pyrex glass tubes above 200° at 1 atm.; the reaction is homogeneous. At 225 — 300° , the reaction is inhibited by oxygen, but at 375° the rate is not affected. H. BURTON.

Decomposition and synthesis of organic compounds by electrical discharges. I. Electrodeless discharge. W. D. HARKINS and D. M. GANS.—See this vol., 318.

Synthesis and pyrolysis of methylallene and ethylacetylene. C. D. HURD and R. N. MEINERT

(J. Amer. Chem. Soc., 1931, 53, 289—300).—Methylallene (Δ^2 -butadiene), b. p. 10–3°, d_4^{20} 0.676, n_D^{20} 1.4205 (tetrabromide, b. p. 97.5°/7 mm., m. p. –2°, d_4^{20} 2.510, n_D^{20} 1.6070), is prepared by the method of Bouis (A., 1928, 1112) by way of $\alpha\beta\gamma$ -tribromobutane and $\beta\gamma$ -dibromo- Δ^2 -butene, b. p. 75°/20 mm., d_4^{20} 1.8881, n_D^{20} 1.5464. Methylallene decomposes completely at 500–550° with a contact time of 36 sec.; 75% is polymerised to liquid products which contain a dimeric methylallene, b. p. 110–115°. The gaseous products consist of small amounts of hydrogen, methane, ethane, ethylene, propylene, and allene. Pyrolysis of ethylacetylene (Δ^2 -butinene), b. p. 8.5° (lit. 8.5° and 14–18°), prepared from sodium acetylide and ethyl sulphate in liquid ammonia, at 580–600° gives about 33% of liquid products similar to those formed from methylallene, allene, and propinene (this vol., 61); hydrogen, paraffin hydrocarbons (main products), ethylene, propylene, and small amounts of allene, acetylene, and propinene are found in the gaseous products. Pyrolyses of allene (*loc. cit.*) and methylallene are very similar.

H. BURTON.

Oxidation of "triisobutylene" by ozone. R. J. McCUBBIN (J. Amer. Chem. Soc., 1931, 53, 356–359).—Treatment of "triisobutylene" (Butlerov, A., 1880, 230) with ozonised oxygen in acetic acid containing 1.5–2% of acetic anhydride, and subsequent decomposition of the ozonide by the addition of water and zinc dust, affords trimethylacetaldehyde, methyl *tert.*-butylmethyl ketone, ditert.-butylmethyl ketone, and methyl α -ditert.-butylethyl ketone. To explain the formation of the last-named ketone, it is necessary to assume that a pinacolic rearrangement occurs during ozonolysis (cf. *loc. cit.*). The original hydrocarbon probably contains $\beta\beta\delta\zeta$ -pentamethyl- Δ^2 -heptene (2 mols.), $\delta\delta$ -dimethyl- β -tert.-butylmethyl- Δ^2 -pentene (1 mol.), and $\beta\delta\delta$ -trimethyl- γ -tert.-butyl- Δ^2 -pentene (1 mol.) (which undergoes the rearrangement). H. BURTON.

Synthesis of squalene. P. KARRER and A. HELFENSTEIN (Helv. Chim. Acta, 1931, 14, 78–85).—Treatment of impure farnesyl bromide, b. p. 125–140°/1 mm., prepared from farnesol or nerolidol by Juvala's method (A., 1930, 1401), with potassium at 100–135°, or, better, with magnesium (activated by methyl iodide) in ether, gives a fraction, b. p. 215–240°/1.1–1.2 mm., containing squalene, since it affords a hexahydrochloride, m. p. 144–145°, crystallographically identical with the squalene hexahydrochloride, m. p. 143–145°, described by Heilbron, Kamm, and Owens (A., 1926, 816). Squalene is, therefore, correctly represented as $(\text{CMe}_2[\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2]\text{CH}\cdot\text{CH}_2)_2$ (cf. A., 1930, 1422). The yield of hexahydrochloride is about 7% (on the farnesyl bromide used). H. BURTON.

Preparation of alkyl iodides. H. S. KING (Proc. Nova Scotian Inst. Sci., 1930, 17, 242–243; cf. *ibid.*, 1924, 16, 87–91).—Methyl alcohol containing 10% of water can be used in the preparation of methyl iodide by the method previously described (*loc. cit.*). The preparation of an alkyl iodide is expedited by covering the iodine with the alcohol and adding the resultant solution to the mixture of phosphorus and

the remainder of the alcohol maintained, in the case of methyl alcohol, at 70–75°. Sufficient alkyl iodide is produced to serve as the solvent for the iodine.

H. BURTON.

Photochemical reactions of gaseous methyl iodide. J. R. BATES and R. SPENCE (J. Amer. Chem. Soc., 1931, 53, 381).—A study of the photochemical decomposition and oxidation of gaseous methyl iodide supports the initial change $\text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{I}$ (cf. Iredale and Mills, A., 1930, 1498). Formaldehyde, paraformaldehyde, and methylal are formed during the oxidation.

H. BURTON.

Preparation of nitromethane. P. P. PRITZL and H. ADKINS (J. Amer. Chem. Soc., 1931, 53, 234–237).—In the preparation of nitromethane from equimolecular quantities of sodium chloroacetate and nitrite (Whitmore and Whitmore, Org. Synth., 1923, 3, 83), approximately 50% of the nitrite is converted into nitromethane. A further 24% affords methazonic acid (by way of nitromethane), whilst the remainder does not react owing to part of the chloroacetate being hydrolysed to glycolate. The yield of nitromethane is increased to 65–70% when an excess of chloroacetate solution is used; this is best added gradually to the nitrite at 100–110°.

H. BURTON.

Preparation of absolute alcohol. E. G. YOUNG (Proc. Nova Scotian Inst. Sci., 1930, 17, 248–255).—The cheapest method of preparing absolute alcohol is to heat 95% alcohol (1 litre) with calcium oxide (300 g.) for 4 hrs., and then distil; the yield is about 80% (cf. Noyes, A., 1923, i, 433). The method of Lyons and Smith (B., 1926, 384) gives a better yield at a slightly higher cost, but the product often possesses a disagreeable odour. The method of Young (J.C.S., 1902, 81, 707) is impracticable.

H. BURTON.

Configurational relationships of phenylated carbinols. P. A. LEVENE and A. WALTY (J. Biol. Chem., 1931, 90, 81–88).—Condensation of *d*-propylene oxide with magnesium *n*-propyl bromide gives *l*-methyl-*n*-butylcarbinol, α_D^{20} –1.75° (α -naphthylurethane, m. p. 81–82.5°, $[\alpha]_D^{25}$ –4.28° in alcohol), consequently the Grignard reaction is not accompanied by a Walden inversion (cf. A., 1926, 597; 1928, 1353). Similarly, magnesium phenyl bromide gives *l*-benzylmethylcarbinol, b. p. 114°/25 mm., $[\alpha]_D^{25}$ –19.8° (α -naphthylurethane, m. p. 111–113°, $[\alpha]_D^{25}$ –31.6°), oxidised by sodium dichromate to benzyl methyl ketone; therefore *l*-benzylmethylcarbinol, *d*-propylene oxide, and *l*-lactic acid are configuratively related.

H. A. PIGGOTT.

Preparation of anhydrous pinacol. H. S. KING and W. W. STEWART (Proc. Nova Scotian Inst. Sci., 1930, 17, 262–267).—Pinacol hydrate is heated with benzene in a flask fitted with a 3 ft. fractionating column, and the benzene in the distillate is separated from water in an automatic separator and returned to the distilling flask. The process is continued until all the water is removed, and the benzene is distilled off, leaving a residue of anhydrous pinacol. The above method is sufficiently accurate to determine the water content of samples of the hydrate. Dehydration by means of calcium carbide in ether gives a product

with a disagreeable odour; the use of anhydrous copper sulphate causes partial decomposition.

H. BURTON.

Homogeneity and polymorphic transformation of pentaerythritol. L. EBERT (Ber., 1931, 64, [B], 114—119; cf. Friederich and Brün, this vol., 62).—The most efficient method for the purification of pentaerythritol is very cautious sublimation in a high vacuum at about 130°; the transparent, thin, quadratic leaflets have m. p. 260.5° (corr.), in agreement with the datum of Friederich and Brün. When heated, tetragonal pentaerythritol passes into a cubic modification; a study of the cooling curve of pentaerythritol fixes the transition temperature at 179.5°.

H. WREN.

High-pressure synthesis of methyl ether and its theoretical basis. E. BIRK and R. NITZSCHMANN (Metallbörse, 1930, 20, 1295—1296, 1351, 1407; Chem. Zentr., 1930, ii, 1941).—The equilibrium constants for the dehydration of methyl alcohol to methyl ether have been determined for temperatures between 240° and 400°, together with their dependence on the concentration. A mathematical study of the formation of methyl ether, by way of methyl alcohol, from carbon monoxide and hydrogen indicates a yield of 0.892—11.25%.

A. A. ELDRIDGE.

Auto-oxidation reactions. II. Mechanism of the auto-oxidation of ethers. N. A. MILAS (J. Amer. Chem. Soc., 1931, 53, 221—233).—The rate of absorption of oxygen by dibenzyl ether in absence and presence of various catalysts has been determined at 40±0.05°. Iodine, picric acid, and *p*-benzoquinone are inhibitors, whilst small amounts of copper, silver, gold, iron, and especially mercury are accelerators. Hydroxybenzyl peroxide, benzaldehyde, and benzoic acid are produced during the oxidation. Ultra-violet irradiation of dibenzyl, *benzyl tert.-butyl*, b. p. 205.6—208° (corr.; slight decomp.), d_4^{20} 0.9439 (prepared from benzyl chloride and sodium *tert.*-butoxide at the ordinary temperature), ethyl *n*-, *iso*-, *sec.*-, and *tert.*-butyl, *n*-propyl *tert.*-butyl, di-*n*-butyl, and methyl *tert.*-butyl ethers, and dioxan in quartz vessels at about 45° accelerates peroxide formation to varying extents. Hydrogen peroxide is formed in all cases, *tert.*-butyl alcohol is isolated from all the alkyl *tert.*-butyl ethers, and formic acid is obtained in small amount from all ethers containing the methyl or ethyl group; dioxan gives some formic acid and glycollaldehyde. The peroxides from ethyl *tert.*-butyl, *n*-propyl *tert.*-butyl, di-*n*-butyl, and ethyl *isobutyl* ethers are oils which explode violently when heated. Their properties differ from those of mono- and di-hydroxyalkyl peroxides. The views of Wieland and Wingler (A., 1923, i, 650) on the auto-oxidation of ethers are held to be untenable; oxidation is considered to occur through oxonium peroxides (cf. A., 1929, 1019).

H. BURTON.

Reaction between organic sulphur compounds and sodium in liquid ammonia. F. E. WILLIAMS [with E. GEBAUER-FUELNEGG] (J. Amer. Chem. Soc., 1931, 53, 352—356).—Diethyl, di-*n*-propyl, and di-*n*-heptyl sulphides react with sodium in liquid ammonia forming the corresponding sodium mercaptides and alkanes: $SR_2 + 2Na + NH_3 \rightarrow$

$R \cdot SNa + NaNH_2 + RH$. Diethyl, di-*n*-propyl, and di-*isoamyl* disulphides are converted into the sodium mercaptides: $S_2R_2 + 2Na \rightarrow 2R \cdot SNa$. Aliphatic mercaptans and liquid ammonia form ammonium mercaptides, converted by sodium into sodium mercaptides and hydrogen: $2R \cdot SNH_4 + 2Na \rightarrow 2R \cdot SNa + 2NH_3 + H_2$.

H. BURTON.

α -Chloroethane- α -sulphonyl chloride. E. MÜLLER and H. RAUDENBUSCH (Ber., 1931, 64, [B], 94—101; cf. A., 1927, 672).—Complete chlorination of β - or α -trithioacetaldehyde in aqueous suspension gives α -chloroethane- α -sulphonyl chloride, b. p. 70—71°/13 mm., in about 50% yield; sulphuric and acetic acids are also formed. The sulphonyl chloride is also produced in glacial acetic acid solution, whereas *heptachlorodiethyl sulphide*, b. p. 35—36°/9 mm., is obtained in presence of carbon tetrachloride. Hypochlorous acid and trithioacetaldehyde give α -chloroethane- α -sulphonyl chloride, but the formation of sulphuric and acetic acids is more marked, in harmony with the observation that the sulphonyl chloride is much more readily oxidised by hypochlorous acid than by chlorine water. α -Chloroethane- α -sulphonamide, m. p. 66°, and α -chloroethane- α -sulphonphenylhydrazide are described. The chloride is hydrolysed by water to α -chloroethane- α -sulphonic acid; the *potassium*, *sodium*, *ammonium*, *barium*, and *silver* salts have been prepared. Treatment of the chloride with anhydrous methyl or ethyl alcohol affords α -chloroethane- α -sulphonic acid in place of the expected ester. *Methyl α -chloroethane- α -sulphonate* can be obtained by use of sodium methoxide, but the simultaneous production of sodium α -chloroethane- α -sulphonate shows that the reaction partly follows the course $CHMeCl \cdot SO_2 \cdot OMe + Me \cdot ONa = CHMeCl \cdot SO_2 \cdot ONa + Me_2O$. Phosphorus pentachloride attacks α -chloroethane- α -sulphonyl chloride with difficulty, yielding ethylidene chloride. Treatment of the chloride with zinc dust in alcohol or acetone, but not in completely anhydrous solvents such as benzene or chloroform, affords *potassium ethanesulphonate*, m. p. 285—286°.

H. WREN.

Preparation of carboxylic anhydrides without the use of phosphorus chlorides. T. PYTASZ and T. I. RABEK (Przemysł Chem., 1930, 14, 529—535).—Pure acetic anhydride may be prepared by allowing sodium chlorosulphonate to react with sodium acetate in acetic anhydride solution, and distilling the product under diminished pressure.

R. TRUSZKOWSKI.

Decomposition of acetic acid in the presence of silica gel. J. A. MITCHELL and E. E. REID (J. Amer. Chem. Soc., 1931, 53, 338—343).—A maximum yield (about 28% on acid used) of acetone is obtained when acetic acid is passed over silica gel at 430—460°. The rate of decomposition of the acetone produced is appreciable above 400°; the presence of water vapour retards this decomposition (cf. Kultashev and Kudrjavzeva, A., 1925, ii, 881). It is calculated from the amount of carbon dioxide produced, in conjunction with the acetone isolated, that 40—60% of the acetone originally formed is decomposed. Some decomposition of the acid into methane and carbon dioxide takes place.

H. BURTON.

Drop reactions for acetic and propionic acids. D. KRÜGER and E. TSCHIRCH (Mikrochem., 1930, 8, 337—338).—The method previously described (A., 1930, 62) may be employed as a drop reaction by adding to the neutral solution 5% lanthanum nitrate solution, 0.01*N*-alcoholic iodine solution and, after mixing, *N*-ammonia solution. The limit of sensitivity is about 0.05 mg. for both acids. H. F. GILLBE.

Partial hydrogenation of linolenic acid and its esters. T. P. HILDITCH (Chem. Umschau, 1930, 37, 354—356).—A reply to Bauer and Ermann (A., 1930, 1271). The results of Hilditch and Vidyarthi (A., 1929, 423) are justified, and the discrepancy between these and the results of Bauer is probably ascribable to differences in the conditions of hydrogenation, e.g., temperature, quantity and activity of the catalyst; further, hydrogenation of esters (cf. Bauer) may proceed differently from the hydrogenation of the free acid. E. LEWKOWITSCH.

[Partial hydrogenation of linolenic acid and its esters.] H. K. BAUER (Chem. Umschau, 1930, 37, 356; cf. preceding abstract).—The experiments (A., 1930, 1271) were made with linolenic esters.

E. LEWKOWITSCH.
Bromides of elæostearic acid. I. Hexabromide. J. VAN LOON (Rec. trav. chim., 1931, 50, 32—36).—When a solution of either α - or β -elæostearic acid and the theoretical quantity of bromine in carbon tetrachloride is submitted to the action of ultraviolet light, a portion of the solvent evaporated, and the residue cooled to -20° , a crystalline hexabromide, m. p. 157° , is obtained, the residue being a liquid hexabromide contaminated with bromine substitution products. The same crystalline hexabromide is similarly obtained from the solid tetrabromide, m. p. 114° . Debromination of either the solid or liquid hexabromide with zinc and alcoholic hydrogen chloride and subsequent hydrolysis of the ester formed affords β -elæostearic acid in quantitative yield.

J. W. BAKER.
 $\alpha\alpha'$ -Dimethyl- and $\alpha\alpha'$ -dibromo- $\alpha\alpha'$ -dimethyl-suberic acids. C. C. STEELE (J. Amer. Chem. Soc., 1931, 53, 283—289).—Ethyl methylmalonate (2 mols.), prepared by way of ethyl α -bromo- and α -cyano-propionate, is condensed with tetramethylene bromide (1 mol.), yielding a mixture of ethyl methyl- Δ^2 -butenyl-malonate and ethyl $\alpha\zeta$ -dimethylhexane- $\alpha\zeta\zeta$ -tetracarboxylate (40% yield), b. p. 210 — $217^\circ/6$ mm.. When the corresponding acid is heated, a mixture of $\alpha\alpha'$ -dimethylsuberic acids, m. p. 91 — 92° and 132 — 133° , is obtained. Bromination of either form in presence of thionyl chloride gives the same $\alpha\alpha'$ -dibromo- $\alpha\alpha'$ -dimethylsuberic acid, m. p. 200 — 201° . When this acid or its methyl ester, b. p. 216 — $219^\circ/30$ mm., is treated with copper-bronze or "molecular" silver, ring closure to a cyclohexane derivative does not take place.

H. BURTON.
Decomposition of citric acid by sulphuric acid. E. O. WING.—See this vol., 315.

Humic acid. J. LUBERTINO (Univ. nac. La Plata fac. agron., 1930, 96 pp.).—A discussion.

CHEMICAL ABSTRACTS.

Propane- $\alpha\beta$ -dithiolacetic acid and propane- $\alpha\beta$ -disulphonylacetic acid. J. A. REUTERSKIÖLD (J. pr. Chem., 1931, [ii], 129, 121—128).— $\alpha\beta$ -Dithiolpropane, prepared by interaction of sodium hydrogen sulphide and $\alpha\beta$ -dibromopropane in alcoholic solution and subsequent purification through the lead salt, yields with concentrated aqueous sodium chloroacetate propane- $\alpha\beta$ -dithiolacetic acid, m. p. 32 — 35° . Thionyl chloride forms the acid chloride, which gives the dianilide. The copper salts $C_7H_{10}O_4Cu.H_2O$ and $C_{14}H_{22}O_8S_4Cu$ and the silver salt have been prepared. The partial resolution of the acid is described. A 15% neutral solution of propane- $\alpha\beta$ -dithiolacetic acid saturated with magnesium sulphate is oxidised by solid permanganate at 0° to propane- $\alpha\beta$ -disulphonylacetic acid, m. p. 185 — 186° . An excess of alkali decomposes it to sulphinoacetic acid and Δ^2 -propenyl- γ -sulphonylacetic acid. When the sodium salt is brominated in aqueous sodium hydrogen carbonate it splits at the double linking and is oxidised, giving finally hexabromodimethyl sulphone, m. p. 131 — 132.5° , and acetic acid.

E. HOPKINS.

Toluene-*p*-sulphonic acid as catalyst in the preparation of acetals. A. JOHANNISSIAN and E. AKUNIAN (Bull. Univ. Etat. R.S.S. Arménie, 1930, No. 5, 235—244; Chem. Zentr., 1930, ii, 552).—In the preparation of acetals from ketones and aldehydes by Claisen's method toluene-*p*-sulphonic acid is preferable as catalyst to hydrochloric acid, sulphuric acid, or ammonium chloride.

A. A. ELDRIDGE.

Gravimetric determination of formaldehyde and hexamethylenetetramine. V. IONESCU and C. BODEA (Bull. Soc. chim., 1930, [iv], 47, 1408—1419).—In the gravimetric determination of formaldehyde with methone (5:5-dimethyldihydroresorcinol) the cold neutral solution free from all other aldehydes is treated with 5—10% excess of methone for 6 hrs. at 20° with occasional agitation. Alternatively the mixture is boiled for 10 min. and then cooled and filtered on a Gooch crucible after $\frac{1}{2}$ hr. and the residue dried at 110 — 115° . If the boiling is continued beyond 15 min. low results are obtained owing to decomposition of the methylenebisdimethyldihydroresorcinol. In acid solution the reaction is not quantitative. Similarly hexamethylenetetramine can be determined in dilute neutral aqueous solution by agitating and boiling for 10 min. with 5—10% excess of methone, and after cooling and keeping for 30 min., collecting the methylenebisdimethyldihydroresorcinol, and drying at 110 — 115° for 1—3 hrs. The reaction time depends on the temperature and at 20° is incomplete in 10 hrs. The method is less accurate for amounts of hexamethylenetetramine above 0.5 g. and accurate results are not obtained in acid solution.

R. BRIGHTMAN.

β -Methyl- Δ^2 -butenal. F. G. FISCHER, L. ERTEL, and K. LÖWENBERG (Ber., 1931, 64, [B], 30—34).—*iso*-Valeraldehyde, prepared from fermentation amyl alcohol, is brominated in chloroform at -25° while irradiated with a powerful Osram lamp, and subsequently treated with ethyl alcohol, thus yielding α -bromo- β -methylbutaldehyde diethylacetal, b. p. 88 — $89^\circ/13$ mm., d_4^{20} 1.1772, n_D^{20} 1.4489, transformed by

Acetylmannoses. VI. Ring structure of the mannose penta-acetates. P. A. LEVENE and R. S. TIRSON (J. Biol. Chem., 1931, 90, 89—98).—1-Bromotetra-acetyl-*D*-mannose, $[\alpha]_D^{25} +123.2^\circ$ in chloroform, prepared from β -mannose penta-acetate, is converted by zinc dust and 50% aqueous acetic acid into triacetylglucal, m. p. 54—55°, $[\alpha]_D^{25} -16.3^\circ$ in alcohol, and by silver acetate in toluene at 95° into α -mannose penta-acetate. The action of silver carbonate in toluene gives a 2:3:4:6-tetra-acetylmannose, m. p. 93°, $[\alpha]_D^{25} +26.3^\circ$ in chloroform, different from the 2:3:4:6-tetra-acetylmannose of Micheel and Micheel (A., 1930, 455); on acetylation this is converted into the original β -mannose penta-acetate. The action of dry sodium methoxide on the bromo-acetylmannose in chloroform gives the tetra-acetylmethylmannoside, m. p. 104—105°, $[\alpha]_D^{25} -22.6^\circ$ in chloroform, of Freudenberg (*ibid.*, 894). Change of structure is unlikely during glucal formation in view of the pyranoside structures of both glucal (Bergmann and Freudenberg, *ibid.*, 70) and bromotetra-acetylglucose; consequently the authors, in contrast to Hudson (*ibid.*, 747), consider that β -*D*-mannose penta-acetate, like the α -compound, has a pyranoside structure. H. A. PIGGOTT.

Methylated tri- and tetra-saccharides from cellulose and starch. K. FREUDENBERG and K. FRIEDRICH (Naturwiss., 1930, 18, 1114; cf. A., 1930, 1412).—*Tridecamethyl- β -methylcelloetraoside*, b. p. 265—275°/0.1 mm., m. p. 139°, $[\alpha]_{D^{18}} -14.6^\circ$ in water, is described. From the decomposition products of acetylated starch are obtained, after methylation, completely corresponding fractions of the same b. p., which are non-crystallisable. The *methylated tri- and tetra-saccharide* have $[\alpha]_{D^{18}} +133^\circ$ and $+140^\circ$ in water, respectively. W. R. ANGUS.

Syntheses of a tetrasaccharide acetate. B. HELFERICH and R. GOOTZ (Ber., 1931, 64, [B], 109—114; cf. A., 1928, 1224; 1930, 748).—*Gentiobiosido- β -D-glucose hendeca-acetate*, m. p. 219—220°, prepared in 59% yield from acetobromogentiobiose and 1:2:3:4- β -tetra-acetyl-*D*-glucose in chloroform in presence of silver carbonate, anhydrous calcium chloride, and iodine, is transformed by hydrogen bromide into *acetobromogentiobiosido-D-glucose*, m. p. 193—194°, $[\alpha]_D^{25} +63.3^\circ$ in chloroform. 1:2:3:4- β -Tetra-acetyl-*D*-glucose transforms the acetobromotrisaccharide into β -*gentiobiosido- β -gentiobiose tetra-deca-acetate*, m. p. 207—209° (corr.) after softening at 135°, $[\alpha]_D^{25} -11.1^\circ$ in chloroform. The free tetrasaccharide shows little tendency to crystallise. The small solubility of the acetate in alcohol is remarkable. The difficulty of obtaining such sugar acetates in a homogeneous state is illustrated by the observation that although analyses and determination of mol. wt. and acetyl groups and of specific rotation give concordant results after 8—12 crystallisations, a constant solubility is attained only after 20 crystallisations. H. WREN.

Constitution of corchorin, the active principle of jute seeds (*Corchorus capsularis*). I. N. K. SEN (J. Indian Chem. Soc., 1930, 7, 905—911).—Corchorin (A., 1930, 826) [*penta-acetyl derivative*, m. p. 158° (decomp.); *bromo-derivative dibromide*,

m. p. 100° (decomp.)] is hydrolysed by 10% sulphuric acid to dextrose and *corchogenin*, $C_{16}H_{28}O_9$, m. p. 112—114° (decomp.) after shrinking at 84° [*dibromide*, m. p. 130—132° (decomp.)]. Corchogenin contains a lactone grouping, does not give an oxime or semicarbazone, does not contain an alkoxy-group, affords an amorphous product, m. p. 165—170° (decomp.), when treated with phenylhydrazine, and is oxidised by potassium permanganate in acetone to *corchoric acid*, $C_{15}H_{24}O_5$, m. p. 67—70°, decomp. 94°. Similar oxidation of corchorin affords *glucocorchoric acid*, $C_{21}H_{34}O_{10}$, m. p. 146—148°, hydrolysed by dilute hydrochloric acid to dextrose and corchoric acid.

H. BURTON.

Processes taking place when polysaccharides are heated in glycerol. H. PRINGSHEIM (Helv. Chim. Acta, 1931, 14, 57).—The author's method of depolymerisation of polysaccharide acetates does not involve the use of glycerol. The criticisms of Karrer and von Krauss (A., 1930, 1415) do not, therefore, apply to his results. H. BURTON.

Autohydrolysis of diastatic dextrans. J. EFFRONT (Compt. rend., 1931, 192, 198—201).—The difficulties experienced in purifying dextrin are due to the formation of maltose by the action of the solvents used. The treatment of dextrin with successive quantities of water increases, particularly when the dilution is high, not only the reducing power of the extract, as measured by its maltose content, but also the reducing power of the residue. The changes which dextrin undergoes on purification were studied by repeated extractions with alcohol followed by an extraction with cold water, evaporating the filtrate to dryness, and again treating with alcohol, the maltose content being measured at the various stages. The reducing power of a dextrin is closely related to its mol. wt. In the saccharification of starch, the reducing dextrin first formed breaks down to give maltose. A. RENFREW.

Amyloid from cellulose. JUSTIN-MUELLER (Bull. Soc. chim., 1930, [iv], 47, 1400—1404).—When 5.82 parts of cellulose (white filter-paper) are treated with 100 parts of sulphuric acid (*d* 1.58) and poured into a large excess of water, cellulose-amyloid is obtained as a powder. The acid and neutral (washed) pastes are insoluble in ammonia, sodium or potassium carbonate, acetic acid, acetone, or ether-alcohol, and are soluble in ammoniacal copper oxide (Péligot's reagent), but are distinguished from cellulose by their solubility in dilute sodium or potassium hydroxide and blue coloration given with iodine in iodide solution. Unlike hydrocellulose, cellulose-amyloid does not reduce Fehling's solution, and on drying is converted by polymerisation and increased cohesion into a dry product which is not completely soluble in concentrated sodium and potassium hydroxides or in boiling ammoniacal copper oxide. The formation of the amyloid from cellulose thus involves successive dehydration, molecule scission in acid media, hydration in aqueous medium, and finally polymerisation. R. BRIGHTMAN.

Distillation products of cellulose. H. B. ARBUCKLE and H. S. DAVIDSON (J. Elisha Mitchell Sci. Soc., 1929, 45, 147—149).—Distillation of

cellulose in a vacuum affords formaldehyde, acetone, diacetyl, formic and acetic acids, phenol, *p*-cresol, pyrocatechol, and guaiacol.

CHEMICAL ABSTRACTS.

Structure of cellulose nitrates. DESMAROUX and MATHIEU.—See this vol., 290.

α - and β -Lignosulphonic acids. P. KLASON (Svensk Kem. Tidskr., 1930, 42, 259—263).—In sulphite waste liquors only 70% of the lignosulphonic acids present can be precipitated by a naphthylamine salt; the unprecipitated acid has been called β -lignosulphonic acid, and the corresponding lignin β -lignin. This latter contains only half the amount of methoxyl found in α -lignin. By precipitation of the β -acid with lead acetate, removal of the lead by hydrogen sulphide, and oxidation with hydrogen peroxide a salt can be obtained on the addition of a naphthylamine salt resembling that of the α -acid, but containing only half as much methoxyl. The β -acid has the formula $C_{19}H_{18}O_6$, that of the corresponding β -lignin being $C_{19}H_{20}O_6$, i.e., a combination of coniferyl alcohol and dihydroxycinnamaldehyde. A solution of the β -acid containing a little hydrochloric acid gives on evaporation to dryness at 60° a dark brown mass, soluble in water to a brown viscous solution which is precipitable by a naphthylamine salt. Analysis of this precipitate gave a formula $C_{46}H_{49}O_{18}NS$ ($=4C_9H_8O_3 + H_2SO_3 + C_{10}H_9N + 3H_2O$). The nature and production of these substances in the cellulose process are discussed.

H. F. HARWOOD.

Phospho- and silico-tungstates of some quaternary bases: analytical applications. L. LEMATTE, G. BOINOT, E. KAHANE, and (MME.) M. KAHANE (Compt. rend., 1930, 191, 1130—1132).—Analysis of the phospho- and silico-tungstates of choline, acetylcholine, α -methylcholine, α -methylacetylcholine, bromocholine, the ethyl ether of betaine, and trimethylallylammonium show that these compounds are anhydrous, and have the general formulæ $12WO_3 \cdot PO_4(NR'R''R''')_3$ and $12WO_3 \cdot SiO_2(NR'R''R''')_4$, respectively, thus disagreeing with Drummond's results (cf. A., 1918, i, 336). The purity attained and constancy of composition are sufficient for their use in the determination of these bases with an accuracy of 2—3%.

C. A. SILBERRAD.

Adrenaline as oxidation catalyst. G. BLIX (Skand. Arch. Physiol., 1929, 56, 131—171; Chem. Zentr., 1930, ii, 903).—Glycine, *d*-alanine, valine, and leucine undergo oxidative deamination by molecular oxygen at 40° in presence of adrenaline. Pyrocatechol, quinol, resorcinol, pyrogallol, and phloroglucinol are also catalytically active. The optimal p_H is 10; amino-acids are measurably oxidised in presence of adrenaline at physiological p_H values. Glycine affords carbon dioxide and formic acid; alanine affords acetaldehyde.

A. A. ELDRIDGE.

Ethyl aminomalonate. Action of alkyl iodides and bromides on ethyl sodioaminomalonate. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1930, 47, 1377—1380).—The reactions of ethyl aminomalonate are reviewed. The sodium derivative reacts with alkyl halides, giving the corresponding alkyl derivative in 50% yield. R. BRIGHTMAN.

Aminoalkylmalonic esters and their derivatives. V. CERCHEZ (Bull. Soc. chim., 1930, [iv], 47, 1381—1385).—Ethyl sodioaminomalonate is obtained by addition of the ester to a solution of sodium ethoxide, or by addition of sodium to a solution in ether; the reaction is slower in methyl isoamyl ether, and does not occur in *n*-butyl ether. With isobutyl iodide ethyl sodioaminomalonate gives 55% of ethyl α -amino- α -isobutylmalonate, b. p. 136°/14 mm. (carbamide, m. p. 194°; phenylcarbamide, m. p. 128°; diamide, m. p. 153°). Ethyl- α -amino- α -allylmalonate, b. p. 134—135°/17 mm. (carbamide, m. p. 173—174°; phenylcarbamide, m. p. 113°), and ethyl amino- α -benzylmalonate (carbamide, m. p. 234°; diamide, m. p. 156°) are similarly obtained.

R. BRIGHTMAN.

Preparation of α -amino-acids by hydrolysis of aminoalkylmalonic esters. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1930, [iv], 47, 1386—1389).—Hydrolysis of aminoalkylmalonic esters with water at 150° or with 10% hydrochloric acid affords α -amino-acids in good yields. Ethyl aminomalonate with water at 150° gives 90% of ethyl aminoacetate and with 10% hydrochloric acid, glycine hydrochloride. Leucine, phenylalanine, and α -amino- Δ^5 -pantoic acid, decomp. about 250°, are similarly obtained.

R. BRIGHTMAN.

Cystine and its absorption spectrum. D. BARNES (Anal. Fis. Quim., 1930, 28, 1386—1406).—The different types of cystine crystal obtained by crystallisation from solutions of various p_H are illustrated; the best yield of cystine is obtained at a definite p_H which is dependent on the concentration of the solution, varying from 4 to 6.5 as the cystine concentration changes from 1.5 to 0.5%. The absorption spectra of hydrochloric acid solutions of cystine and of alanine have been examined at wavelengths from 2300 to 4000 Å. and from 2100 to 3800 Å., respectively. The molecular absorption coefficient-wave-length curves for the two compounds are similar and agree with those obtained by Ward (A., 1924, i, 272); the extinction coefficients increase continuously with decrease of wave-length, and there is no evidence of selective absorption. The structure of cystine is aliphatic, and not cyclic as suggested by Ward. From the wave-length at which absorption commences the heat of dissociation of cystine has been calculated to be 70.8 kg.-cal./mol., and that of alanine 83 kg.-cal./mol. It is suggested that the cystine molecule is easily ruptured at the S-S linking.

H. F. GILLBE.

Crystallised alkali salts of *l*-cystine. G. TOENNIES and T. F. LAVINE (J. Biol. Chem., 1931, 90, 203—213; cf. Voss and Guttmann, A., 1930, 1170).—The sodium (+1H₂O), $[\alpha]_D^{25}$ —89.6° in water (calculated on free cystine), —265° in methyl alcohol, potassium, $[\alpha]_D^{25}$ —88.9° in water, —254° in methyl alcohol, and lithium, $[\alpha]_D^{25}$ —113.5° in water, salts of *l*-cystine are prepared by precipitation of alkaline alcoholic cystine solutions with acetonitrile. They are stable in aqueous solution, and regenerate cystine (determined polarimetrically) completely on acidification, but the sodium and potassium salts decompose in methyl-alcoholic solution with liberation of ammonia.

H. A. PIGGOTT.

Synthesis of cyanic acid and carbamide by the ammoniacal oxidation of carbon. G. LAUDE (Compt. rend., 1930, 191, 1135—1137; cf. A., 1921, i, 652).—Carbon derived from (a) camphor and (b) acetylene, 95.97—97 and 98.2—99.06% C, respectively, has been oxidised in quantities of 0.1 g. at a time by means of 1 g. of copper, 30 c.c. of concentrated ammonia, and 20 g. of potassium permanganate (added in four portions) at 40—45°, the period of oxidation being about 30 hrs. The product from (a) gave 11.39% of cyanic acid, that from (b) 6.3%.

C. A. SILBERRAD.

Chlorates and perchlorates of some bases prepared from calcium cyanamide. S. MICEWICZ (Przemysł Chem., 1926, 10, 56—58, 136—137; Chem. Zentr., 1930, ii, 379).—Dicyanodiamidine chlorate, $C_2H_7O_4N_4Cl$, decomposes at 129—130°; perchlorate, subl. above 260°, and explodes on continued heating. Guanidine chlorate, $CH_6O_3N_3Cl$, m. p. 100—101°, is less stable than the perchlorate, m. p. 245—246°. Carbamide is soluble in dilute chloric acid, explosive decomposition occurring at 40—50°; the perchlorate, hygroscopic, has m. p. 66—67°. Thiocarbamide is vigorously decomposed by chloric acid; the hygroscopic perchlorate, m. p. 106—107°, explodes when heated.

A. A. ELDRIDGE.

Action of thionyl chloride on anilic acids. W. H. WARREN and R. A. BRIGGS (Ber., 1931, 64, [B], 26—30).—Anilic acids become converted into anils when boiled with eight times their weight of thionyl chloride until evolution of sulphur dioxide and hydrogen chloride ceases. The following examples are cited: oxanilic acid, m. p. 149°, into *oxanil*, not melted below 320°; malonanilic acid into *malonanil*, m. p. 249°; succinanilic acid into *succinanil*, m. p. 156°; glutaranilic acid, m. p. 126—127°, into *glutaranil*, not molten below 320° [possibly a polymeride of the glutaranil, m. p. 144—145°, obtained by Bödtker (Diss., Leipzig, 1891) from aniline and glutaric acid]; phthalanilic acid, m. p. 158°, into *phthalanil*, m. p. 203°; camphoranilic acid into *camphoranil*, m. p. 116°; *diphenanilic acid*, m. p. 176°, from the anhydride and aniline in benzene, into *diphenanil*, m. p. 199°.

H. WREN.

Silica gel as a catalyst in the preparation of nitriles. J. A. MITCHELL and E. E. REID (J. Amer. Chem. Soc., 1931, 53, 321—330).—When acetic acid and ammonia (excess) are passed over silica gel (activated by heating at 210° in a current of dry air) at about 500° with a contact time of 25 sec., the yield of acetonitrile is almost quantitative. Above 500°, the catalyst is poisoned, the yield diminishes, and ammonium carbonate is produced. The commercial and pure silica gels have the same order of activity. The following nitriles are prepared similarly from the appropriate acids (the figures in parentheses are the percentage yields): propionitrile (85), butyronitrile (90), *n*-valeronitrile (80), isovaleronitrile (94), hexonitrile (90), heptonitrile (93), dodeconitrile (55), phenylacetoneitrile (87), and β -phenylpropionitrile (81). No nitrile could be obtained from palmitic acid. Acetonitrile, butyronitrile, and benzonitrile are obtained in yields of 87, 75, and 77%, respectively, when *n*-butyl acetate and butyrate, and ethyl benzoate

are passed over silica gel with an excess of ammonia. The rates of hydrolysis of benzamide by water and of the formation of acetamide from ammonium acetate are not affected by silica gel; the catalyst is effective only in the dehydration of the amides.

H. BURTON.

Catalytic dehydrogenation of dicyclic hydrocarbons. N. D. ZELINSKI and I. N. TITZ (Ber., 1931, 64, [B], 183—188; cf. A., 1926, 277).—*cyclopentyl* chloride and benzene in presence of aluminium chloride yield *phenylcyclopentane*, b. p. 217°, d_4^{20} 0.9474, n_D^{20} 1.5280, hydrogenated at 220—225° in presence of platinised charcoal to *cyclohexylcyclopentane*, b. p. 214°, d_4^{21} 0.8780, n_D^{21} 1.4728; at 300°, the last-named compound is dehydrogenated to *phenylcyclopentane*. *Phenylcyclopentylmethane*, b. p. 233—235°, d_4^{21} 0.9345, n_D^{21} 1.5206, prepared in addition to dibenzyl and a little *dicyclopentyl* by the action of sodium on benzyl and *cyclopentyl* chlorides, is stable in presence of platinised charcoal at 300°. When hydrogenated at 220°, it passes into *cyclohexylcyclopentylmethane*, b. p. 225—227°, d_4^{21} 0.8789, n_D^{21} 1.4775, dehydrogenated at 300° to *phenylcyclopentylmethane*. The pentamethylene ring, even when a component of a dicyclic system, is therefore stable to dehydrogenation.

Repetition of the previous work (*loc. cit.*) shows that the product of the action of magnesium *cyclohexyl* bromide on *cyclopentanone* is almost exclusively *dicyclohexyl* (formed from the halide by the Würtz-Fittig reaction) and that the dehydrogenated product previously described is diphenyl. The expected tertiary alcohol is obtained only in minimal amount from magnesium *cyclopentyl* chloride and *cyclohexanone* or from magnesium *cyclohexyl* bromide and 3-methylcyclopentanone.

H. WREN.

Alleged electrochemical sulphonation of an aromatic hydrocarbon. F. FICHTER, H. E. SUENDERHAUF, and A. GOLDACH (Helv. Chim. Acta, 1931, 14, 249—253).—The sulphur-containing acid produced during the electrochemical oxidation of toluene in presence of alcohol and sulphuric acid is not *p*-sulphobenzoic acid as stated by Puls (A., 1901, i, 318), but is ethylsulphuric acid. The same acid (isolated as the barium salt) is formed from alcohol and sulphuric acid in absence of toluene.

Maleic and fumaric acids are produced during the electrochemical oxidation of acetophenone in presence of *N*-sulphuric acid.

H. BURTON.

Decomposition of phenyl iodide dichloride. III. E. V. ZAPPI and V. DEULOFEU (Anal. Asoc. Quim. Argentina, 1930, 18, 124—132; cf. A., 1930, 79).—A reply to Guglielmelli and others (*ibid.*, 758).

R. K. CALLOW.

Preparation and properties of some ethyl arylsulphonates and a comparative investigation of their velocities of hydrolysis with those of the corresponding ethyl arylcarboxylates. L. DEMÉNY (Rec. trav. chim., 1931, 50, 60—71).—The following ethyl arylsulphonates have been prepared by the action of sodium ethoxide on the appropriate sulphonyl chloride in dilute alcoholic solution: ethyl benzene-, *o*-, b. p. 160—163°, m. p. 15°, *m*-, m. p. 42°, and *p*-, m. p. 92°, *-nitrobenzene*-, and *p*-toluene-

sulphonates. In general, the velocity of hydrolysis of the sulphonic esters in 30 vol.-% alcohol in 0.001*N*-alkaline solution is about one tenth that of the corresponding carboxylic ester. With sulphonic esters the effective hydrolysing agent is considered to be water and the velocity depends only slightly on the concentration of alkali used. The mean values for the unimolecular velocity coefficient $k \times 10^4$ in 30% alcohol at 25° for the above sulphonic esters are, respectively, 3.8, 75, 24, 26, and 1.9 (alkalinity 0.001—0.008*N*), the values of the bimolecular coefficient k for the corresponding carboxylates being 0.46, 1.23, 11.4, 19.0, and —, respectively (alkalinity 0.003—0.005*N*). Introduction of a nitro-group in the *m*- or *p*-positions has a similar accelerating effect in both series, but in the *o*-position its effect is small in the case of the carboxylic esters, whilst it has a powerfully accelerating influence in the sulphonic ester series.

J. W. BAKER.

Arylsulphonalkylamides. L. DEMÉNY (Rec. trav. chim., 1931, 50, 51—59).—By the action of an alcoholic solution of the appropriate amine on various arylsulphonyl chlorides a series of arylsulphonalkylamides has been prepared, the following being new: *benzenesulphon-n-hexylamide*, m. p. 17°, and *-n-heptylamide*, m. p. 20°; *p-bromobenzenesulphon-n-amyldamide*, m. p. 55° (not sharp), *-n-hexylamide*, m. p. 55°, and *-n-heptylamide*, m. p. 65°; *p-toluenesulphon-n-butylamide*, m. p. 43°, *-n-amyldamide*, a colourless oil, *-n-hexylamide*, m. p. 62°, and *-n-heptylamide*, m. p. 45°; *mesitylenesulphon-n-propylamide*, m. p. 54°, *-n-butylamide*, m. p. 44°, *-n-amyldamide*, m. p. 42°, *-n-hexylamide*, m. p. 64°, *-n-heptylamide*, m. p. 45°. The m. p. of these derivatives and those previously prepared (A., 1930, 81) are in general agreement with the various laws connecting m. p. and constitution, a minimum value occurring in the case of the *n*-amyldamine derivatives. J. W. BAKER.

Ditolyl series. I. A. ANGELETTI [with A. BRAMBILLA] (Gazzetta, 1930, 60, 967—974).—2-Iodo-2'-nitro-4 : 4'-dimethyldiphenyl (*o*-iodo-*o'*-nitro-ditolyl), m. p. 83—84°, prepared from 2-nitro-2'-amino-4 : 4'-dimethyldiphenyl (cf. Mascarelli and Gatti, A., 1930, 205) by way of the diazo-compound, is accompanied by a small quantity of ditolylene-iodonium iodide (?) and, as in the preparation of the following compounds, by 4 : 4'-dimethyldiphenylene oxide (cf. Niementowski, A., 1902, i, 21). It seems that decomposition of the diazo-nitro-compound gives first the 2'-nitro-2-hydroxy-compound, which loses nitrous acid to form the dimethyldiphenylene oxide. 2-Bromo-, m. p. 73—74°, and 2-chloro-2'-nitro-4 : 4'-dimethyldiphenyl, m. p. 85—86°, were also prepared, but attempts to obtain 2'-nitro-2-hydroxy-4 : 4'-dimethyldiphenyl were unsuccessful. T. H. POPE.

Halogen substitution. II. P. PFEIFFER and P. SCHNEIDER (J. pr. Chem., 1931, [ii], 129, 129—144).—Coloured unstable carbonium salts, similar to those formed from bromine vapour and auxochrome-substituted α -diarylethylenes (cf. A., 1928, 633), are also given by the parent hydrocarbons. The following hydrocarbons were examined as to (a) colour of solutions in sulphuric acid (formation of a carbonium sulphate) and (b) colour produced by bromine vapour

(a perbromide), and were converted by the theoretical amount of bromine in solution into the mono- and di-bromo-substitution products, which were examined similarly: diphenyl- and di-*p*-tolyl-ethylene, no reaction; α -dinaphthylethylene, m. p. 107°, from magnesium naphthyl bromide and ethyl acetate and subsequent dehydration of the *carbinol*, m. p. 146°, formed, (a) deep malachite-green, (b) indistinct red; β -bromo- α -dinaphthylethylene, m. p. 148°, (a) bluish-green, (b) reddish-brown; tetrabromo- α -dinaphthylethylene, m. p. 69—70°, from the hydrocarbon and excess bromine in chloroform, (a) intense grass-green; *p*-diphenylphenylethylene, m. p. 94—95°, from the corresponding ketone and magnesium methyl iodide (cf. Schlenk and Bergmann, A., 1928, 1031), (a) cherry-red, (b) grass-green; β -bromo- α -*p*-diphenylphenylethylene, m. p. 162°, (a) reddish-violet, (b) dark violet; β -dibromo- α -*p*-diphenylphenylethylene, m. p. 155°, (a) reddish-violet; di-*p*-diphenylethylene, m. p. 211°, (a) reddish-violet, (b) deep green; β -bromo- α -di-*p*-diphenylethylene, m. p. 187—188°, (a) green, changing to bluish-green on warming; with oleum deep blue, and (b) reddish-brown; β -dibromo- α -di-*p*-diphenylethylene, m. p. 194—195°, α -di-*p*-diphenyl- Δ^a -propene, m. p. 165—166°, (a) deep reddish-violet, (b) deep green; β -bromo- α -di-*p*-diphenyl- Δ^a -propene, m. p. 150—152°, (a) bluish-violet on warming, (b) greyish-black; α -phenyl- β -di-*p*-diphenylethylene, m. p. 192—193°, (a) violet, (b) grass-green; α -bromo- α -phenyl- β -di-*p*-diphenylethylene, m. p. 201—202°, (a) deep bluish-green with oleum. An attempt to produce α -dinaphthyl- β -phenylethylene from phenylethyl acetate and magnesium naphthyl iodide yielded only diphenylacetoacetic ester.

E. HOPKINS.

2-Phenyl-1 : 1-dimethylindene. J. C. EARL and C. A. SMYTHE (J. Proc. Roy. Soc. New South Wales, 1930, 44, 90—95).—Aluminium bromide can be used in the same way as aluminium chloride for the removal of aromatic hydrogen (cf. Scholl, A., 1913, ii, 56, 734; 1922, i, 258, 261, 331, 336), and can also be used for the removal of aliphatic hydrogen. The interaction of aluminium bromide, trimethylethylene dibromide, and benzene yields 2-phenyl-1 : 1-dimethylindene, m. p. 51°, b. p. 190—205°/36—38 mm., which, according to conditions, is oxidised to phthalic acid or *o*- α -benzoyl- α -methylenebenzoic acid, m. p. 198°, converted by acetic anhydride into 3-acetoxy-3-phenyl-4 : 4-dimethyl-3 : 4-dihydrobenzisopyrone, m. p. 137°. 3-Nitro-2-phenyl-1 : 1-dimethylindene, m. p. 139—140°, is described. G. DISCOMBE.

Reduction of naphthalene by alkali metals in liquid ammonia. C. B. WOOSTER and F. B. SMITH (J. Amer. Chem. Soc., 1931, 53, 179—187).—Determinations of the amount of hydrogen (or ethane) evolved when the reaction mixtures from naphthalene and excess of sodium in liquid ammonia are treated with ammonium bromide (or ethyl bromide) indicate that 4 atoms of the metal per 1 mol. of naphthalene are consumed. Hydrolysis of the resultant sodio-derivative gives 1 : 2 : 3 : 4-tetrahydronaphthalene, indicating that the sodium atoms add in the 1 : 2 : 3 : 4-positions. This tetrasodio-derivative is shown to be approximately three quarters ammono-

lysed in solution at -33.5° , by determinations of the amounts of sodium peroxide (from the excess of sodium) and nitrite (from sodamide) formed when the reaction mixture is oxidised with oxygen. Potassium and naphthalene react in essentially the same manner. The results support Willstätter, Seitz, and Bumm's theory (A., 1928, 756) of reductions using sodium amalgam. Those hydrocarbons, including naphthalene, shown by Lebeau and Picon (A., 1914, i, 825, 946) to be reducible by sodium and liquid ammonia, all furnish alkali metal additive compounds.

H. BURTON.

Interaction of *tert*-butyl chloride and naphthalene. W. GUMP (J. Amer. Chem. Soc., 1931, 53, 380—381).—When *tert*-butyl chloride (2 mols.) is heated with naphthalene (1 mol.) in presence of a small amount of aluminium chloride, a mixture of two *ditert*-butylnaphthalenes, b. p. 319° , m. p. $82-83^{\circ}$, and b. p. 320° , m. p. $145-146^{\circ}$, separable by fractional crystallisation from alcohol, is obtained. These are probably identical with the supposed 1:2'- and 1:1'-dinaphthyls of Wegscheider (A., 1884, 1185), obtained during the reaction between naphthalene and isobutyl chloride. A *tert*-butylnaphthalene could not be prepared from equimolecular amounts of the reactants.

H. BURTON.

Anthracene derivatives. III. E. DE B. BARNETT and J. A. LOW (Ber., 1931, 64, [B], 49—56).—In spite of the impossibility of a *peri*-co-ordination, the derivatives of 1:4-dimethylantracene resemble the corresponding derivatives of 1:4-, 1:5-, and 4:5-dichloro- and 1:5-diphenoxy-anthracene much more closely than those of anthracene itself. Since the assumption that the departure from "normal anthracene properties" is conditioned by different factors in the methyl and chloro-derivatives appears unjustifiable, the hypothesis of a *peri*-co-ordination is considered untenable in spite of the numerous observations in its favour.

o:2:5-Dimethylbenzoylbenzoic acid, m. p. 149° , prepared from phthalic anhydride and *p*-xylene in presence of aluminium chloride, is reduced by activated zinc dust, sodium hydroxide, and ammonia to *o*:2:5-dimethylbenzylbenzoic acid, m. p. 136° , converted by hot 80% sulphuric acid into 1:4-dimethylantrone, m. p. 116° . 1:4-Dimethylanthranyl acetate, from the anthrone by pyridine and acetic anhydride, has m. p. 162° . Reduction of 1:4-dimethylantrone with activated zinc dust and ammonia gives 1:4-dimethyl-9:10-dihydroanthranol, m. p. 134° , from which 1:4-dimethylantracene, m. p. 76° , is derived. Successive treatment of 1:4-dimethylantrone with magnesium methyl iodide and with hydrochloric acid in glacial acetic acid yields 1:4:9-trimethylantracene, m. p. 81° . 9-Benzyl-1:4-dimethylantracene, m. p. 135° , is converted by bromine in carbon disulphide into 10-bromo-9-benzylidene-1:4-dimethyl-9:10-dihydroanthracene, m. p. 180° , from which the corresponding 10-piperidino-, m. p. 150° , 10-methoxy-, m. p. $118-119^{\circ}$, and 10-ethoxy-, m. p. 130° , derivatives are obtained. 10-Bromo-1:4-dimethylantrone, decomp. about 160° , is transformed into 10-piperidino-1:4-dimethylantrone, m. p. 133° , 10-anilino-1:4-dimethylantrone, m. p. 192° , 10-methylanilino-1:4-dimethyl-

anthrone, m. p. 179° , 10-*p*-dimethylaminophenyl-1:4-dimethylantrone, m. p. 154° , and 10-methoxy-1:4-dimethylantrone, m. p. 76° . 10-Bromo-1:4-dimethylantrone is converted by benzene and aluminium chloride into 10-phenyl-1:4-dimethylantrone, m. p. 144° , which when treated successively with magnesium methyl iodide and hydrochloric acid in glacial acetic acid gives 10-phenyl-1:4-dimethyl-9-methylene-9:10-dihydroanthracene, m. p. 129° , oxidised by chromic acid to 10-phenyl-1:4-dimethylantrone. 10-Phenyl-9-benzylidene-1:4-dimethyl-9:10-dihydroanthracene, m. p. 170° , is described. 9:10-Diphenyl-1:4-dimethylantracene, m. p. 189° , is derived from 10-phenyl-1:4-dimethylantrone.

H. WREN.

Fluoranthene. O. KRUBER (Ber., 1931, 64, [B], 84—85).—Treatment of a neutral tar-oil fraction, b. p. $370-390^{\circ}$, with sodium in solvent naphtha at 160° yields a solid sodium derivative from which tetrahydrofluoranthene, m. p. 75° , is obtained after decomposition with water; the filtrate from the sodium compound readily affords pyrene. Oxidation of tetrahydrofluoranthene with sodium dichromate in glacial acetic acid gives (?) fluorenone-8-propionic acid, m. p. $137-138^{\circ}$. Tetrahydrofluoranthene unites with sodium and the mixture of compounds is transformed by carbon dioxide into carboxylic acids, from which an acid, $C_{17}H_{14}O_2$, m. p. 188° after softening, is obtained; when heated above its m. p. or distilled with lime, it affords tetrahydrofluoranthene. It is unlikely that the tar-oil fraction contains tetrahydrofluoranthene.

H. WREN.

Method of reducing aromatic nitro-compounds. T. E. DE KIEWIET and H. STEPHEN (J.C.S., 1931, 82—84).—Crystalline stannous chloride ($SnCl_2 \cdot 2H_2O$) is heated with excess of acetic anhydride until completely dehydrated; the resulting solution reduces nitro-compounds to acetamido- or, often where possible (exceptions are *m*-chloronitrobenzene, the nitrobenzoic acids, and *o*-nitrophenol), to *p*-chloroacetamido-compounds. *p*-Chloronitrobenzene gives *p*-chloroacetanilide in absence of free hydrogen chloride, and 2:4-dichloroacetanilide in its presence; *o*-, *m*-, and *p*-nitrobenzoic acids give the corresponding aminobenzoic acids; *p*-nitrophenol and its chloro-derivatives give acetamidophenyl acetates, but *o*-nitrophenol and similar derivatives give acetamidophenols, apparently by hydrolysis of intermediately formed 1-methylbenzoxazoles. 3-Chloro-4-nitrophenol, m. p. 120° , obtained by nitration of *m*-chlorophenol (cf. Uhlemann, Ber., 1869, 2, 1161; Chem. Fabr. Griesheim-Elektron, G.P. 143,449), gives 3-chloro-4-acetamidophenyl acetate, m. p. 127° .

H. A. PIGGOTT.

Hydrogenation of aniline under pressure in the presence of cerium and lanthanum as promoters. V. S. SADIKOV and A. J. SCHAGALOV (J. Russ. Phys. Chem. Soc., 1930, 62, 1635—1642).—The influence of small quantities (1%) of cerium and lanthanum oxides as promoters to the main catalysts (osmium and nickel) in the hydrogenation of aniline under pressure was investigated. With osmium, the addition of cerium oxide does not affect the time of hydrogenation, although the consumption of hydrogen

is decreased. The yield of benzene and *cyclohexylamine* is much greater, whilst that of *dicyclohexylamine* is much less, and more aniline is left unreduced, so that cerium oxide appears to act as an inhibitor on osmium. With nickel instead of osmium, the presence of cerium oxide somewhat improves the final yield, but the main factor in the efficiency of the catalyst appears to be the preliminary heat treatment of the latter, which is rendered more sensitive to it by addition of cerium oxide. If lanthanum oxide is used, this sensitiveness is still further increased, whilst the tendency to promote the condensation of the reduction products is diminished, the *cyclohexylamine* content in the final mixture increasing from 33% in the case of cerium oxide to 71.2% in the case of lanthanum oxide, and that of *dicyclohexylamine* falling from 52% to 33%. M. ZVEGINTZOV.

Action of alcohols and esters on aniline hydrochloride. S. A. BUSSE and A. I. TRAVIN (J. Russ. Phys. Chem. Soc., 1930, 62, 1685—1690).—Aniline hydrochloride and benzyl alcohol when heated together gave a 59% yield of phenylbenzylamine, m. p. 35.5°. Using benzyl acetate, the yield was more than 79%. Oxidation with ferric chloride or sulphate gave benzaldehyde; oxidation with nitrosodimethylaniline gave benzaldehyde together with some azoxydimethylaniline, m. p. 241°. With *n*-octyl alcohol aniline gives *phenyloctylamine*, b. p. 158—158.5°/4 mm., d_4^{20} 0.9089, n_D^{20} 1.5132, which yielded octaldehyde on oxidation.

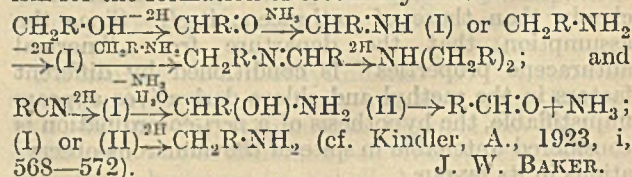
M. ZVEGINTZOV.

Derivatives of 1-chloro-2-nitronaphthalene. A. P. J. HOOGEVEEN (Rec. trav. chim., 1931, 50, 37—40).—2-Acetonaphthalide is converted, through the chloroamine, by an excess of bleaching powder solution in dilute acetic acid in alcohol at 16° into 1-chloro-2-acetonaphthalide, which affords 1-chloro-2-nitronaphthalene (Hodgson and Kilner, A., 1926, 279) after hydrolysis, diazotisation, and treatment of the diazo-solution with potassium nitrite in the presence of cuprous-cupric sulphite. It is converted by heating with an alcoholic solution of the appropriate amine in a sealed tube at 180° into 1-amino-, 1-methylamino-, m. p. 114°, and 1-ethylamino-, m. p. 77°, 2-nitronaphthalene, and by alcoholic sodium disulphide into 2:2'-dinitrodinaphthyl disulphide, m. p. 204°.

J. W. BAKER.

Mechanism of chemical reactions. II. Mechanism of the synthesis of secondary and tertiary amines by reduction. K. KINDLER [with W. DEHN and W. PESCHKE] (Annalen, 1931, 485, 113—126).—Reduction of benzylamine or β -phenylethylamine with palladium-black and hydrogen in boiling alcohol gives, respectively, quantitative and 10% yields of the secondary bases dibenzylamine and di-(β -phenylethyl)amine, the velocity of reduction of benzylamine also being the greater in glacial acetic acid or xylene. Similar reduction of β -phenylethylamine in the presence of benzyl alcohol in xylene affords mainly (90%) *N*-benzyl- β -phenylethylamine (also obtained by catalytic reduction of benzylidene- β -phenylethylamine) and only 6% of di-(β -phenylethyl)amine, determined by the amount of ammonia evolved. Reduction of thiobenzamide with aluminium amalgam and moist ether affords 85% of benzylamine and 8%

of dibenzylamine, and proceeds more rapidly than the similar reduction of phenylthioacetamide, which affords 26% and 66% of the primary and secondary bases, respectively. Reduction of the mixture of α -amino- β -phenylethyl alcohol and phenylacetaldehyde (obtained by the action of ammonia on phenylacetaldehyde) with aluminium amalgam and water affords di-(β -phenylethyl)amine, in addition to the primary base, similar reduction of α -dimethylamino- β -phenylethyl alcohol yielding β -phenylethyldimethylamine (Decker and Becker, A., 1912, i, 844). Reduction of phenylacetonitrile in acetic acid and ammonium acetate with hydrogen and palladium-black at 65°/2.5 atm. gives, in addition to β -phenylethylamine and the corresponding secondary base, β -phenylethylidene- β -phenylethylamine, reduced to di-(β -phenylethyl)amine in 60% yield. The proportion of primary and secondary bases formed depends on the acid present during the reduction and in aqueous-alcoholic ethyl acetate, glacial acetic acid, and acetic acid containing hydrogen chloride, with hydrogen and palladium-black at 35°/2.5 atm., the proportion of these products is 25, 50, and 90% and 70, 40, and 1%, respectively. The much greater velocity of reduction of benzonitrile compared with that of phenylacetonitrile results in the almost exclusive formation of the primary base in the first case, whilst in the latter a large amount of the secondary amine is also formed. Similar reduction of phenylacetonitrile in the presence of dipropylamine affords β -phenylethyldipropylamine in addition to the normal product di-(β -phenylethyl)amine. These results confirm the following mechanism for the formation of secondary bases:



J. W. BAKER.

Conversion of aldehydes into higher molecular amines. A. SKITA, G. PFEIL, and [in part] H. WINKLER (Annalen, 1930, 485, 152—173).—The amine, b. p. 110—112°/15 mm., obtained by catalytic reduction of *n*-propylidenecyclohexylamine (Skita and Wulff, A., 1927, 559) with colloidal platinum in alcoholic acetic acid is cyclohexyl-(β -methyl-*n*-amyl)amine (III) (hydrochloride, m. p. 139°; phenylurethane, m. p. 99°), identical with a specimen obtained by similar reduction of β -methyl- Δ^3 -pentenyldienecyclohexylamine (II), b. p. 118—119.5°/15 mm., obtained by condensation of α -methyl- Δ^3 -pentenaldehyde (I) with cyclohexylamine. In the original reduction complete hydrolysis first occurs to give propaldehyde which by an aldol condensation followed by loss of water affords the pentenaldehyde I. This condenses with cyclohexylamine to the Schiff's base II, which is less readily hydrolysed and is reduced to III:

$$\begin{aligned} 2\text{CH}_2\text{Me}\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_{11} &\rightarrow \text{C}_6\text{H}_{11}\cdot\text{NH}_2 + \text{CH}_2\text{Me}\cdot\text{CHO} \\ &\rightarrow \text{CH}_2\text{Me}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CHO} \text{ (I)} \xrightarrow{\text{C}_6\text{H}_{11}\cdot\text{NH}_2} \\ &\text{CH}_2\text{Me}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_{11} \text{ (II)} \rightarrow \\ &\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_{11} \text{ (III)}. \end{aligned}$$

Similar results are obtained with Schiff's bases derived from other aliphatic (but not aromatic) aldehydes and

cyclohexylamine, although the above case is the only one in which hydrolysis is complete. The structure of the reduction products is proved by their identity with the reduction products of the intermediate Schiff's bases synthesised from cyclohexylamine and the appropriate unsaturated aldehyde. Thus ethylidenecyclohexylamine is reduced to cyclohexylethylamine (8%) (picrate, m. p. 231°) and cyclohexyl-n-butylamine (39%) (also from Δ^{β} -butenylidenecyclohexylamine, b. p. 90—91°/15 mm.); *n*-butylidene-, isovalerylidene-, *n*-heptylidene-, and γ -phenylpropylidene-cyclohexylamine, by similar reduction, afford, respectively, cyclohexyl-(β -ethyl-*n*-hexyl)amine (78%), b. p. 140—148°/15 mm. [hydrochloride, m. p. 95°; picrolonate, m. p. 225—226° (decomp.)] (also from β -ethyl- Δ^{β} -hexylidenecyclohexylamine, b. p. 139—143°/13 mm.); cyclohexyl-(ϵ -methyl- β -isopropyl-*n*-hexyl)amine (15%), b. p. 143—145°/11 mm. (hydrogen oxalate, m. p. 193.5—194.5°; hydrochloride, m. p. 105°) (also from ϵ -methyl- β -isopropyl- Δ^{β} -*n*-hexylidenecyclohexylamine, b. p. 146—152°/16 mm.); cyclohexyl-(β -amyl-*n*-nonyl)amine (42.3%), b. p. 208—210°/17 mm. (hydrochloride, m. p. 90°; hydrogen oxalate, m. p. 153°) (also from β -amyl- Δ^{β} -*n*-nonenylidenecyclohexylamine, b. p. 208—211°/11 mm.); cyclohexyl-(ϵ -phenyl- β -benzyl-*n*-amyl)amine (hydrochloride, m. p. 169—170°; hydrogen oxalate, m. p. 172°) (also from ϵ -phenyl- β -benzyl- Δ^{β} -*n*-pentenylidenecyclohexylamine, b. p. 265—270°/16 mm.), together with the normal reduction products, of which cyclohexyl-*n*-heptylamine, b. p. 132—135°/16 mm. (hydrochloride, m. p. 211—212°), is new. From isovalerylidene-ethylamine is obtained *N*-(ϵ -methyl- β -isopropyl-*n*-hexyl)ethylamine, b. p. 213—220° [picrolonate, m. p. 221—222° (decomp.)]. When the reduction of the Schiff's base is effected in the presence of another aldehyde this may also undergo an aldol condensation with the aldehyde formed by hydrolysis of the Schiff's base and mixtures of several amines are then formed by the mechanism given above. Thus reduction of propylidenecyclohexylamine in the presence of acetaldehyde affords, in addition to the products obtained above, cyclohexyl-(β -methylbutyl)amine (29.5%), b. p. 97—99°/15 mm. (hydrochloride, m. p. 234°; phenylurethane, m. p. 118°) (also from β -methyl- Δ^{β} -butenylidenecyclohexylamine, b. p. 100—105°/15 mm.), whilst with benzaldehyde as the second component are obtained cyclohexyl-(γ -phenyl- β -methylpropyl)amine (11%), b. p. 164—168°/15 mm. (hydrochloride, m. p. 184°; phenylurethane, m. p. 116°) (also from γ -phenyl- β -methyl- Δ^{β} -propenylidenecyclohexylamine, b. p. 168—176°/14 mm.), and cyclohexylbenzylamine. Reduction in the presence of furfuraldehyde affords cyclohexyl-(γ -furyl- β -methylpropenyl)amine (8%), b. p. 166—172°/12 mm. (hydrochloride, m. p. 180°) (also from γ -furyl- β -methyl- Δ^{β} -propenylidenecyclohexylamine, b. p. 158—162°/12 mm.), together with its dihydro- (0.7%), b. p. 155—160°/12 mm., and tetrahydro- (8%), b. p. 144—149°/12 mm. (hydrogen oxalate, m. p. 165°)-derivatives (the position of the double linking in all three products is undetermined), and cyclohexylfurylamine, b. p. 123—124° (phenylurethane, m. p. 113°) (also from furfurylidenecyclohexylamine, b. p. 131.5—135.5°/18 mm.). Reduction of isobutylidenecyclohexylamine in the presence of formaldehyde affords cyclohexyl-(γ -hydroxy-

$\beta\beta$ -dimethylpropyl)amine, b. p. 123—125°/12 mm., m. p. 38° (hydrochloride, m. p. 224°; phenylurethane, m. p. 150°) (also from γ -hydroxy- $\beta\beta$ -dimethylpropylidenecyclohexylamine, b. p. 108—110°/12 mm.).

J. W. BAKER.

[Possible yellow content of the acidic, red solutions of methyl-yellow.] A. HANTZSCH and A. BURAWOY (Ber., 1930, 63, [B], 3172—3176; cf. A., 1930, 1280).—In reply to Thiel (A., 1930, 1573), reasons are advanced in favour of the view that in salt solutions of *p*-aminoazobenzenes in 2*N*-hydrochloric acid, which in agreement with Thiel contain practically no free base, an equilibrium exists between the yellow azoid and red quinonoid salts.

H. WREN.

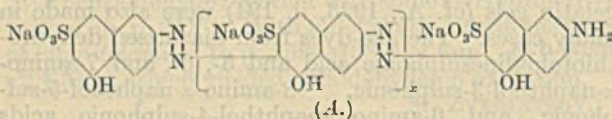
Azo-dyes and their intermediates. V. Constitution and degree of dispersion of azo-dyes. VI. Relation between molecular size and properties of azo-dyes. P. RUGGLI and A. ZIMMERMANN (Helv. Chim. Acta, 1931, 14, 101—126, 127—141).—V. The adsorption of various azo-dyes (all as pure sodium salts) on cotton, in absence and presence of sodium sulphate, has been investigated by the method previously described (cf. A., 1924, ii, 464; B., 1926, 436). Determinations of the viscosity of solutions and their rate of diffusion through 1% gelatin gels (cf. A., 1925, ii, 194) were also made in many cases. The azo-dyes from diazotised dehydrothiolutidinesulphonic acid and 5-, 6-, and 7-amino- α -naphthol-3-sulphonic, 8-amino- α -naphthol-5-sulphonic, and 6-amino- β -naphthol-4-sulphonic acids show small affinities; these and the rates of diffusion through gelatin are somewhat less than the corresponding values for "Erika B" (prepared from diazotised dehydrothioxylidine and α -naphthol-3 : 8-disulphonic acid). The dyes from diazotised 4-aminoazobenzene-4'-sulphonic acid and the above acids are less substantive and show a higher rate of diffusion than the above. The affinities of the dyes from tetrazotised benzidine and 2 mols. of the above acids are generally higher (much more so in presence of sodium sulphate), but not nearly so good as Congo-red; the dye from 6-amino- β -naphthol-4-sulphonic acid gives a much smaller value than the others, although its rate of diffusion through gelatin is very similar to that of the other members of the series; the difference in the adsorption can be ascribed to the constitution, since coupling takes place, in this case only, in the 1-position.

The bisazo-dye obtained from tetrazotised benzidine and 2 mols. of 6-amino- α -naphthol-3-sulphonic acid (J acid) is compared as a typical primary type with those (secondary) prepared by first coupling dehydrothiolutidine (I) or α -naphthylamine (II) with J acid, and then coupling the resultant azo-compounds (after diazotisation) with a further mol. of the acid. The mol. wt., atom numbers, and degree of sulphonation (=wt. of total SO₃Na groups \times 100/mol. wt.) of the three bisazo-dyes are of the same order. The secondary compounds are adsorbed to about three times the extent of the primary dye in absence of sodium sulphate; in presence of the sulphate, the compound from I is adsorbed to a greater extent than Congo-red, whilst its rate of diffusion through gelatin is considerably less than that from II or Congo-red.

The order of coupling does not affect the substantive properties.

A series of bisazo-dyes of the "Biebrich scarlet" type (cf. Nietzki, A., 1880, 664; 1881, 178) is prepared from diazotised aminoazobenzene, its 4'-sulphonic and 3:4'-disulphonic acids with β -naphthol, β -naphthol-6-sulphonic, -3:6-disulphonic, and -3:6:8-trisulphonic acids. The products obtained (all containing 1—3 sulpho-groups) are not substantive except that formed from 4-aminoazobenzene-4'-sulphonic acid and β -naphthol. This is adsorbed to the same extent as a regular substantive dye; the relative viscosity of a 1% solution is much higher than that of any other member of the series examined, and it does not diffuse through gelatin. The colloidal character of the dye is ascribed to association caused by the isolated sulpho-group originating a strong dipole moment. The effect of the number of sulpho-groups on the solubility and colour reaction with sulphuric acid is determined.

VI. Mono-, bis-, tris-, and tetrakis-azo-dyes (A , where $x=0, 1, 2$, and 3, respectively), are prepared by diazotising J acid and coupling with excess of the sodium salt of the same acid, diazotising the purified monoazo-dye, and again coupling as before, and so on. A polyazo-dye of unknown value of x , and in which



the final NH_2 is probably replaced by OH , is obtained by the action of alkali on diazotised J acid, when self-coupling occurs. The colours given by the dyes in sulphuric acid are not characteristic, but when the solutions are poured into water, orange, red, reddish-violet, violet, and blue precipitates, respectively, are obtained. The shades on cotton and in water show the expected shift towards the blue as the series is ascended, but this is only slight after the bisazo-dye. The affinity for cotton of the monoazo-derivative is much smaller than that of the other compounds (in presence of sodium sulphate), which approximate to those of the substantive type, and are all approximately equal. The rate of diffusion of the monoazo-compound into gelatin is much higher than that of any of the others (the polyazo-derivative does not diffuse); the relative viscosities of the bis- and polyazo-compounds are the same and are higher than those of the other compounds.

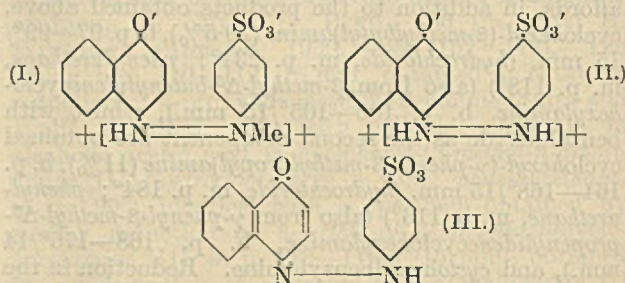
H. BURTON.

Naphthalene series. III. Action of hydrogen sulphite on p -nitrobenzeneazo- α -naphthol. N. N. VOROSCHCOV and P. A. BJELOV (Ber., 1931, 64, [B], 77—83).— p -Nitrobenzeneazo- β -naphthol, m. p. 249°, is converted by protracted ebullition with aqueous sodium hydrogen sulphite in presence of chloroform and ethyl alcohol into the yellow additive compound (I); it is decomposed with regeneration of the initial $\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ material in alkaline solution, showing that the nitro-group has not suffered reduction. (A similar stability of the nitro-group is observed with p -nitrobenzeneazo- α -naphthol.) The

corresponding *barium* (anhydrous and monohydrated) and *copper* (anhydrous and octahydrated) salts are described. In aqueous solution the tendency of the sodium salt towards dissociation increases with the dilution. It increases similarly with increasing concentration of hydroxyl ions, whereas hydrochloric acid has a stabilising action which is accentuated up to about 0.5 equivalent of acid but subsequently not considerably enhanced.

H. WREN.

Constitution of azo-indicators. I. α -Naphthol-orange. K. H. SLOTTA and W. FRANKE (Ber., 1931, 64, [B], 86—94).—Attempts to determine the acid constant of α -naphthol-orange failed since its conductivity in aqueous solution is so small that it cannot be even approximately determined. Electro-metric titration of weighed amounts of the indicator with alkali hydroxide coupled with observations of the colour of the solution shows that the change from yellow to red takes place after addition of exactly one equivalent of hydroxide; a further change of colour is not observed after the addition of a second equivalent of hydroxide. Confirmation of the view that the second hydrogen atom is not connected with the indicator properties is found in the observation that the monoalkyl derivatives behave in a precisely similar manner and are therefore similarly constituted. Treatment of monomethylnaphthol-orange with hydriodic acid does not give methyl iodide, which is obtained by the use of ammonium iodide above 200°. The methyl group is therefore attached to an azo-nitrogen atom, and since fission of the compound with sodium hyposulphite affords 4-amino- α -naphthol the methyl group must be united to the nitrogen vicinal to the benzene nucleus. Treatment of the mono-methyl compound with ethereal diazomethane gives a dimethyl compound void of indicator properties; treatment of this with sodium hyposulphite yields 4-methylamino- α -naphthol, and it does not give methyl iodide when treated with phosphorus and hydriodic acid. For the "acid" form of methyl-naphthol-orange the constitution I is therefore



advanced, whereas the structures II and III are ascribed to the yellow "acidic" and the red "alkaline" form of naphthol-orange. Confirmation is found in the direct production of the dimethyl compound from the acidic form and diazomethane in ether.

The following compounds are incidentally described: α -naphthol-orange, decomp. 260°; methyl- α -naphthol-orange, decomp. 260°; 4-methoxyazobenzene-4'-sulphonic acid; 4- p -nitrobenzamido- α -naphthol, decomp. 276°; ethyl-, decomp. 263—265°; n -propyl-, decomp. 268°; n -butyl-, decomp. 269—270°; n -hexyl- α -

naphthol-orange, decomp. 267° ; *dimethylnaphthol-orange*, m. p. 178° ; *4-methyl-p-nitrobenzamido- α -naphthol*, m. p. 216° .
H. WREN.

Action of ethyl nitrate on phenylhydrazine in presence of sodium ethoxide. E. BAMBERGER and O. BILLETER (Helv. Chim. Acta, 1931, 14, 219—232).—When a mixture of phenylhydrazine and ethyl nitrate is added gradually with stirring to cold alcoholic sodium ethoxide, a mixture of methylformazyl, m. p. 125 — 125.3° , sodium nitrite, benzene, aniline, β -acetylphenylhydrazine, and small amounts of phenyl azide, azobenzene, acetic acid, nitrogen, and (probably) diphenyl are produced. The various reactions which probably occur are discussed. Methylformazyl (cf. A., 1903, i, 284) is conveniently prepared by adding benzenediazonium chloride to a cold solution of acetaldehydephenylhydrazine in alcoholic sodium acetate. *Nitromethylformazyl*, $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2(+0.5\text{EtOH})$, m. p. 154° , is obtained similarly using *p*-nitrobenzenediazonium chloride. Much of the work has been published previously (Vierteljahrsschr. Naturf. Ges. Zurich, 1903, 48, 329).
H. BURTON.

[Reduction of normal diazo-hydrates.] E. BAMBERGER (Helv. Chim. Acta, 1931, 14, 242—249).—The formation of β -benzoylhydrazine from benzaldehyde and phenyldi-imide (Angeli, A., 1930, 205) is not considered to be analogous to the production of phenylazohydroxyanilide, $\text{O}\cdot\text{NPh}\cdot\text{NH}\cdot\text{NPh}$, from nitrosobenzene and phenyldi-imide (*loc. cit.*), since the former reaction involves the migration of a hydrogen atom. Angeli's synthesis of benzhydroxamic acid from benzaldehyde and nitrosyl probably results through the intermediate formation of α -nitrosobenzyl alcohol (cf. A., 1902, i, 197). The remainder of the paper has been reviewed previously (A., 1900, i, 193).
H. BURTON.

Identification of phenols. C. F. KOELSCH (J. Amer. Chem. Soc., 1931, 53, 304—305).—The phenol (1 g.) is heated with a 50% solution of chloroacetic acid (2.5 c.c.) and 33% sodium hydroxide solution (3.5 c.c.) at 100° (bath) for 1 hr., the solution acidified, and the resultant aryloxyacetic acid extracted with ether. The following are new: *o*-, m. p. 143 — 145° , and *m*-chlorophenoxy-, m. p. 108 — 110° ; *m*-bromophenoxy-, m. p. 107 — 108.5° ; *o*-, m. p. 134 — 135° , and *m*-iodophenoxy-, m. p. 114 — 115.5° , and *p*-methoxyphenoxy-acetic acids, m. p. 110 — 112° .
H. BURTON.

Preparation and properties of tri-, tetra-, and penta-chlorophenols. G. J. TIESSENS (Rec. trav. chim., 1931, 50, 112—120).—Experimental details are given for the preparation and determination of the electrical conductivity in dilute aqueous solution of various polychlorophenols, a preliminary account of which has already been published (A., 1929, 1173).
J. W. BAKER.

Chlorination of iodophenols. III. *o*-Iodophenol. S. BUCHAN and H. MCCOMBIE (J.C.S., 1931, 137—144; cf. *ibid.*, 1913, 103, 1762).—Chlorination of *o*-iodophenol in carbon tetrachloride at 0° gives an unstable iododichloride, which rapidly decomposes to give *4-chloro-2-iodophenol*, m. p. 78° ,

the constitution of which is proved by its synthesis from the benzyl ether, m. p. 84 — 85° , of *4-chloro-2-nitrophenol*, through the amino- and iodo-benzyl ethers. *4-Chloro-2-iodophenyl acetate* (an oil) and benzyl ether, m. p. 60° , may be obtained either from *4-chloro-2-iodophenol*, or by decomposition of the iododichlorides of *o*-iodophenyl acetate and benzyl ether (both oils). *o*-Iodophenyl phenylcarbamate, m. p. 121 — 122° , and benzoate, m. p. 34° , and *4-chloro-2-iodophenyl phenylcarbamate*, m. p. 128° , and benzoate, m. p. 88° , form relatively stable iododichlorides, m. p. 125° , 98 — 101° , 146° , and 103 — 104° (decomp. in every case), respectively; the first of these with acetic acid and aqueous potassium iodide gives *o*-iodophenyl 2:4-dichlorophenylcarbamate, m. p. 145° , identified by synthesis from *o*-iodophenol and 2:4-dichlorophenylcarbimide.

4-Chloro-2-iodophenol on chlorination as above gives an unstable iododichloride, converted by decomposition into *4:6-dichloro-2-iodophenol*, m. p. 62° , also obtained by chlorination of *o*-iodophenol; its acetate, m. p. 59° , and benzyl ether, m. p. 62° , are obtained either from it, or by decomposition of the iododichlorides from corresponding *4-chloro-2-iodophenol* derivatives; their iododichlorides decompose in the course of a few days with regeneration of the parent substance. The benzoate, m. p. 89° , and phenylcarbamate, m. p. 181° (prepared from *4:6-dichloro-2-iodophenol* only) do not appear to form iododichlorides. A little trichloro-*o*-iodophenol, m. p. 52 — 54° , is formed by decomposition of the iododichloride from *4:6-dichloro-2-iodophenol*.

2-Iododiphenyl ether, m. p. 55 — 56° , synthesised by standard methods from the 2-nitro-compound, gives an unstable iododichloride, m. p. 81 — 82° (decomp.). The iododichloride, m. p. 98° (decomp.), of ω -*o*'-iodophenoxyacetophenone, m. p. 123° (from *o*-iodophenol, ω -chloroacetophenone, and sodium ethoxide), is moderately stable. *o*-Iodophenol with carbonyl chloride and pyridine gives the carbonate, m. p. 88° [iododichloride, stable, m. p. 108° (decomp.)]; with toluene-*p*-sulphonyl chloride the *p*-toluenesulphonate, m. p. 80° [iododichloride, stable, m. p. 95 — 97° (decomp.)]; and with allyl bromide and sodium ethoxide the allyl ether (dibromide), which with chlorine gives the iododichloride, m. p. 84° (decomp.), of *o*-iodophenyl β -*y*-dichloropropyl ether; the iododichloride, m. p. 118° (decomp.), of the dibromide decomposes slowly into *4-chloro-2-iodophenyl* β -*y*-dibromopropyl ether, m. p. 52° . *o*-Iodophenyl ethyl carbonate (from ethyl chloroformate and the phenol in aqueous sodium hydrogen carbonate) does not give an iododichloride.

Chlorination of *o*-iodophenol in carbon tetrachloride at 60 — 70° gives hexachlorocyclohexadienone and chloranil. Iodine monochloride and *o*-iodophenol give *4-chloro-2:6-di-iodophenol*, m. p. 106 — 107° , which forms an unstable iododichloride. Chlorination of diphenyl carbamate in chloroform at 0° gives *4-chlorophenyl 2:4-dichlorophenyl carbamate*, m. p. 157° , identical with the product of interaction of *p*-chlorophenol and 2:4-dichlorophenylcarbimide, m. p. 61° . The last is prepared from 2:4-dichloroaniline and carbonyl chloride at 350 — 400° .

H. A. PIGGOTT.

Chlorination and nitration in methyl-alcoholic solution. E. PĚÁZEK (Rocz. Chem., 1930, 10, 761—776).—Aromatic hydrocarbons and β -naphthol do not undergo chlorination in methyl-alcoholic solution, the chlorine entering into combination only with the solvent. Phenol, *m*-cresol, and anisole readily yield monochloro-derivatives, quinol yields a mixture of 2:3- and 2:5-dichloroquinol, with only traces of quinone, whilst pyrocatechol and resorcinol yield uncrystallisable, tarry products. Anthracene is converted into anthraquinone, veratrole gives a dichloro-derivative, guaiacol yields exclusively trichloroguaiacol, m. p. 107°, salicylic acid yields exclusively 5-chloro-2-hydroxybenzoic acid, 3-hydroxybenzoic acid is converted chiefly into 2-chloro-3-hydroxybenzoic acid, with the 6-chloro-derivative as a by-product, whilst 4-hydroxybenzoic acid gives a mixture of products containing 3:5-dichloro-4-hydroxybenzoic acid. *p*-Nitrophenol yields 2-chloro-*p*-nitrophenol, *o*-nitrophenol gives a mixture of 6- and 4-chloro-*o*-nitrophenol. Phenol-4-sulphonic acid, aniline, and *o*- and *p*-acetotoluides yield the same products as in other solvents. *o*-, *m*-, and *p*-Diacetylphenylenediamines give exclusively dichloro-derivatives, *p*-nitroaniline yields 2-chloro-*p*-nitroaniline, with an admixture of 2:6-dichloro-*p*-nitroaniline; *o*-nitroaniline yields chiefly 4-chloro-*o*-nitroaniline together with 4:6-dichloro-*o*-nitroaniline; *m*-nitroaniline gives a mixture of 4-chloro-*m*-nitroaniline, 4:6-dichloro-*m*-nitroaniline, and 2:4:6-trichloro-*m*-nitroaniline; the last named is the sole product of exhaustive chlorination. *o*-Aminobenzoic acid does not undergo chlorination, whilst the *m*- and *p*-acids yield the same dichloro-derivatives as are obtained using ordinary solvents, together with some trichloroaniline resulting from decarboxylation of the original acid. On the whole, purer products are obtained in greater yield in methyl than in ethyl alcohol. Nitration can be performed in methyl-alcoholic solution only of phenolic substances; phenol gives a mixture of 2- and 4-nitrophenol, anisole yields 2- and 4-nitroanisole, 2- and 4-chlorophenols give respectively a mixture of 2-chloro-4- and -6-nitrophenol and 4-chloro-2-nitrophenol, veratrole yields 4-nitroveratrole, quinol dimethyl ether the 2-nitro-derivative, and *m*-cresol yields 4-nitro-*m*-cresol, together with the 2- and 6-nitro-derivatives. R. TRUSZKOWSKI.

Reaction of *p*-anisidine and ethyl methylacetoacetate. W. O. KERMACK and J. F. SMITH (J.C.S., 1931, 221—222).—The compound, m. p. 51° (cf. A., 1930, 1298), isolated from the product of condensation of *p*-anisidine with ethyl methylacetoacetate appears from its nitrogen content to be derived from 2 mols. of base and 1 mol. of ester; this conclusion is supported by the formation of a completely solid product, m. p. 40—46°, by the reagents in these proportions, the yield of aceto-*p*-anisidine obtained on treatment with acetic anhydride, and the mol. wt. in benzene (199, 202), which points to dissociation of a compound of the type $C_{14}H_{19}O_3N, C_7H_5ON$, and is inconsistent with the formula $C_{14}H_{19}O_3N$.

H. A. PIGGOTT.

Catalytic preparation of 2:4-diaminophenol. W. E. BRADT (J. Physical Chem., 1930, 34, 2711—

2718).—The reduction of 2:4-dinitrophenol to the diamine by means of hydrogen in the presence of a nickel catalyst, prepared by the reduction of nickel carbonate in hydrogen at 288°, has been investigated. A maximum yield of 95.1% of 2:4-diaminophenol (determined by titration with sodium nitrite) is obtained at 96° with 5 g. of 2:4-dinitrophenol in 20 c.c. of absolute alcohol, 2.0 g. of nickel catalyst, at a pressure of 500 lb. per in.² of electrolytic hydrogen. Higher temperatures cause a slight decrease in yield with the formation of ammonia at 125°, and an increased time of reduction beyond 2 hrs. gives only a slight increase. Absolute ethyl alcohol dehydrated over anhydrous copper sulphate at the ordinary temperature is the best solvent. For a given weight of catalyst an optimum concentration of 2:4-dinitrophenol exists, and an increase in the ratio of the weight of catalyst to that of the nitrophenol from 0.2 to 0.4 also increases the yield. The maximum yield isolated as crystalline dihydrochloride is 50%. L. S. THEOBALD.

Addition of phenols to the ethylenic linking. Reaction mechanism and synthesis of phenolic ethers. J. B. NIEDERL and S. NATELSON (J. Amer. Chem. Soc., 1931, 53, 272—277).—When Δ^8 -pentene and diisobutylene are treated with phenols in presence of sulphuric acid at 0°, and the mixture is kept for a week at the ordinary temperature, phenyl alkyl ethers are obtained. Addition of sulphuric acid to the double linking first occurs; the resultant compound reacts with the phenol, forming the ether and sulphuric acid. A similar mechanism is proposed for the interaction of phenols and unsaturated alcohols, ethers, aldehydes, ketones, acids, and esters; the ethers rearrange in presence of sulphuric acid. The following are prepared: *m*-tolyl α -methylbutyl ether, b. p. 238°, d^{20}_D 0.920, n^{20}_D 1.500 (also obtained from sodium *m*-tolyl-oxide and β -bromopentane in alcohol), converted by nitric acid into trinitro-*m*-cresol; *o*-, b. p. 234°, d^{20}_D 0.915, n^{20}_D 1.493, and *p*-tolyl, b. p. 225°, d^{20}_D 0.920, n^{20}_D 1.505, α -methylbutyl ethers; phenyl, b. p. 190°/40 mm., 258°/760 mm., m. p. 12°, d^{20}_D 0.950, n^{20}_D 1.510, *o*-tolyl (I), b. p. 271°, m. p. 6°, d^{20}_D 0.881, n^{20}_D 1.472, *m*-tolyl, b. p. 273°, d^{20}_D 0.895, n^{20}_D 1.476, and *p*-tolyl, b. p. 272°, d^{20}_D 0.889, n^{20}_D 1.470, $\alpha\alpha\gamma\gamma$ -tetramethylbutyl ethers. When I is heated with zinc and hydrogen chlorides at 200°, rearrangement into $\alpha\alpha\gamma\gamma$ -tetramethylbutyl-*o*-cresol, m. p. 49—50°, occurs. H. BURTON.

Derivatives of dulcin [*p*-ethoxyphenylcarbamide]. E. WERTHEIM (J. Amer. Chem. Soc., 1931, 53, 200—203).—When a mixture of *p*-ethoxyphenylcarbamide and ethyl chloroformate is heated, first over a free flame until homogeneous and then at 100°, ethyl *p*-ethoxyphenylallophanate, m. p. 139—140°, is obtained. This is converted by ammonia at 100° into *p*-ethoxyphenylbiuret, m. p. 185—186°. The carbamide and ethyl chloroformate react at 175°, forming a mixture of *s*-di-*p*-ethoxyphenylcarbamide and *s*-di-*p*-ethoxyphenylbiuret, m. p. 208—209°. *p*-Methylthiol-, m. p. 164—165°, and *p*-ethylthiol-phenylcarbamides, m. p. 149—150°, and *p*-methylthiol-, m. p. 198—199°, and *p*-ethylthiol-phenylthiocarbamides, m. p. 136—137°, are prepared by the

usual methods. The last-named thiocarbamides are bitter; the other compounds are tasteless.

H. BURTON.

Detection of β -naphthol. G. DE HAAS (Pharm. Weekblad, 1931, 68, 29—32).—Addition of glacial acetic acid and concentrated sulphuric acid successively to solutions containing β -naphthol in dilutions up to 1:10⁵ produces a yellowish-green colour at the common surface; on shaking, the mixture becomes fluorescent. Colorations are obtained with other hydroxy-compounds, but no fluorescence.

S. I. LEVY.

Action of bromine on naphthylamine- and aminonaphthol-sulphonic acids. G. HELLER [with H. ARNOLD and J. SCHMIDT] (Z. angew. Chem., 1930, 43, 1132—1137).— α -Naphthylamine-4-sulphonic acid and bromine (2 mols.) in warm acetic acid give 2:4-dibromo- α -naphthylamine. α -Naphthylamine-5-sulphonic acid and 1 mol. of bromine yield a bromo-derivative, which could not be diazotised or coupled with diazotised aniline in acid or alkaline solution; with an excess of bromine in water, 2:4-dibromo- α -naphthylamine-5-sulphonic acid results. This is converted by heating with water and aniline into a bromoanilino- α -naphthylamine-5-sulphonic acid. 2:4-Dibromo- and bromoanilino- α -naphthylamine-8-sulphonic acids are prepared similarly. β -Naphthylamine-6-sulphonic acid is brominated in acetic acid to the 1-bromo-derivative (sodium salt); the -5- and -7-sulphonic acids also afford 1-bromo-derivatives, which when diazotised and coupled with alkaline β -naphthol give red azo-dyes. Definite products could not be isolated from β -naphthylamine-1- and -8-sulphonic acids. Sodium bromo- β -naphthylamine-6:8-disulphonate and a sodium dibromo- β -naphthylamine-6(or 8)-sulphonate are prepared from β -naphthylamine-6:8-disulphonic acid, whilst the -3:6-disulphonic acid affords a dibromo- β -naphthylamine-3(or 6)-sulphonic acid. In all the above brominations, bromine has no oxidising action on the amino-group (cf. A., 1928, 409).

Treatment of 2-amino-8-naphthol-3:6-disulphonic acid with an excess (20 mols.) of bromine in acetic acid at 100° affords 1:3:6:7-tetrabromo-2-amino-5:8-naphthaquinone (I), m. p. 241° [acetyl derivative, m. p. 255° (decomp.); diacetyl derivative, m. p. 160—161°], reduced by stannous chloride and acetic acid to tribromo-2-amino-5:8-dihydroxynaphthalene, not melted at 300°, and converted by an excess of aniline into tribromo-2-aminoanilino-5:8-naphthaquinone, m. p. 215—216° after previous sintering. 2-Amino-5-naphthol-7-sulphonic acid (dibromo-derivative, obtained by the action of 2 mols. of bromine in acetic acid) can also be converted into I, also formed when a solution of 2-amino-8-naphthol-6-sulphonic acid in slightly diluted sulphuric acid is treated with an acetic acid solution of bromine at 35°. Bromination of 1-amino-8-naphthol-4-sulphonic and -2:4-disulphonic acids in warm aqueous acetic acid gives 2:4:7-tribromo-1-amino-5:8-naphthaquinone, m. p. about 235° after previous sintering. Sodium hydrogen 1-amino-8-naphthol-4:6-disulphonate is brominated in acetic acid to 2:4:5(or 7)-tribromo-1-amino-8-naphthol-6-sulphonic acid, whilst in sulphuric acid 1:2:4-tribromo-5:8-naphthaquinone-6-sulphonic

acid [potassium salt (+2.5H₂O)] results. 2:4:6:7-Tetrabromo-1-amino-5:8-naphthaquinone, m. p. 255° after previous sintering, prepared in one experiment from the above sodium salt and an excess of bromine in sulphuric and acetic acids at 40°, is also formed by similar treatment of 1-amino-8-naphthol-5-sulphonic acid. Sodium 1-amino-8-naphthol-3:6-disulphonate and bromine in potassium chloride solution afford potassium 2:4(?)-dibromo-1-amino-5:8-naphthaquinhydrone-3:6-disulphonate, C₂₀H₈O₁₆N₂Br₄S₄K₄·4H₂O, deep violet, reduced by stannous chloride to a colourless substance, C₁₀H₇O₈NBr₂S₂, which with nitrous acid gives first a violet and then a brownish-yellow coloration. 1-Amino-2-naphthol-4-sulphonic acid and bromine in aqueous acetic acid at 100° yield 3:4-dibromo-1:2-naphthaquinone, m. p. 171°, formed by way of the naphthaquinone-4-sulphonic acid (cf. Böniger, A., 1894, i, 199); when a similar reaction mixture is boiled, 2-bromo-3-hydroxy-1:4-naphthaquinone, m. p. 196—198°, results. Potassium 4-bromo-1:2-naphthaquinone-6-sulphonate (+H₂O) is obtained when (sodium) 1-amino-2-naphthol-4:6-disulphonate is brominated in boiling aqueous acetic acid and the resulting solution treated with potassium chloride.

H. BURTON.

cycloHexanediols. B. ROTHSTEIN (Ann. Chim., 1930, [x], 14, 461—598).—A detailed account and discussion of results most of which have previously been summarised (A., 1928, 518, 632, 1129, 1130; 1929, 60, 1064, 1441; 1930, 84, 463, 768). The action of organic acids and their derivatives on cyclohexane-1:2-diols affords esters of the same configuration as the parent diol, but in the cases of the 1:3- and 1:4-diols partial stereoisomeric change in the direction *cis*→*trans* occurs. The action of hydrogen halides on the 1:2-diol yields only resinous products and the 1:2-dihalogeno-derivatives can be obtained only by (*cis*-) addition of halogen to cyclohexene. The "pseudo-migration" mechanism suggested in explanation of the identity of the halogeno-derivatives obtained by the action of hydrogen halide (or phosphorus trihalide) on the 1:3- or 1:4-diols is confirmed by the observation that no migration of the halogen occurs when the halogeno-derivatives are treated with the hydrogen halide under the same reaction conditions. Conversely, acetic acid does not add on to the double linking in cyclohexene derivatives and silver acetate reacts with the dihalogeno-derivatives by direct substitution without stereoisomeric change. Determination of the configuration of the 1:3-diols by optical resolution of the *trans*-derivative has so far proved unsuccessful, but configurations are assigned by a comparative study of the m. p. and solubilities of the 1:3- and 1:4-diols with those of known configuration in the 1:2-diol series, the relationships m. p. *cis*<m. p. *trans*, and solubility *cis*>*trans* being general. The following appears to be new. Separation of the product of catalytic reduction of pyrocatechol is effected by conversion of the *cis*-diol into its isopropylidene ether, b. p. 75—76°/17 mm. (by the action of acetone and anhydrous hydrogen chloride in the presence of sodium sulphate), which is hydrolysed to the *cis*-cyclohexane-1:2-diol, m. p. 98° (42%) [diacetate, *d*₄²⁰ 1.0836, *n*_D²⁰ 1.4429 (cf. Verkade and others, A., 1930, 337); *cinnamate*,

b. p. 138°/11 mm. (corr.), d_4^{25} 1.0648, n_D^{25} 1.5528], leaving the *trans*-diol, m. p. 104° (52%) (*cinnamate*, m. p. 90—91°), the solubility of the two stereoisomerides in dry commercially pure acetone at 20° being 7.195 and 6.595, respectively. *cis-cyclohexane-1:3*-diol (monobenzoate, d_4^{25} 1.1328, n_D^{25} 1.5348) crystallises in three polymorphous forms. The solubility of the *cis*- and *trans*-1:3-diols in pure, dry acetone at 17.5° is, respectively, 8.335 and 7.935, and of their di-*p*-nitrobenzoates, m. p. 154.5° and 176.5°, is 2.89 and 1.09, respectively, at 20°. *cis-cyclohexane-1:4*-diol di-cinnamate has d_4^{25} 1.0466, n_D^{25} 1.5548; *cis-cyclohexane-1:3*-diol gives *dipropyl*, b. p. 113°/15 mm., d_4^{25} 0.9006, n_D^{25} 1.4430; *diisobutyl*, b. p. 160—162°/16 mm., d_4^{25} 0.9006, n_D^{25} 1.4489; and *dibenzyl*, b. p. 205—207°/1 mm., d_4^{25} 1.0739, n_D^{25} 1.5440, *ethers*. The configuration of *cis*-1:2-dibromocyclohexane, b. p. 101—103°/13 mm., d_4^{25} 1.7759, n_D^{25} 1.5445 (by addition of bromine to cyclohexene, above), is proved by its conversion into the *cis*-diol through the *cis*-diacetate. Contrary to Lindemann and Baumann (A., 1930, 209), the dibromo-derivative, m. p. 112°, obtained by the action of hydrogen bromide on the 1:3-diols, and to which these authors assigned the *cis*-1:3-configuration, is actually the *trans*-1:4-dibromo-compound and is accompanied by the *cis*-1:4-dibromo-derivative, m. p. 48° (dimorphous), and a liquid *dibromocyclohexane*, b. p. 114—115°/15 mm., d_4^{25} 1.7834, n_D^{25} 1.5531, which is probably a 1:3-derivative. Hydrobromic acid (65%) converts cyclohexane-1:4- or -1:3-diols *diisobutyl ether* and the 1:3-diols *dibenzyl ether* into a mixture of *trans*-1:4-dibromocyclohexane, m. p. 112°, and its isomeride, m. p. 48°; similar results are obtained with concentrated hydrochloric acid or phosphorus tribromide. J. W. BAKER.

Two stereoisomeric isoeugenols. F. BOEDECKER and H. VOLK (Ber., 1931, 64, [B], 61—66).—Technical isoeugenol, f. p. about 0°, is converted by dissolution in 15% aqueous sodium hydroxide into the crystalline sodium derivative of isoeugenol, b. p. 141—142°/13 mm., m. p. 30—33°, d_4^{25} 1.0852, n_D^{25} 1.5782. Treatment of the product obtained from the mother-liquor from the sodium salt with benzoyl chloride and sodium hydroxide yields a benzoate, m. p. 59—61°, hydrolysed to the second form of isoeugenol, b. p. 134—135°/13 mm., d_4^{25} 1.0851, n_D^{25} 1.5726, which could not be caused to solidify. The isomeric isoeugenols (crystalline and liquid) are converted into their respective methyl ethers, m. p. 16—17°, b. p. 143—144°/11 mm., d_4^{25} 1.0528, n_D^{25} 1.5692, and b. p. 138—140°/12 mm., d_4^{25} 1.0521, n_D^{25} 1.5616, and acetates, m. p. 79°, and b. p. 160—162°/13 mm., n_D^{25} 1.5418. Bromination of isoeugenyl acetate, m. p. 79°, affords mainly the dibromide, m. p. 132°, mixed with a smaller amount of the isomeric dibromide, m. p. 79°; the relative proportion of the products is reversed when the acetate, b. p. 160—162°/13 mm., is used as initial material. Debromination of either dibromide similarly leads to a mixture of acetates. Conversion of the liquid into the crystalline isoeugenol is effected by debromination of the mixed bromide obtained from the liquid acetate, separation of the bulk of the crystalline acetate from the product of repetition of the complete process with the residue, followed finally

by hydrolysis of the solid acetate thus obtained. The reverse transformation is effected by debromination and hydrolysis of the small amounts of the bromide, m. p. 79°, obtained by bromination of the acetate of the crystalline isoeugenol. Treatment of the product with sodium hydroxide leads to the isolation of the crystalline isoeugenol. On grounds of analogy, the *trans*- and *cis*-configurations are ascribed to the crystalline and liquid isoeugenols, respectively.

H. WREN.

Stereochemistry of diphenylbenzenes. *meso*- and *r*-3:6-Dibromo-2:5-di-(3-bromo-2:4:6-trimethylphenyl)quinols and the corresponding quinones. XII. P. R. SHILDNECK and R. ADAMS (J. Amer. Chem. Soc., 1931, 53, 343—352; cf. A., 1930, 1588).—*p*-Benzoquinone and mesitylene react in presence of aluminium chloride below 5° forming 2:5-di-(2:4:6-trimethylphenyl)quinol, m. p. 225—226° (corr.), which when brominated in chloroform at 50—60° affords two (*meso*- and *r*-) 3:6-dibromo-2:5-di-(3-bromo-2:4:6-trimethylphenyl)quinols (I), m. p. 334—335° (corr.; slight decomp.), and (II), m. p. 294—295° [corresponding diacetates, m. p. 285—286° (corr.) and 237—238° (corr.), respectively]. Oxidation of I and II with *p*-benzoquinone in alcohol gives the corresponding orange-coloured 3:6-dibromo-2:5-di-(3-bromo-2:4:6-trimethylphenyl)-*p*-benzoquinones, m. p. 295—296° (decomp.) and 284—285° (decomp.), respectively. These are reduced by stannous chloride in pyridine to the respective quinols and are oxidised by alkaline hydrogen peroxide to 3-bromo-2:4:6-trimethylbenzoic acid, m. p. 168° (corr.), also prepared by brominating 2:4:6-trimethylbenzoic acid in carbon tetrachloride in presence of iron filings at 120—130° (bath). Treatment of I or II with liquid bromine gives the same 3:6-dibromo-2:5-di-(3:5-dibromo-2:4:6-trimethylphenyl)quinol, m. p. (block) 395—398° [diacetate, m. p. 297° (corr.)], oxidised by *p*-benzoquinone in alcohol to 3:6-dibromo-2:5-di-(3:5-dibromo-2:4:6-trimethylphenyl)-*p*-benzoquinone, m. p. (block) 390—393°. This is reducible to the original quinol and is oxidised by alkaline hydrogen peroxide to 3:5-dibromo-2:4:6-trimethylphenylbenzoic acid, m. p. 210—211° (corr.), also formed by the action of liquid bromine on 3-bromo-2:4:6-trimethylbenzoic acid at the ordinary temperature. H. BURTON.

Migration of acyl from sulphur to nitrogen. H. P. LANKELMA and A. E. KNAUF (J. Amer. Chem. Soc., 1931, 53, 309—312).—Treatment of the hydrochloride (I) of 4-chloro-2-aminothiophenol, m. p. 198—201° (decomp.; lit. 120°), prepared by reduction of 4:4'-dichloro-2:2'-dinitrodiphenyl disulphide with tin and alcoholic hydrochloric acid, with benzoyl chloride in boiling dimethylaniline gives 5-chloro-2-phenylbenzothiazole, m. p. 139°; 5-chloro-2-methylbenzothiazole, m. p. 68—69°, is prepared similarly, using acetic anhydride. When I is heated with benzoyl chloride in dimethylaniline at 100°, 4-chloro-2-benzamidophenyl thiobenzoate, m. p. 158—159°, is formed. This is hydrolysed by alcoholic potassium hydroxide at the ordinary temperature to 4-chloro-2-benzamidothiophenol, m. p. 105—106° (acetate, m. p. 129—130°, hydrolysed to the original thiophenol), which when

crystallised from alcohol passes into 5-chloro-2-phenylbenzthiazole. Treatment of I with acetic anhydride in dimethylaniline at 100° gives 4-chloro-2-acetamidophenyl thioacetate, m. p. 150—151°, hydrolysed to 4-chloro-2-acetamidothiophenol, m. p. 92—94°, which when crystallised from alcohol passes into 5-chloro-2-methylbenzthiazole. Hydrolysis of 4-chloro-2-acetamidophenyl thiobenzoate, m. p. 141—142°, gives 5-chloro-2-phenylbenzthiazole, showing that the benzoyl group migrates from sulphur to nitrogen. H. BURTON.

Determination of constitution by changing the order in which groups are introduced into the benzene nucleus. J. W. DIENSKE (Rec. trav. chim., 1931, 50, 21—31).—Mainly experimental details of results previously described (this vol., 78; Challenger and Collins, A., 1924, i, 953) on the conversion of *p*-halogenoaniline and *p*-thiocyananiline into identical *p*-halogenocyanobenzene. Improved yields are obtained by using a solution of cuprous thiocyanate in the Sandmeyer reaction (Thurnauer, A., 1890, 749). The formation of di-iododiphenyl disulphide observed by Challenger and Collins (*loc. cit.*) when cuprous thiocyanate acts on diazotised *p*-iodoaniline was not confirmed, a substance, m. p. 88—100°, being obtained. By similar reactions are obtained: *p*-thiocyanobenzonitrile, m. p. 127·5°, and *p*-dithiocyanobenzene, m. p. 108·5° (Challenger and Peters, A., 1928, 750, give m. p. 106°), nitrated by absolute nitric acid at 0° to its 2-nitro-derivative, m. p. 146·5° (*loc. cit.*, m. p. 143—144°). The use of potassium hydrosulphide for hydrolysis of aromatic thiocyanoderivatives to thiophenols and disulphides is unnecessary, since these products are readily obtained by hydrolysis with boiling 10% potassium hydroxide or moderately concentrated sulphuric acid and thus from *p*-bromo- and *p*-iodo-thiocyanobenzene are obtained mixtures of *p*-bromo- or *p*-iodo-thiophenol and 4:4'-dibromo- or 4:4'-di-iodo-diphenyl disulphides, respectively. J. W. BAKER.

Condensation of benzyl alcohol with cyclohexene in the presence of phosphorus pentoxide. D. N. KURSAOV (J. Russ. Phys. Chem. Soc., 1930, 62, 1691—1695).—The condensation of benzyl alcohol and cyclohexene in the presence of phosphorus pentoxide takes place readily with the formation of much tarry matter which cannot be purified, and benzyl- Δ^1 -cyclohexene, b. p. 127·2—128·4°/15 mm., d^{20}_4 0·9634, n^{20}_D 1·5400, which on oxidation with alkaline potassium permanganate yielded benzoic acid and a neutral compound, m. p. 105—106°, which could not be identified. M. ZVEGINZOV.

Conjugated systems. VI. Preparation of the geometrical isomerides of styrylmethylcarbinol and phenylbutadiene. VII. Reactions of the geometrical isomerides of styrylmethylcarbinol. I. E. MUSKAT and M. HERRMAN (J. Amer. Chem. Soc., 1931, 53, 252—260, 260—271).—VI. When the reaction product (A) from magnesium methyl bromide and cinnamaldehyde is decomposed with dilute acid and the residue from the completely acid-free ethereal extract distilled, trans-styrylmethylcarbinol, b. p. 117°/4 mm., n^{21}_D 1·5550, is obtained. When this is distilled in presence of a trace of acid, cis-styrylmethyl-

carbinol, b. p. 144°/21 mm., n^{21}_D 1·5536, is isolated. The *cis*- and *trans*-carbinols are also formed from magnesium methyl iodide and cinnamaldehyde; the reaction product is decomposed with sulphurous acid, and the resulting acid-free extract contains the *trans*-form. The *cis*-carbinol eliminates water very readily, even on keeping, forming *cis*- α -phenylbutadiene, b. p. 86°/11 mm. (cf. Klages, A., 1906, i, 661). Decomposition of A with 50% sulphuric acid affords trans- α -phenylbutadiene, b. p. 76°/11 mm., n^{28}_D 1·5920, also formed when the *cis*-isomeride is kept in presence of a trace of acid and then distilled, or when trans- α -methylcinnamyl chloride, b. p. 104°/6 mm., is heated with pyridine.

VII. trans-Styrylmethylcarbinol furnishes a phenylcarbimide derivative, m. p. 94°, identical with that described by Klages (*loc. cit.*), and an acetate, b. p. 141—144°/15 mm., previously prepared by Burton (A., 1929, 554). When the carbinol is heated to 180°, the main product formed is a compound, C₂₀H₂₂O, b. p. 200°/6 mm. (tetrabromide, m. p. 179°). *cis*-Styrylmethylcarbinol does not give a phenylcarbimide derivative; it is dehydrated by acetic anhydride, forming mainly dimeric α -phenylbutadiene, but it yields with ethereal hydrogen chloride *cis*- α -methylcinnamyl chloride, b. p. 108°/6 mm. Catalytic reduction of both carbinols by Adams' method shows that the *cis*-form is reduced more readily; γ -phenyl- α -methylpropyl alcohol, b. p. 105°/6 mm. (phenylcarbimide derivative, m. p. 113°), is produced in each case. The *cis*-carbinol (oxide, b. p. 117°/3·5 mm.) is oxidised more rapidly by perbenzoic acid than is the *trans*-isomeride (oxide, b. p. 118°/4 mm.). When the *trans*-oxide is heated with 2*N*-sulphuric acid, a compound, b. p. 200°/4 mm., is formed by elimination of 1 mol. of water from 2 mols. of the oxide. The styrylmethylcarbinol of Klages (*loc. cit.*) is probably a mixture of *cis*- and *trans*-forms; that prepared by Burton (*loc. cit.*) appears to be the *trans*-modification. H. BURTON.

Constitution of colourless and coloured triphenylmethane derivatives. I. LIFSCHITZ (Ber., 1931, 64, [B], 161—182).—Reply is made to the criticism of Hantzsch and Burawoy (A., 1930, 901) of the work of the author and Girbes (A., 1928, 1001). The properties of colourless and coloured triphenylmethyl derivatives are explained on the basis that in the great majority of compounds Ar₃CX the C·X linking is heteropolar. Whether isomeric, truly homopolar compounds exist is not immediately material. In conformity with Werner's theories, these compounds by intrusion of suitable groups can yield true, complex salts, [Ar₃C···R]⁺X⁻, the ions of which may be stable or undergo further transformation either by solvation or addition of neutral molecules to the anion or by isomerisation of the cation to the quinonoid form $\left[\text{Ar}_3\text{C} \begin{array}{c} \diagup \text{R} \\ \diagdown \text{R} \end{array} \right]^+$ X⁻,

the actual parent of the halochromic carbonium ions. The homopolar compounds (e.g., triphenylmethane, triphenylcarbinol esters, tetraphenylmethane), provided they do not contain special chromophores, are colourless and yield non-characteristic absorption spectra. The heteropolar derivatives, Ar₃C···X (triphenylmethyl halides, thiocyanates, perchlorates)

and $[\text{Ar}_3\text{C} \cdots \text{R}]\text{X}'$, in so far as absorption is not caused by the group R, are colourless and do not give more characteristic absorption spectra than the homopolar compound, whereas the quinonoid derivatives are coloured and show powerful selective absorption of the short waves of the visible region. A review of the literature shows that these theories are not at variance with recorded data as far as mol. wt. and behaviour in connexion with Beer's law are concerned. The halochromic compounds are structural analogues of Wurster's dyes, the quinhydrones and related compounds, the additive products of ketones, and the triphenylmethane dyes. It is not valid to assume that solutions of a particular triphenylmethylecarbinol invariably contain the same complex or that, for example, solutions of a perchlorate in chloroform or *s*-tetrachloroethane are comparable with that of the carbinol in anhydrous sulphuric acid. The quinonoid nature of the halochromic compounds is illustrated by comparison of their behaviour with that of the fuchsones, dibromofuchsones, and diphenylquinonedi-imine particularly towards *NN'*-diphenyl-*p*-phenylenediamine.

H. WREN.

Naphthalene series. II. Diaryl- and triaryl-methane derivatives of dimethyl- α -naphthylamine. B. GOKHLE and F. A. MASON (J.C.S., 1931, 118—126).—4:4'-Tetramethyldiamino-1:1'-dinaphthylcarbinol, m. p. 184—186° (rapidly heated), is formed in minute yield by oxidation of the corresponding methane base (Morgan, *ibid.*, 1900, 77, 283) by chloranil in acetic acid, but not by other oxidising agents commonly employed in such cases. Methylal may be used in place of formaldehyde in the preparation of the methane. The chloride and anilide of 4-dimethylamino-1-naphthoic acid (cf. A., 1889, 150) were prepared; attempts to synthesise 4:4'-tetramethyldiamino-1:1'-dinaphthyl ketone from the former and dimethyl- α -naphthylamine, or by oxidation of the corresponding methane, failed. Interaction of the acid chloride with dimethylaniline in presence of aluminium chloride in the cold, however, gives *p*-dimethylaminophenyl 4-dimethylamino-1-naphthyl ketone, m. p. 128.5—129°, and this condenses further with dimethylaniline under the influence of phosphoryl chloride, with apparent formation of "Naphthoblau" (Noelting and Philipp, A., 1908, i, 295); reduction of the ketone with sodium amalgam and alcohol gives the corresponding carbinol, m. p. 62—63°. Hexamethyltriaminotrinaphthylmethane, m. p. 266—267.5°, is obtained by condensation of dimethyl- α -naphthylamine with ethyl orthoformate and aluminium chloride at 70°; the condensation could not be effected by means of zinc chloride. 4-Amino-dimethyl- α -naphthylamine (benzoyl derivative, m. p. 195°) is obtained by reduction of the corresponding nitroso-compound by zinc dust and acid; it is not converted into a dye of the methylene-blue type by oxidation in presence of dimethyl- α -naphthylamine and sodium thiosulphate.

The absorption maxima of the blue solutions in acetic acid of *pp'*-tetramethyldiaminodiphenylcarbinol and the two carbinols described above agree with those calculated on Moir's theory.

H. A. PIGGOTT.

Heteropolar carbon compounds. XII. New dyes of the aniline-blue series, and perchlorates of important triphenylmethane dyes. W. DILTHEY and R. DINKLAGER (J. pr. Chem., 1931, [ii], 129, 24—30).—*Tri-p*-diphenylene-, decomp. about 225°, 4:4':4''-tri-(*p*-phenoxyphenyl)-, decomp. about 230°, and 4:4':4''-tri-(*p*-phenylthiolphenyl)-pararos-aniline, decomp. 220—230° (as hydrochlorides), are prepared by interaction of *p*-aminodiphenyl, *p*-aminodiphenyl ether, and *p*-aminodiphenyl sulphide, respectively, and pararos-aniline base at 120—180° in presence of benzoic acid. It is found that the bathochromic effects of these substituents are little, if at all, greater than that of the phenyl nucleus (aniline-blue), a fact which is considered to support the "carbenium" formula for these dyes (cf. A., 1929, 1067).

The following m. p. of dye perchlorates, obtained by rapidly heating the carefully dried substances, are regarded as comparative (*ibid.*, 1293): malachite-green, m. p. about 200°; brilliant-green, m. p. 183°; rhodamine 3B, m. p. 167°; crystal-violet, m. p. 239—240°; methylene-blue, m. p. 231—232°; Victoria-blue, decomp. 320°; pararos-aniline, m. p. 317° (decomp.).

H. A. PIGGOTT.

Synthetic bases closely related to ephedrine. E. CHERBULIEZ, F. NEUMEIER, and H. LOZERON (Helv. Chim. Acta, 1931, 14, 186—200).—Treatment of cinnamyl acetate with iodine and mercuric oxide in moist ether gives an iodohydrin, converted by methylamine in alcohol at 100° into β -methylamino- α -phenylpropane- α - γ -diol [dl- ω -hydroxyephedrine], b. p. 175—178°/14 mm., m. p. 110° (hydrochloride, m. p. 159.5°), also prepared by the same method from cinnamyl alcohol and benzoate. The following β -methylamino- γ -alkoxy- α -phenylpropyl alcohols [alkoxyephedrines] are prepared similarly from the appropriate cinnamyl alkyl ethers: γ -methoxy-, b. p. 148°/12 mm. (hydrochloride, m. p. 151—153°); γ -ethoxy-, b. p. 148—150°/10 mm. (hygroscopic hydrochloride); γ -propoxy-, b. p. 151—153°/12 mm.; γ -butoxy-, b. p. 155—157°/13 mm., and γ -allyloxy-, b. p. 155—157°/12 mm. Cinnamyl ethyl ether, b. p. 125—126°/11 mm., is prepared from cinnamyl alcohol and ethyl sulphate in presence of alkali; cinnamyl propyl, b. p. 131—132°/13 mm., butyl, b. p. 138°/13 mm., and allyl ethers, b. p. 131—132°/12 mm., are obtained from sodium cinnamoxide and the requisite alkyl iodide in benzene. When cinnamyl alcohol is treated with iodine and mercuric oxide in methyl alcohol and the resultant product heated with alcoholic methylamine, β -methylamino- γ -methoxy- γ -phenylpropyl alcohol, b. p. 143°/11 mm., m. p. 83.5° (hygroscopic hydrochloride; hydrogen oxalate, m. p. 143°), is obtained in 31% yield. The yields of the above substances, for which pharmacological data are given, vary from 5 to 40%.

H. BURTON.

Nickelic compound of benzamidoxime. J. V. DUBSKY and M. KURÁŠ (Chem. Listy, 1930, 24, 464).—The salt $(\text{NH}_2\text{CPh}\cdot\text{NO})_3\text{Ni}$ is produced by the oxidation of an ammoniacal solution of a nickellous salt containing benzamidoxime.

R. TRUSZKOWSKI.

Action of ozone on benzoic acid and phenylated fatty acids. H. RUPE and H. HIRSCHMANN (Helv.

Chim. Acta, 1931, **14**, 49—56).—Treatment of phenylacetic acid with ozone (10—12%) in carbon tetrachloride for 24 hrs. at 0—15°, and subsequent decomposition of the triozone produced with water, gives small amounts of unchanged acid, formic and malonic acids, and glyoxal. β -Phenylpropionic and benzoic acids afford small amounts of succinic and oxalic acids, respectively, in addition to glyoxal and formic acid. Benzoic acid is the most stable of the three acids to ozone; its triozone, which is the most unstable, is, however, obtained in the largest amount. A considerable part of the phenylacetic and β -phenylpropionic acids is completely oxidised (cf. A., 1916, i, 409).

H. BURTON.

α -Benzyl- δ -methyl- Δ^7 -hexenoic acid and the lactone of γ -hydroxy- α -benzyl- δ -methyl- n -hexoic acid. G. DARZENS and A. LEVY (Compt. rend., 1930, **191**, 1455—1457).—Dry hydrogen bromide at 130—140° converts γ -methyl- Δ^6 -buten- α -ol into the corresponding bromide, b. p. 120° (95% yield), which reacts with ethyl sodiobenzylmalonate to give ethyl benzyl-(γ -methyl- Δ^6 -butenyl)malonate, b. p. 184—187°/9 mm. This is hydrolysed by alcoholic potassium hydroxide to give the corresponding malonic acid, decomp. at 160—170° in a vacuum into a mixture of α -benzyl- δ -methyl- Δ^7 -hexenoic acid, b. p. 157—160°/7 mm., m. p. 49.5° (80%), and the lactone

$\text{CH}_2\text{Ph}\cdot\text{CH}\begin{matrix} \text{CH}_2\cdot\text{CHPr}^3 \\ \text{CO}\cdot\text{O} \end{matrix}$, b. p. 148—150°/6 mm., m. p. 25° (20%). All attempts to cyclise the acid or the lactone to the corresponding tetrahydronaphthalene derivative (A., 1926, 1239) were unsuccessful.

J. W. BAKER.

3-Iodo- β -naphthoic acid. H. GOLDSTEIN and E. CORNARIUS (Helv. Chim. Acta, 1931, **14**, 200—203).—3-Iodo- β -naphthoic acid, m. p. 214° (methyl ester, m. p. 55°; ethyl ester, m. p. 78°; amide, m. p. 241°; anilide, m. p. 205°), is prepared by the usual method from 3-amino- β -naphthoic acid.

H. BURTON.

Catalytic effect of magnesium alcohols on the reaction of Grignard reagents with carbon dioxide. C. R. KINNEY and M. L. MAYHUE (J. Amer. Chem. Soc., 1931, **53**, 190—199).—The amount of triphenylacetic acid obtained when magnesium triphenylmethyl chloride is treated with carbon dioxide is diminished by the addition of small amounts of triphenylcarbinol; when the amount of carbinol is 15.3 mol.-%, the yield of the acid, under the usual experimental conditions, is zero. Addition of benzaldehyde also causes a marked diminution in the yield. The yields of phenylacetic, benzoic, and valeric acids from magnesium benzyl chloride, phenyl bromide, and butyl bromide are also depressed by the addition of benzyl alcohol, phenol, and butyl alcohol, respectively. In these cases, the addition of more than 6 mol.-% does not cause such a pronounced diminution in the amount of the respective acid as with magnesium triphenylmethyl chloride.

Cleavage of tetraphenylethane could not be accomplished with magnesian iodide at 300° in an atmosphere of carbon dioxide.

H. BURTON.

Reaction of phenyl *o*-acetoxybenzoate. H. SZANCER (Pharm. Zentr., 1931, **72**, 68—69).—Phenyl

o-acetoxybenzoate (Phennin) (0.02 g.), sodium nitrite (0.002 g.), and water (0.5 c.c.), superposed on sulphuric acid (1 c.c.), give a red ring and, after mixing, a green solution which becomes lemon-yellow (distinction from salol; Ekkert, this vol., 88) when made alkaline.

H. E. F. NOTTON.

Two modifications of methyl *p*-hydroxybenzoate. L. KOFLER and A. KOFLER (Mikrochem., 1931, **9**, 45—51).—Two modifications of methyl *p*-hydroxybenzoate, m. p. 110° and 126°, respectively, are described. The first is formed by rapid cooling of the sublimate and the second by slow cooling. The former is transformed into the latter on recrystallisation. The two forms are readily distinguishable under the polarising microscope. E. S. HEDGES.

Preparation of 4-nitrophthalimide and derivatives. L. F. LEVY and H. STEPHEN (J.C.S., 1931, 79—82).—A 78% yield of 4-nitrophthalimide, unaccompanied by 3-nitrophthalimide, is obtained by the action of nitric acid on phthalimide dissolved in sulphuric acid containing 10% of free sulphur trioxide. Nitration under similar conditions of *N*-phenylphthalimide gives *p*-nitroaniline and phthalic acid, and of phthalic anhydride 4-nitrophthalic acid only. 4-Aminophthalimide (A., 1908 i, 651) [acetyl derivative, m. p. 331° (decomp.)] gives with phthalic anhydride at 180° 4-phthalimidophthalimide, m. p. 319° (decomp.), and is converted by standard methods into 4-chloro- and 4-hydroxy-phthalimides (Graebe and Rée, J.C.S., 1886, **49**, 524, 529).

H. A. PIGGOTT.

Preparation of ellagic acid. F. ZETZSCHE and M. GRAEF (Helv. Chim. Acta, 1931, **14**, 240—242).—Crystalline sodium sulphite is added to an aqueous extract of Turkish tannin and the mixture boiled for 1 hr., whereby sodium ellagate (4% of original tannin) separates; carbon dioxide is evolved during the process owing to the decomposition of gallic acid. Ellagic acid (tetra-acetyl derivative, m. p. 317—319°) is best purified by crystallisation from pyridine and then decomposing the resulting pyridine salt with dilute hydrochloric acid. Pyrogallol is extracted from the mother-liquors after separation of the above sodium salt; subsequent evaporation of the residual solution affords sodium gallate.

H. BURTON.

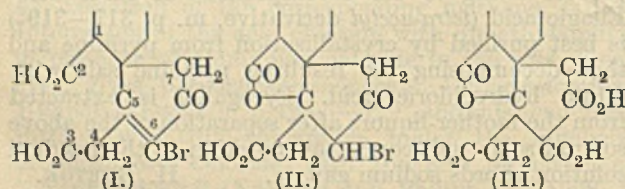
Action of potassium hydroxide on tetracarboxylic esters of the dimalonate series. Preparation of ethylphenylpropionic acids. H. T. LO (Bull. Chem. Soc. Japan, 1930, **5**, 326—333).—Ethyl *o*-xylylenedimalonate yields on hydrolysis with alcoholic potassium hydroxide and subsequent decarboxylation at 150—155°, besides *o*-phenylenedipropionic acid (Perkin, J.C.S., 1888, **53**, 18), *o*-ethylphenylpropionic acid, m. p. 103° (silver salt; ethyl ester, b. p. 131°/10 mm.), the yield of the latter increasing with the concentration of the alkali hydroxide used for hydrolysis. *o*-Phenylenedipropionic acid does not lose carbon dioxide when distilled in a vacuum or when boiled with alcoholic potassium hydroxide. *p*-Ethylphenylpropionic acid, m. p. 114—115° (silver salt; ethyl ester, b. p. 141°/15 mm.), is similarly formed when ethyl *p*-xylylenedimalonate (Kipping, *ibid.*, 35) is hydrolysed. Ethyl *m*-xylylenedimalonate

(Kipping, *loc. cit.*) affords under similar conditions almost exclusively *m*-phenylenedipropionic acid.

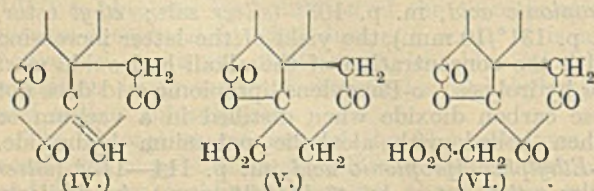
R. CHILD.

Bile acids. XXXI. Constitution of ψ -choloidanic acid. H. WIELAND, L. ERTTEL, and E. DANE. **XXXII. New degradation of deoxybilianic acid.** E. DANE and H. WIELAND (*Z. physiol. Chem.*, 1930, 194, 107—118, 119—123).—XXXI. When ψ -choloidanic acid, $[\alpha]_D^{25} +14.6^\circ$ in alcohol (tetramethyl ester, m. p. 132° , $[\alpha]_D^{25} +8.27^\circ$ in alcohol) (cf. A., 1923, i, 41), is heated, a mixture of 15% of pyro- ψ -choloidanic acid [the methyl ester, m. p. 192° , is identical with the compound formed when dimethyl ψ -choloidanate is heated (cf. *loc. cit.*)], and an acid, $C_{22}H_{32}O_5$, m. p. 199° , which is not affected by sodium hydroxide solution or reducing agents, is produced. When pyro- ψ -choloidanic acid is treated with *N*-sodium hydroxide, three equivalents are consumed, and a tricarboxylic acid, $C_{23}H_{32}O_7$, m. p. 212° (dimethyl ester), is produced; an anhydride ring is opened. The last-named acid is stable to permanganate, but is oxidised by chromic and acetic acids to a small amount of an acid, $C_{23}H_{32}O_{10}$, m. p. 180 — 182° (decomp.). It is concluded from these results that ψ -choloidanic acid is a lactonic tetracarboxylic acid; one of the carboxyl groups is in the side-chain, and the loss of carbon dioxide is accompanied by the formation of a cyclic ketone, since the pyro-acid reacts with bromine.

Bromination of deoxybilianic acid in acetic acid containing a little iodine at 75° affords a dibromo-derivative, m. p. 215° (decomp.), converted by methyl-alcoholic potassium hydroxide into bromodeoxybilianic acid, $C_{24}H_{33}O_7Br$, m. p. 218° (decomp.) (trimethyl ester, m. p. 93°), represented by the partial structure I. This is reduced by zinc and hydrochloric acid to deoxybilianic acid and oxidised by nitric acid (*d* 1.4) to ψ -choloidanic acid (as III), probably by way of the lactone (II). The formation



of ψ -choloidanic during the oxidation of deoxybilianic acid (cf. *loc. cit.*) is explained by the formation of a hydroxyl group on C_5 , subsequent lactonisation, and fission of the ring between C_6 and C_7 . Pyro- ψ -choloidanic acid is formulated as IV; the production of only a dimethyl ester from IV is explained by the spontaneous lactonisation of the corresponding free acid to V.



XXXII. Oxidation of bromodeoxybilianic acid with alkaline potassium permanganate at 30° gives

6-keto-5-hydroxydeoxybilianic acid, m. p. 223 — 225° (oxime, m. p. 200°); the following changes occur:

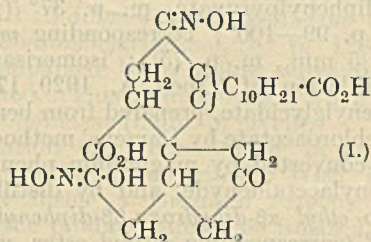
$>\overset{5}{C}CBr \cdot \longrightarrow >C(OH)CBr(OH) \cdot \longrightarrow >C(OH)CO \cdot$. Esterification of this with diazomethane affords a trimethyl ester, m. p. 154° , whilst with methyl-alcoholic hydrogen chloride, a trimethyl ester, m. p. 178° , results. The ketohydroxy-acid is converted by hydrochloric and acetic acids into the diketolactonic acid (VI), m. p. 258 — 260° (slight decomp.), also formed as the main product of the attempted oxidation of the hydroxy-acid with nitric acid (*d* 1.4), reduced by hydrogen in presence of platinum oxide and acetic acid to 6-ketodeoxybilianic acid, m. p. 255° after previous sintering (trimethyl ester, m. p. 108°). Oxidation of the hydroxy-acid with nitric acid (*d* 1.51) yields a small amount of a pentacarboxylic acid, $C_{24}H_{36}O_{11}$, m. p. 180° (decomp.).

H. BURTON.

Bile acids. XXXIII. Bromination of dehydrocholic and dehydrodeoxycholic acids. H. WIELAND and T. NOGUCHI (*Z. physiol. Chem.*, 1931, 194, 248—259).—Dehydrocholic acid and bromine (1 mol.) in acetic acid at about 15° give a bromo-derivative, m. p. 182 — 183° (decomp.) [ethyl ester, m. p. 192° (decomp.)], prepared by similar bromination of ethyl dehydrocholate, converted by cold 0.1*N*-potassium hydroxide into a hydroxydehydrocholic acid (+ H_2O), m. p. 187° (decomp.). With 2 mols. of bromine at 15 — 20° , α -dibromodehydrocholic acid (+AcOH), m. p. 200° (decomp.), (+EtOH) decomp. 206° , (+0.5Et₂O) decomp. 174° , results. This is converted by 0.5*N*-potassium hydroxide into a dihydroxydehydrocholic acid (+Et₂O), m. p. 198° (decomp.), and an isomeride (?), m. p. 212 — 213° (decomp.), whilst treatment with barium hydroxide solution affords a hydroxytriketocholenic acid (+0.5AcOH), m. p. 257° (decomp.). When dehydrocholic acid is treated with an excess of bromine in acetic acid at 50 — 65° , β -dibromodehydrocholic acid (+AcOH), m. p. 265 — 266° (decomp.), is obtained. This results from the action of the evolved hydrogen bromide on higher bromo-derivatives. Dehydrocholic acid and 5 mols. of bromine in acetic acid below 30° give a tetrabromodehydrocholic acid, m. p. 213° with blackening, and an impure tribromo-derivative, m. p. 202 — 203° (decomp.) (recrystallisation of this from acetic acid gives a product approximating to a tetrabromo-derivative, but the m. p. is unaltered); with 8 mols. of bromine at the ordinary temperature, an impure pentabromodehydrocholic acid, m. p. 192° with blackening, results. Bromination of dehydrodeoxycholic acid (improved method of preparation given) with 3 mols. of bromine at 50° furnishes a mixture of two tribromo-derivatives, (a), (+0.5AcOH), m. p. 212 — 213° (decomp.), m. p. (solvent-free) 184° (decomp.), and (b), (+0.5AcOH), m. p. 215° (also formed when dehydrodeoxycholic acid is treated with 6 mols. of bromine in the cold). Not more than three atoms of bromine could be introduced into dehydrodeoxycholic acid. H. BURTON.

Bile acids. XXIX. M. SCHENCK (*Z. physiol. Chem.*, 1931, 194, 33—42; cf. Schenck and Kirchhof, A., 1930, 1435).—Nitric acid (*d* 1.4) converts the oximes of isodeoxybilianic and cilianic acids, $C_{24}H_{37}O_7N$ and $C_{24}H_{35}O_{10}N$, respectively, into the

corresponding keto-acids. Although there appears to be transitory formation of a nitroso-compound by the action of nitric acid on *isobilanic acid oximelactam*, the product isolated is the keto-lactamtricarboxylic acid, $C_{24}H_{35}O_8N$ (A., 1929, 1070). Under the same conditions, *isobilanic acid dioxime* affords in small yield a nitroso-compound, $C_{24}H_{33}O_8N$, decomp. 220–222°, probably identical with that obtained from *bilanic acid dioxime* (A., 1928, 1007).



Neither the nitrohydroxamic acid, $C_{24}H_{33}O_9N_2$ (A., 1929, 558), nor its oximino-derivative (I) undergoes the Beckmann–Wallach change when treated with sulphuric acid.

A. COHEN.

Production of benzaldehyde from benzyl chloride. P. SCHORIGIN, I. KIZBER, and E. SMOLIANINOVA (J. Appl. Chem., Russia, 1930, 3, 721–726).—When boiled with aqueous calcium nitrate, benzyl chloride affords benzaldehyde (60–65%) and benzoic acid (10%). The presence of aluminium or copper retards oxidation by the nitric acid which is liberated. Free nitric acid may be employed.

CHEMICAL ABSTRACTS.

Formation of thioamides from acylated aldehydecyanohydrins. VII. J. F. OLIN and T. B. JOHNSON (Rec. trav. chim., 1931, 50, 72–76).—Acyl derivatives of aliphatic aldehydecyanohydrins are best prepared by shaking together molecular proportions of the aldehyde, the acyl chloride, and powdered sodium or potassium cyanide with crushed ice until the odour of the acyl chloride disappears. Conversion of these derivatives into the corresponding thioamides is best effected by saturating a solution of the acylated cyanohydrin and triethanolamine in alcoholic solution with hydrogen sulphide. Unlike pyridine, the triethanolamine does not cause dissociation of the thioamide into hydrogen sulphide and the parent nitrile. Thus from the appropriate acylated cyanohydrin are prepared (80–90% yield): α -benzoyloxy-, $\text{CHPh}(\text{OBz})\cdot\text{CS}\cdot\text{NH}_2$, m. p. 139°, and α -acetoxy-, m. p. 104°, -phenylacetothioamide; benzoyloxyacetothioamide, m. p. 103°, α -benzoyloxypropionthioamide, m. p. 104°, and α -benzoyloxy-n-butyrothioamide, m. p. 106°. All these derivatives are destroyed by hydrolysis with mineral acids or alkalis.

J. W. BAKER.

Isomerisation of hydroxyaldehydes. IV. Transformation of α -bromo- β -phenylpropaldehyde and α -hydroxy- β -phenylpropaldehyde. S. DANILOV and E. VENUS-DANILOVA (J. Russ. Phys. Chem. Soc., 1930, 62, 1697–1711).— α -Bromo- β -phenylpropaldehyde, obtained by direct bromination of hydrocinnamaldehyde, gives a stable monohydrate, m. p. 87.5–88°, and a semicarbazone, m. p. 136.5°. When heated with an aqueous suspension of barium carbonate, the bromoaldehyde is converted into

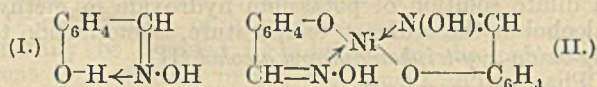
α -hydroxy- β -phenylpropaldehyde, m. p. 51.5–52°, b. p. 120–121°/4 mm. (oxime, m. p. 123°; semicarbazone, m. p. 136.5°; osazone, m. p. 137°; benzoyl derivative, m. p. 70°), together with some hydrocinnamic acid. If silver oxide is used instead of barium carbonate, α -hydroxy- β -phenylpropionic acid, m. p. 98°, is also formed. On oxidation, the aldehyde yielded a variety of products, among them phenylacetaldehyde, b. p. 88–89°/12 mm. (semicarbazone, m. p. 155°), and α -hydroxy- β -phenylpropionic acid. When heated in alcoholic sulphuric acid solution in a sealed tube, the aldehyde isomerises with the formation of acetylphenylcarbinol, b. p. 130–132°/13 mm. (semicarbazone, m. p. 194°), and the corresponding α -diketone, benzoylacetyl, b. p. 113–115°/13 mm.; dioxime, m. p. 238–239°. The carbinol, on treatment by Grignard's method with magnesium phenyl bromide, yielded β -dihydroxy- β -diphenylpropane, m. p. 103–104°, which gave acetophenone on oxidation.

M. ZVEGINTZOV.

Acetylation of *o*-hydroxy-aldehydes. T. MALKIN and M. NIERENSTEIN (J. Amer. Chem. Soc., 1931, 53, 239–242).—Treatment of salicylaldehyde, β -resorcyraldehyde, and phloroglucinaldehyde with acetic anhydride in presence of ether and potassium carbonate gives the corresponding *O*-acetyl, *diacetyl*, m. p. 69°, and *triacetyl*, m. p. 101°, derivatives. In absence of ether, formation of benzylidene acetate occurs. The triacetylphloroglucinaldehyde of Pratt and Robinson (A., 1925, i, 826; cf. Robertson and Robinson, A., 1927, 974) is 2 : 4 : 6-triacetoxybenzylidene acetate (Herzig and Wenzel, A., 1904, i, 251).

H. BURTON.

Co-ordination compounds of oximes. II. Nickel and cobalt compounds of *o*-hydroxybenzaldoxime. O. L. BRADY (J.C.S., 1931, 105–107).—Nickel and cobalt complexes of salicyldoxime are described. To account for the attack of its oximino- and not its phenolic hydroxyl group on acetylation, the formula (I) is suggested for the oxime, which has



the physical properties of a co-ordination compound. The corresponding structure (II) is advanced for the nickel (and cobalt) complexes.

H. A. PIGGOTT.

2-Hydroxy-4-methoxy- and 4-hydroxy-2-methoxy-benzaldehydes. T. E. DE KIEWIET and H. STEPHEN (J.C.S., 1931, 84–85; cf. A., 1898, i, 581; 1922, i, 555).—*m*-Methoxyphenol is condensed with hydrogen cyanide and hydrogen chloride in dry ether in the cold, the resulting aldimide hydrochlorides (after 24 hrs.) hydrolysed by a large excess of water, and the aldehydes separated by distillation in steam in which 2-hydroxy-4-methoxybenzaldehyde alone is volatile. The phenylhydrazone, m. p. 158°, *p*-nitrophenylhydrazone, m. p. 255° (decomp.), and semioxamazone, m. p. 242°, of 4-hydroxy-2-methoxybenzaldehyde, and the *p*-nitrophenylhydrazone, m. p. 226.5°, semioxamazone, m. p. 247°, and semicarbazone, m. p. 230°, of 2-hydroxy-4-methoxybenzaldehyde are described.

H. A. PIGGOTT.

Catalytic production of acetophenone. I. G. LAKOMKIN (J. Appl. Chem., Russia, 1930, 3, 555—572).—Acetophenone is obtained by interaction of acetic and benzoic acids in presence of thorium dioxide or preferably manganous oxide. The quantity of catalyst used affects the yield only if the acid vapours are not preheated. The yield is maximal at 600°; preheating of the reacting vapours is recommended.

CHEMICAL ABSTRACTS.

Action of organic magnesium compounds on $\alpha\beta$ -oxido-ketones and -esters. E. P. KOHLER, N. K. RICHTMYER, and W. F. HESTER (J. Amer. Chem. Soc., 1931, 53, 205—221).— α -Benzoyl- β -phenylethylene oxide, prepared by a modification of Weitz and Scheffer's method (A., 1921, i, 868), is converted by an excess of magnesium phenyl bromide at the ordinary temperature into triphenylcarbinol (phenyl-diethylcarbinol is produced similarly using magnesium ethyl bromide) and resinous material. The reaction involves the intermediate formation of benzophenone, since triphenylcarbinol is also obtained from magnesium phenyl bromide and α -benzoyl- β -anisylethylene oxide, whilst magnesium mesityl bromide and α -acetyl- β -phenylethylene oxide give acetylmesitylene. When α -benzoyl- β -phenylethylene oxide is treated with 1 mol. of magnesium phenyl bromide at -10° , and the mixture decomposed with ice-cold acid, $\beta\gamma$ -oxido-

$\alpha\gamma$ -triphenylpropyl alcohol (I), $\text{CPh}_2\text{CH}(\text{O})\text{CH}_2\text{CPh}_2\text{OH}$, m. p. 129—130°, is produced. This is unaffected by magnesium phenyl bromide at -10° , but is converted at the ordinary temperature into triphenylcarbinol. Treatment of I with methyl alcohol containing a little hydrochloric acid gives $\alpha\beta$ -dihydroxy- γ -methoxy- $\alpha\gamma$ -triphenylpropane, m. p. 154—155° (oxidised by chromic and acetic acids to methyl benzoate and benzophenone), also prepared by the action of magnesium phenyl bromide on phenyl α -hydroxy- β -methoxy- β -phenylethyl ketone (*dimethylacetal*, m. p. 122°, obtained from phenyl $\alpha\beta$ -dibromo- β -phenylethyl ketone and methyl-alcoholic sodium methoxide). When I is treated with a dilute solution of potassium hydroxide in methyl alcohol at the ordinary temperature, isomerisation to $\beta\gamma$ -oxido- $\alpha\gamma\gamma$ -triphenylpropyl alcohol (II),

$\text{CPh}_2\text{CH}(\text{O})\text{CH}_2\text{CPh}_2\text{OH}$, m. p. 103°, occurs. This is oxidised by chromic and acetic acids to α -benzoyl- $\beta\beta$ -diphenylethylene oxide, m. p. 124—125°, and with magnesium phenyl bromide yields diphenylacetaldehyde and benzhydrol: $(\text{II}) + \text{Ph}\cdot\text{MgBr} \longrightarrow \text{CPh}_2\text{CH}\cdot\text{OMgBr} + \text{Ph}\cdot\text{CHO}$; $\text{Ph}\cdot\text{CHO} + \text{Ph}\cdot\text{MgBr} \longrightarrow \text{CHPh}_2\cdot\text{OMgBr}$. Treatment of II with magnesium methyl iodide gives diphenylacetaldehyde, benzaldehyde, and a small amount of probably *diphenylacetylphenylcarbinol*, m. p. 128°. When II is exposed to air, autoxidation occurs and the main product formed is the peroxide, $\text{CPh}_2\text{CH}(\text{O})\text{O}(\text{O})\text{CHPh}\cdot\text{OH}$, which decomposes at about 160° into benzaldehyde, formic acid, and benzophenone, and reacts with magnesium methyl iodide, forming $\alpha\alpha$ -diphenylpropylene glycol, m. p. 94—95°, also prepared from ethyl lactate and an excess of magnesium phenyl bromide, and α -phenylethyl alcohol. Dibromodibenzoylmethane reacts with magnesium phenyl bromide, forming phenyl α -bromo-

β -hydroxy- $\beta\beta$ -diphenylethyl ketone, m. p. about 180° (decomp.), converted by methyl-alcoholic sodium methoxide into α -benzoyl- $\beta\beta$ -diphenylethylene oxide. This reacts with magnesium phenyl bromide and ethyl iodide, yielding diphenylacetaldehyde in each case: $\text{CPh}_2\text{CH}(\text{O})\text{CH}_2\text{CPh}_2\text{OH} + \text{R}\cdot\text{MgX} \longrightarrow \text{CPh}_2\text{CH}\cdot\text{OMgX} + \text{Bz}\cdot\text{R}$.

The ethyl diphenylglycidate of Pointet (A., 1909, i, 234) and of Bardon and Ramart (A., 1926, 950) is ethyl $\beta\beta$ -diphenylpyruvate, m. p. 37° (*phenylhydrazone*, m. p. 99—100°; corresponding *methyl ester*, b. p. 175°/5 mm., m. p. 75°); isomerisation occurs during distillation (cf. Troell, A., 1929, 171). Crude ethyl diphenylglycidate, prepared from benzophenone and ethyl chloroacetate by Darzens' method (A., 1905, i, 116), is converted by magnesium phenyl bromide into diphenylacetaldehyde, and by distillation with steam into ethyl $\alpha\beta$ -dihydroxy- $\beta\beta$ -diphenylpropionate, m. p. 130° (corresponding *methyl ester*, m. p. 130—131°). $\beta\beta$ -Diphenylpyruvic acid phenylhydrazone has m. p. (block) 245° (decomp.; lit. 189°). Triphenylcarbinol is also obtained when ethyl $\beta\beta$ -dimethylglycidate and α -phenyl- β -nitrophenylglycidate are treated with magnesium phenyl bromide. There is no evidence that oxido-compounds form 1:4-additive products with Grignard reagents (cf. Bardon and Ramart, *loc. cit.*)

The initial product of the reaction between ethyl $\beta\beta$ -diphenylpyruvate and magnesium phenyl bromide is ethyl α -hydroxy- $\alpha\beta\beta$ -triphenylpropionate, m. p. 118—120°. The further reaction products are phenyl α -hydroxy- $\alpha\beta\beta$ -triphenylethyl ketone, m. p. 123°, and $\alpha\beta$ -dihydroxy- $\alpha\beta\gamma\gamma$ -pentaphenylpropane, m. p. about 190° (decomp.). When the last-named compound is heated in acetic acid a mixture of benzhydrol and phenyl benzhydrol ketone is obtained; in absence of the acid small amounts of benzophenone and $\alpha\beta\beta$ -triphenylethyl alcohol are produced also.

H. BURTON.

Benzoin condensation. Influence of the nature of radicals on the formation of mixed benzoin. M. TIFFENEAU and (MLLE.) J. LEVY (Compt. rend., 1931, 192, 287—290).—By the ordinary benzoin condensation benzaldehyde with *o*-methoxybenzaldehyde, anisaldehyde, piperonal, and furfuraldehyde, and anisaldehyde with *o*-methoxybenzaldehyde afford (>50% yield) only one benzoin, namely, benzoyl-*o*-methoxyphenyl- (*semicarbazone*, m. p. 178—179°); *p*-methoxybenzoylphenyl-, m. p. 105.5—106.5°; 3:4-methylenedioxybenzoylphenyl-, m. p. 120° (*semicarbazone*, m. p. 180—182°); *furfuroylphenyl*-, m. p. 135—136° (*semicarbazone*, m. p. 192—193°); and *p*-methoxybenzoyl-*o*-methoxyphenyl-, m. p. 101—102° (*semicarbazone*, m. p. 204°), *-carbinol*, respectively. Benzaldehyde and *m*-methoxybenzaldehyde afford *m*-methoxybenzoylphenyl- and benzoyl-*m*-methoxyphenyl-*carbinol*, whilst anisaldehyde and piperonal give *p*-anisoyl-3:4-methylenedioxyphenyl- and 3:4-methylenedioxybenzoyl-*p*-anisyl-, m. p. 98—99° (*semicarbazone*, m. p. 191°), *-carbinol*. Mixtures of isomeric benzoin are thus obtained when the affinities of the two aryl groups are approximately equal.

J. W. BAKER.

Reactivity of substituents in the five-carbon ring. V. JACOBI (J. pr. Chem., 1931, [ii], 129,

55—96).—Interaction of equimolecular quantities of 1:3-diketohydrindene and terephthalaldehyde at 110—120° gives 1:3-diketo-2-p-aldehydobenzylidene-hydrindene, m. p. 173°; excess of the former gives 2:2'-terephthalylidenebis-1:3-diketohydrindene, m. p. 293°. In each case a yellow substance of high m. p. is also formed. The action of magnesium methyl iodide on 1:3-diketohydrindene leads to enolisation, and only by use of a large excess of the Grignard reagent is 1:3-dihydroxy-3-methylindene (or 3-hydroxy-1-keto-3-methylhydrindene), b. p. 126°/10 mm., again accompanied by a yellow substance of high m. p., formed. This is dehydrated when heated to 3-keto-1-methylindene (no m. p. given).

The isolation of 5-bromoindene in a crystalline form, m. p. 36°, is described. With magnesium in ether it forms a Grignard reagent only with difficulty; the product cannot be isolated in a state of purity, but its formation is proved by regeneration of indene on decomposition with water or dilute acids.

1:2:5-Tribromohydrindene is obtained as an unstable oil by addition of bromine to 5-bromoindene in light petroleum. With 10% alcohol it gives 1:5-dibromo-2-hydroxyhydrindene, m. p. 80.5—81.5°. Interaction of indene dibromide with absolute alcohol gives 1-bromo-2-ethoxyhydrindene, and with methyl alcohol 1-bromo-2-methoxyhydrindene. Distillation of the former under reduced pressure gives 1-bromoindene, b. p. 135.5—136°, oxidised by dilute nitric acid to phthalic acid; its constitution is proved by its conversion by magnesium, followed by carbon dioxide, in dry ether into indene-1-carboxylic acid, m. p. about 70°, identified by difference. Bromination of 1-bromoindene resulted in a small amount of substitution only, no direct addition being observed.

Distillation of indene dibromide at atmospheric pressure gives 3-bromoindene, b. p. 110—120°/11 mm., oxidation of which with dilute nitric acid gives phthalic acid. Action of magnesium in ether precipitates the magnesium indyl bromide, converted by carbon dioxide into indene-3-carboxylic acid, m. p. about 160°, 3:3'-di-indyl ketone, m. p. 235°, and indene. Unlike the 1-bromo-compound, 3-bromoindene readily adds bromine to give 1:2:3-tribromohydrindene, converted by 10% alcohol into 1:3-dibromo-2-hydroxyhydrindene, m. p. 90°.

Bromination of indene in a hot, dilute aqueous suspension gives a tribromoindene, m. p. 133.5—134°, which, from its oxidation by dilute nitric acid to a dibromophthalic acid, m. p. 135°, must be dibrominated in the benzene nucleus. H. A. PIGGOTT.

Polymerisation and pyrogenic decomposition of phenylacetic anhydride. I. *cyclo*Butane- α -diones. P. KALNIN (Latvian Univ. Raksti, 1930, 1, 468).—A preliminary note. During the fractionation of phenylacetic anhydride in a vacuum considerable decomposition occurs, with the production of phenylacetic acid and a residue of a red substance which gives the reactions of an α -diketone. The red substance is considered to be diphenylcyclobutane- α -dione, formed by unsymmetrical polymerisation of the enolic form of the anhydride and elimination of 2 mols. of phenylacetic acid. F. L. USHER.

B B

Sulphonic acid derivatives of naphthaquinone chloroimines and di-imines. W. SWIENTOSŁAWSKI, A. PILTZ, and F. KRACZKIEWICZ (Rocz. Chem., 1931, 11, 40—48).—Potassium β -naphthaquinone-1-chloroimine-4-sulphonate, the corresponding 1-bromo-derivative, potassium β -naphthaquinone-2-chloroimine-4-sulphonate, and α -naphthaquinonedichloroimine-6-sulphonate are prepared by halogenating the appropriate aminonaphthol- or naphthylenediamine-sulphonic acid and salting out the product with potassium chloride as formed at a low temperature.

R. TRUSZKOWSKI.

New compound of benzaldehyde and anthrahydroquinone. H. A. BEATTY (J. Amer. Chem. Soc., 1931, 53, 378—380).—A solution of anthrahydroquinone in benzaldehyde containing a trace of hydrochloric acid gradually deposits (in absence of oxygen) a compound, $C_{28}H_{20}O_3$, m. p. 211—212° (corr.), probably formed by elimination of 1 mol. of water between 2 mols. of benzaldehyde and 1 mol. of oxanthrone (the tautomeric form of anthrahydroquinone). The compound is conveniently obtained when a mixture of anthraquinone, benzoic acid, alcohol, and benzaldehyde is exposed to sunlight in absence of oxygen, whereby photo-reduction of the quinone occurs; the volatile products are distilled with steam, and the residue is treated successively with alcohol and sodium hyposulphite to remove resinous material and unchanged anthraquinone, respectively. The compound is hydrolysed by alcoholic hydrochloric acid to benzaldehyde and anthrahydroquinone. H. BURTON.

Reduction products of the hydroxyanthraquinones. XII. G. F. ATTREE and A. G. PERKIN (J.C.S., 1931, 144—173; cf. A., 1930, 607).—The hydroxy- and methoxy-9-anthrone (-anthranols) described below are prepared by reduction of the corresponding hydroxy- or methoxy-anthraquinones with stannous chloride and hydrochloric acid (cf. Goodall and Perkin, A., 1924, i, 527).

Demethylation of a methoxyanthraquinone may generally be avoided by addition of the reducing agent to a solution in hot acetic acid and allowing to cool; partial demethylation may be effected during reduction by boiling for a limited time. Prolonged boiling may lead to the reduction of both carbonyl groups. In the majority of cases the anthrone is readily oxidised by ferric chloride in alcohol and acetic acid to the corresponding dianthrone, which is formed in varying yield, often accompanied by the anthraquinone; it is suggested that the latter is formed by reaction in the anthranol form. In comparatively few cases could further oxidation to the corresponding dianthaquinones, helianthrone, and naphthadanthrones be effected (cf. A., 1924, i, 300; 1925, i, 1160). The following are described: 3-methoxy-9-anthrone, m. p. 108—109° (by reduction of 2-methoxyanthraquinone with copper and sulphuric acid at 140°: purified through the anthranol acetate, m. p. 152—154°); 3:3'-dimethoxy-9:9'-dianthrone, m. p. 215—217°; the dianthranyl diacetate, m. p. 228—230°, is oxidised by iodine in pyridine to 3:3'-dimethoxydianthaquinone (A., 1925, i, 1160), further oxidised by insol-

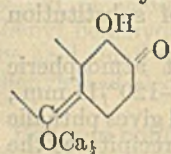
ation in pyridine to 2:2'-dimethoxynaphthodianthrone (*loc. cit.*); 3:6-dihydroxyanthrone, m. p. 183—184° (A., 1882, 975) 3:3':6:6'-tetrahydroxydianthrone, decomp. indef. 270—300° (hexa-acetyl derivative, m. p. 280—282°); 3:6-dimethoxyanthrone, m. p. 158—160° (acetyl derivative, m. p. 180—181°) [by reduction of the dimethyl ether, m. p. 215—217°, of isoanthraflavic acid (methyl sulphate and alkali) by copper and sulphuric acid]; 3:3':6:6'-tetramethoxydianthrone, m. p. 242—243° (diacetyl derivative, m. p. 255—256°); 6-hydroxy-3-methoxyanthrone, m. p. 234—236° (diacetyl derivative, m. p. 197—199°); 6:6'-dihydroxy-3:3'-dimethoxydianthrone, m. p. 292—295° (tetra-acetyl derivative, m. p. 229—231°); 3:7-dihydroxyanthrone; 3:3':7:7'-tetrahydroxydianthrone, m. p. 315—318° (hexa-acetyl derivative, darkens 290°); 2:3-dihydroxyanthrone (A., 1903, i, 840); 2:2':3:3'-tetrahydroxydianthrone [tetra-acetoxy-compound, m. p. 274—277° (acetic anhydride); 2:2':3:3'-tetra-acetoxy-9:9'-dianthranyl diacetate, m. p. 293—295° (acetic anhydride and pyridine)]; 2:3-dimethoxyanthrone, m. p. 143—146° (acetyl compound, m. p. 169—171°); 2:2':3:3'-tetramethoxydianthrone, m. p. 243—245° (diacetyl derivative, m. p. 194—196°), readily oxidised by alkaline persulphate to 2:2':3:3'-tetramethoxydianthraquinone, m. p. 290—291°, which is converted by insolation in a mixture of benzene and alcohol into 2:2':3:3'-tetramethoxy-helianthrone, m. p. 287—288°, and -naphthodianthrone, the last being the sole product if the action of light is prolonged; 4:4'-dihydroxydianthrone, m. p. 256—258° (tetra-acetyl derivative, m. p. 265—267°); 1:5-dihydroxyanthrone (cf. A., 1902, i, 773); 1:5-dimethoxyanthrone, m. p. 181—182° (acetyl compound, m. p. 169—171°); 1:1':5:5'-tetramethoxydianthrone, m. p. 305—307°; 1-hydroxy-5-methoxyanthrone, m. p. 131—133° (diacetyl derivative, m. p. 161—163°); 1:1'-dihydroxy-5:5'-dimethoxydianthrone, m. p. 287—289° (tetra-acetyl derivative, m. p. 250—252°); 1:8-dimethoxyanthrone, m. p. 196—197° (by reduction of chrysazin dimethyl ether by zinc and ammonia); 1:1':8:8'-tetramethoxydianthrone, m. p. above 340°; 1-hydroxy-8-methoxyanthrone, m. p. 183—185° (diacetyl derivative, m. p. 164—165°); 1:1'-dihydroxy-8:8'-dimethoxydianthrone, m. p. above 330° (acetyl derivative, m. p. 284—287°); 3:4-dimethoxyanthrone, m. p. 162° [acetyl derivative, m. p. 146—148°; methyl ether, m. p. 116—118° (by methylation of 3:4-dihydroxyanthrone with methyl sulphate and alkali; cf. Graebe and Thode, A., 1906, i, 863; preparation of the dimethoxyanthrone by these authors' method is improved by use of pyridine as solvent)].

1-Hydroxyanthrone is not affected by ferric chloride at 100°. 1-Methoxyanthrone, m. p. 129—131°, prepared by use of copper and sulphuric acid, differs in m. p. from the "1-methoxyanthrone" of Graebe and Bernhard (A., 1906, i, 865), which is probably its methyl ether; it is not acetylated by acetic anhydride and pyridine, a property that appears characteristic of α -hydroxy- and α -methoxy-anthrone.

1:1'-Dimethoxydianthrone (diacetyl derivative, m. p. 290—291°) is best prepared by air oxidation in alkaline methyl alcohol; if much alcohol is employed 1:1'-dimethoxydianthraquinone, m. p. 315—

316°, is formed, also produced by oxidation of the dianthrone with iodine in pyridine at 60°; it is oxidised by insolation in acetone to 4:4'-dimethoxynaphthodianthrone and -helianthrone, hydrolysed by 40% hydrobromic acid at 180° to 4:4'-dihydroxynaphthodianthrone, scarlet, and -helianthrone, orange-red, all melting above 360°. An improved method of preparation of 1-hydroxy-2-methoxyanthrone (Miller and Perkin, A., 1926, 174) is described. It is oxidised to 1:1'-dihydroxy-2:2'-dimethoxydianthrone (tetra-acetyl derivative, m. p. 242—245°) by the methods already described, and also by boiling its solution in nitrobenzene, or by the action of alkali hypiodite in alcohol, or diazomethane in acetone. 4:4'-Dihydroxy-3:3'-dimethoxyhelianthrone, m. p. above 330°, is formed from the anthrone by the action of iodine or arsenic acid in pyridine, or by continued boiling of its nitrobenzene solution, and to some extent by attempted acetylation of the dianthrone at the h. p.; it cannot be acetylated or reduced, but is demethylated by hydrochloric and acetic acids at 180° to 3:3':4:4'-tetrahydroxyhelianthrone, m. p. above 360° (3:3'-diacetoxy-compound, m. p. about 325°), which possesses poor affinity as a mordant dye, but is sulphonated by 20% fuming sulphuric acid at 100° to a product (isolated as crude sodium salt) with marked affinity for wool, which it dyes in deep reddish-brown to slate-blue shades. As causes of the low tinctorial power of this hydroxyhelianthrone the marked chelation of the α -hydroxyl groups, which prevents the formation of a tetra-acetyl derivative, and the absence of an hydroxyl group in the *p*-position to the carbonyl group, are suggested, tinctorial power being regarded as due to a quinonoid type of metallic complex (annexed formula). Oxidation of 1:2-dihydroxyanthrone with ferric chloride or the minimum quantity of nitrobenzene gives 1:1':2:2'-tetrahydroxydianthrone [tetra-acetyl derivative, m. p. 245—247° (acetic anhydride and pyridine)]; excess of the latter, or iodine in pyridine, gives 3:3':4:4'-tetrahydroxyhelianthrone, converted by sulphuric acid at 160° into a substance isolated in small amount as acetyl derivative (probably 4:4'-dihydroxy-3:3'-diacetoxy-naphthodianthrone).

Attempted reduction of 1:3-dimethoxyanthraquinone with copper and sulphuric acid fails, but zinc and ammonia in water or pyridine gives (probably) 10-hydroxy-1:3-dimethoxyanthranol, m. p. 156—158°, and stannous chloride gives (after acetylation) 1:3-diacetoxyanthranyl acetate, m. p. 154—155°, identified by hydrolysis to 1:3-dihydroxyanthrone, also obtained by reduction of purpuroxanthin with stannous chloride. A stannous chloride reduction of anthrarufin dimethyl ether at 65° for 3 hrs. gives 10-hydroxy-1:5-dimethoxyanthrone, m. p. 153—155°. Oxidation of 6-acetoxy-3-methoxyanthranyl acetate (above) with chromic and acetic acids gives the acetyl derivative, m. p. 194—196°, of isoanthraflavic acid monomethyl ether, m. p. 283—285°; the last-named is also obtained by oxidation of the anthrone, and in minute amount by methylation of isoanthraflavic acid. 2:2':3:3'-Tetrahydroxyhelianthrone (tetra-



acetyl derivative, m. p. 295—297°) and *-naphthadanthrone* (tetra-acetyl derivative, m. p. above 360°) are obtained by demethylation of the corresponding methoxy-derivatives with hydrochloric and acetic acids at 190° and 215°, respectively. The former readily dyes mordanted calico and wool, for which the latter has little affinity; its acetyl derivative is oxidised by chromic acid to 2 : 2' : 3 : 3'-tetra-acetoxy-1 : 1'-dianthraquinonyl, m. p. 200° with subsequent re-solidification and re-melting at 268—270° (tetra-hydroxy-compound, m. p. above 360°).

H. A. PIGGOTT.

Reaction of aromatic 1 : 4-diketone monoximes occurring in place of the Beckmann transformation. I. R. SCHOLL, H. SEMP, and E. STIX [with, in part, W. MESSE] (Ber., 1931, 64, [B], 71—77).—The poor yield of anthraquinone-1-carboxyxylylide obtained by the action of alcoholic hydrogen chloride on *m*-xylyl 1-anthraquinonyl ketoxime (cf. A., 1927, 885) has led to examination of the behaviour of glacial acetic and sulphuric acids, which leads to the formation in good yield of an anhydride, $C_{23}H_{15}O_2N$, m. p. 240°. The theoretically possible products of the Beckmann transformation of the oxime, anthraquinone-1-carboxy-*m*-xylylide and 1-*m*-xylamidoanthraquinone, m. p. 261—262°, are converted by the reagents into anthraquinone-1-carboxylic acid and 1-aminoanthraquinone, respectively. Anhydride formation does not take place between the oxime hydroxyl and a hydrogen atom of the *ortho*-methyl group, since, although *p*-xylyl 1-anthraquinonyl ketoxime, m. p. 223° after softening and becoming yellow at 218°, is transformed into an anhydride, $C_{23}H_{15}O_2N$, m. p. 265—266° after darkening at 255°; similar behaviour is exhibited by *p*-tolyl 1-anthraquinonyl ketoxime (anhydride, $C_{22}H_{13}O_2N$, m. p. 236—237°) and phenyl 1-anthraquinonyl ketoxime (anhydride, $C_{21}H_{11}O_2N$, m. p. 291°), whereas phenyl *m*-xylyl ketoxime could not be caused to yield an anhydride, but affords only the products of the Beckmann transformation. The possibility that anhydride formation involves a hydrogen atom in aromatic union is examined at the instances of phenyl, *m*-xylyl, and *p*-xylyl 2-methylantraquinonyl 1-ketoximes, which are unchanged by short treatment with the reagent, but transformed under more drastic conditions into 2-methylantraquinone-1-carboxylic acid and black, ill-defined products, and mesityl 1-anthraquinonyl ketoxime, which decomposes in a different direction. The possibility that the anhydride is an acridine derivative is negated by the observation that anthraquinone-1 : 2-acridone is converted by distillation with zinc dust into 2-anilinoanthracene, m. p. 197—198° (picrate) (also derived from 2-anilinoanthraquinone), whereas the anhydride affords a sublimate from which a homogeneous product could not be isolated.

p-Xylyl 1-anthraquinonyl ketone, m. p. 205°, anthraquinone-1-carboxyanilide, m. p. 288—289°, and 2-methylantraquinone-1-carboxyanilide, m. p. 287—288°, are incidentally described.

H. WREN.

Deguelin. I. Preparation, purification, and properties of deguelin, a constituent of tropical fish-poisoning plants. E. P. CLARK (J. Amer.

Chem. Soc., 1931, 53, 313—317).—Details are given for the isolation of the compound, m. p. 171° (A., 1930, 967) (now termed *deguelin*), from derris and cubé roots. Deguelin, $C_{23}H_{22}O_6$, is oxidised by alkaline potassium ferricyanide to *dehydrodeguelin*, $C_{23}H_{20}O_6$, m. p. 233°, oxidised by chromic and acetic acids to *dehydrodeguelone*, $C_{23}H_{18}O_7$, m. p. 292° (corr.) after darkening at about 280°. Treatment of dehydrodeguelin with alcoholic potassium hydroxide and zinc dust affords *deguelic acid*, $C_{23}H_{24}O_8$, m. p. 189° (corr.), converted by acetic anhydride and sodium acetate into dehydrodeguelin. Deguelin is a dimethoxylactone; it occurs also in the leaves of *Cracca* (*Tephrosia*) *vogelii* and the roots of *C. toxicaria*.

H. BURTON.

Relation between rotenone, deguelin, and tephrosin. E. P. CLARK (Science, 1931, 73, 17—18).—Oxidation of deguelic acid with hydrogen peroxide yields derric acid. Tephrosin with sulphuric and acetic acids or with acetic anhydride forms dehydrodeguelin. Derric acid constitutes one half of the molecule of rotenone, deguelin, and tephrosin.

L. S. THEOBALD.

Senegin and its fission products. O. DAFERT and E. KALMAN (Pharm. Acta Helv., 1930, 5, 71—77; Chem. Zentr., 1930, ii, 1999).—Senegin, a saponin extracted from senega root by means of alcohol, m. p. 240°, contains C 52.29, H 7.17%. It is hæmolytic at a dilution of 1 in 6×10^4 . Treatment with sulphuric acid affords dextrose 41.09, methylpentose 11.12, and arabinose 11.06%, and Wedekind and Krecke's compound having m. p. 270° (A., 1924, i, 976).

A. A. ELDRIDGE.

Action of Beckmann's mixture on monocyclic terpenes. II. Terpinolene and "origanene." T. A. HENRY and H. PAGET (J.C.S., 1931, 25—32).—Terpinolene on oxidation with Beckmann's mixture gives, in addition to the principal products lævulic and acetic acids, a small quantity of an unsaturated keto-lactone (I), to which the constitution of β -thujaketo-lactone, m. p. 48—50° [semicarbazone, m. p. 222—223° (corr., decomp.)], is given, since on catalytic reduction it yields homoterpenyl methyl ketone. With permanganate I yields lævulic acid, but prolonged treatment with Beckmann's mixture at 60° yields terebic acid, catalytically reduced to terebic acid. Hydrolysis of I by warm alkali gave an unsaturated acid (II), m. p. 130°, considered to be β -isopropenyl- ϵ -keto- Δ^7 -heptenoic acid, since on reduction it gives ϵ -keto- β -isopropylheptenoic acid. It is considered that these reactions are best explained by the assumption that the first step in the oxidation is the formation of a tetrahydric alcohol by addition of four hydroxyl groups to the two double linkings. The presence of "origanene" in Cyprus origanum oil is confirmed (cf. Pickles, J.C.S., 1908, 93, 866). Crystallographic data are given for two terpinolene tetrabromides, the new tetrabromide having m. p. 119°. Both yield terpinolene on debromination.

J. D. A. JOHNSON.

Natural and synthetic rubber. VI. Pyrolysis of natural rubber in presence of metallic oxides. T. MIDGLEY, jun., and A. L. HENNE (J. Amer. Chem. Soc., 1931, 53, 203—204).—Pyrolysis of pale crêpe rubber in presence of magnesium or zinc oxides gives

the same products as are obtained in their absence (A., 1929, 702), but in different proportions. Zinc oxide has approximately the same effect as magnesium (*loc. cit.*).
H. BURTON.

Menthone series. IX. Resolution of *dl*-menthol and *dl*-camphor-10-sulphonic acid. J. READ and W. J. GRUBB (J.C.S., 1931, 188—195).—*dl*-Menthol may be resolved by fractional crystallisation of its *d*(or *l*)-camphor-10-sulphonate, obtained by the action of *d*(or *l*)-camphor-10-sulphonyl chloride in quinoline. The esters are pure (40%) after four crystallisations (twice from light petroleum and twice from ethyl acetate), but hydrolysis, which is best carried out with hot 50% aqueous oxalic acid, gives only 10% of pure *d*(or *l*)-menthol together with *d*(or *l*)-camphor-10-sulphonic acid and *d*(or *l*)- Δ^3 -menthene. Similarly *dl*-camphor-10-sulphonic acid may be resolved, using *d*- and *l*-menthols, since *d*-menthol is thus made readily accessible. The menthol esters of camphor-10-sulphonic acid when heated at 153° decompose smoothly into the menthols and the Δ^3 -menthenes. Crystallographic data are given for *l*-menthyl *d*-camphor-10-sulphonate.

J. D. A. JOHNSON.

Optically active diazo-compounds. Diazo-camphane. U. HEUBAUM and W. A. NOYES (J. Amer. Chem. Soc., 1930, 52, 5070—5078).—Treatment of *s*-dibornylcarbamide with nitrogen trioxide in ether at -15° gives the *mononitroso*-derivative, m. p. 73—75° (decomp.), which decomposes slowly at the ordinary temperature to the original carbamide. Nitrosobornylurethane, $[\alpha]_D +11^\circ$ in ether, and nitrosonebornylurethane, $[\alpha]_D -18.5^\circ$ in ether, prepared similarly from the corresponding urethanes, are converted by 2% methyl-alcoholic sodium methoxide in ether at -20° into diazocamphane and diazonecamphane, respectively. Rotatory powers for ethereal solutions of these are given for various wavelengths; the dispersion curve for each compound has its maximum at about 5750 Å., this anomaly being due to an absorption band situated at about 5650 Å. The difference in shape of the dispersion curves, the isolation of a small amount of *l*-bornyl chloride, $[\alpha]_D -33.2^\circ$ in ether, from the decomposition products of diazocamphane by treatment with ethereal hydrogen chloride, and the formation of *d*-bornyl chloride by similar decomposition of diazonecamphane indicate that the diazo-compounds possess different structures. The main product of decomposition of both diazo-compounds is, however, tricyclene, thus indicating that they possess (in part) the same structure. It is suggested that the diazo-compounds may exist as equilibrium mixtures of much cyclic and little chain forms (cf. Lindemann, Wolter, and Groger, A., 1930, 586).
H. BURTON.

Addition of hydrogen to acetylene derivatives. XVIII. Synthesis and hydrogenation of di(hydroxybornyl)acetylene. J. S. SALKIND and W. O. MOCHNATSCH (J. Russ. Phys. Chem. Soc., 1930, 62, 1643—1647).—*s*-Di(hydroxybornyl)acetylene, m. p. 201—202°, which gives an intense red coloration with sulphuric acid, was obtained by Grignard's method by warming camphor with the magnesium derivative of acetylene dibromide for 20 hrs. Hydro-

genation in the presence of even considerable quantities of colloidal palladium as catalyst was very slow, but with palladium-black *s*-di(hydroxybornyl)ethylene, m. p. 165—167°, giving a yellow coloration with sulphuric acid, was rapidly obtained, whilst complete reduction to *s*-di(hydroxybornyl)ethane, m. p. 204°, required about 5½ hrs.
M. ZVEGINTZOV.

Oxidation of 5-hydroxycamphor from campherol. Y. ASAHINA and M. ISHIDATE (Ber., 1931, 64, [B], 188—192; cf. A., 1928, 526; 1929, 72).—Repeated crystallisation of crude campherol from light petroleum, hydrolysis of 5-acetoxycamphor, or treatment of crude hydroxycamphor with 10% potassium hydroxide followed by crystallisation from light petroleum gives 5-hydroxycamphor, m. p. 222°, $[\alpha]_D^{25} +43.8^\circ$ in ethyl alcohol. 5-Acetoxycampherosemicarbazone, m. p. 180—185°, is hydrolysed by sodium carbonate to 5-hydroxycampherosemicarbazone, m. p. 233°. Cautious oxidation of 5-hydroxycamphor affords a *labile* 5-ketocamphor, m. p. 195—200°, $[\alpha]_D^{25} +70.6^\circ$ in alcohol, which decolorises permanganate in water or acetone and bromine in chloroform. Repeated crystallisation from glacial acetic acid converts it into *p*-diketocamphane, stable towards permanganate. With semicarbazide it gives *p*-diketocamphanedisemicarbazone, m. p. 295°. Oxidation of *labile* 5-ketocamphor with aqueous potassium permanganate at 0° gives stable 5-ketocamphor, m. p. 210°, $[\alpha]_D^{25} +103^\circ$, and 1:5:5-trimethylcyclopentane-2:4-dione-1-acetic acid, m. p. 251° (disemicarbazone, m. p. 251°), also formed by autooxidation of the *labile* compound, the enolic content of which increases during preservation.

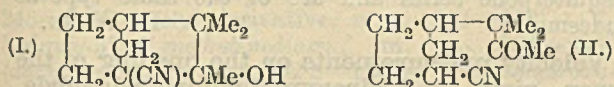
H. WREN.

Camphor and terpenes. V. So-called campherocyanohydrins. J. HOUBEN and E. PFANKUCH (Annalen, 1930, 483, 271—304; cf. A., 1927, 364).—In view of the suggestions of Lapworth and others (A., 1927, 1080) the nature of the compounds described by Passerini (A., 1925, i, 1290) and by Houben and Pfankuch (A., 1927, 364) has been investigated. Passerini's compound is identified with camphene-1-carboxylamide (Houben and Willfroth, A., 1913, i, 970, 1196). Thus, the three forms prepared from the optical varieties of camphor, viz., a racemic form, a *l*-form (sample described of $[\alpha]_D -47.8^\circ$), and a *d*-form, prepared by the action of potassium cyanide on per-nitrosocamphor from pure *d*-camphor in presence of triethylamine ($[\alpha]_D +78.5^\circ$), all melt at 209—210°, not depressed by camphene-1-carboxylamide prepared from bornyl chloride, for which a value $[\alpha]_D +32^\circ$ has been recorded (*loc. cit.*). The observations of Passerini on the acid hydrolysis of the compound could not be confirmed, the action of hydrochloric acid leading to a chlorocamphanecarboxylamide. No formation of an imino-ether takes place with dry alcoholic hydrogen chloride; alkaline hydrolysis of the *dl*-“cyanohydrin” affords (90% yield) *dl*-camphene-1-carboxylic acid, m. p. 109—110°. *d*-Camphene-1-carboxylic acid, $\begin{array}{c} \text{CH}_2\text{CH} \text{---} \text{CMe}_2 \\ | \quad \quad | \\ \text{CH}_3 \quad \quad \text{CH}_3 \end{array}$ (similarly from the *d*-“cyanohydrin”), m. p. 83—84°, $[\alpha]_D^{25} +95.5^\circ$, gives with *l*-camphene-1-carboxylic acid from *l*-bornyl

chloride, the above racemate. The acid so obtained by hydrolysis is further characterised by oxidation with ozone to camphenonic acid (new m. p. 134°; oxime, m. p. 171—172°) (*d*-acid, m. p. 106°, $[\alpha]_D^{20} +75^\circ$). Similar ozonisation of the *d*-“cyanohydrin” affords *d*-camphenonamide, m. p. 152—153°, $[\alpha]_D^{20} +55^\circ$. Further, the acid from the *d*-cyanohydrin is hydrogenated to D-1-dihydrocamphene-1-carboxylic acid, m. p. 56—57° (amide, through the chloride, m. p. 174—175°, $[\alpha]_D^{20} -16.7^\circ$); direct hydrogenation of the *d*-“cyanohydrin” affords the last-mentioned amide, whilst the *dl*-compound gives quantitatively the dihydrocamphene-1-carboxylamide, m. p. 189—190°, described by Houben and Willfroth (*loc. cit.*). *d*-Camphene-1-carboxylic acid, m. p. 83—84°, is readily converted through the chloride into the original *d*-“camphorecyanohydrin,” m. p. 208—210°, which with acetic anhydride gives *d*-camphene-1-nitrile, b. p. 108—110°, m. p. 38—40°, $[\alpha]_D^{25} +40.5^\circ$ (no imino-ether formation with alcoholic hydrogen chloride). Treatment of either active form of the cyanohydrin with alcoholic hydrogen chloride causes the rotation gradually to approach zero, the formation of an intermediate compound, $C_{11}H_{17}ON \cdot 2HCl$, being postulated; on treatment with water the original compound is re-formed, and inversion of the rotation may occur.

The mechanism of the formation of camphene-1-carboxylamide from pernitrosocamphor is discussed; in this connexion the *silver* salt and *methyl* ester, m. p. 102°, of Passerini's intermediate compound are described.

To Houben and Pfankuch's compound is ascribed the constitution I. Hydrolysis of I cannot be



effected without other alteration of the molecule; the action of sodium methoxide causes isomerisation to 3-(α -dimethylacetonyl)cyclopentamethylene-1-nitrile (II), b. p. 172—174°/17 mm., the corresponding ketonic acid (III), b. p. 186—188°/10 mm., $[\alpha]_D^{20} -2.6^\circ$ (*dl*-acid also prepared) (*semicarbazone*, m. p. 200—202°), resulting on hydrolysis with methyl-alcoholic potassium hydroxide. *dl*-III is broken down to *dl*-camphene-camphoric acid, m. p. 134—135°, by the action of hypobromite, *l*-III similarly giving a mixture of active and inactive acids from which *l*-camphene-camphoric acid, m. p. 142—143°, $[\alpha]_D -1.0^\circ$, is isolated.

D-1-6-Bromocamphane-1-carboxylic acid, m. p. 118—120° (efferv.), $[\alpha]_D^{20} -15.5^\circ$ (by addition of hydrogen bromide to *d*-camphene-1-carboxylic acid), on treatment with dilute alkali is converted into a mixture of the original acid and D-1-6-hydroxycamphane-1-carboxylic acid, m. p. 142—143°, $[\alpha]_D^{20} -17^\circ$, which is stable to alkaline hydrolysis, but readily passes into *d*-camphene-1-carboxylic acid, m. p. 83°, on treatment with dilute acids; the corresponding *methyl* ester, m. p. 59—60°, $[\alpha]_D^{20} -19.5^\circ$, is converted by sodium methoxide into the *methyl* ester of III, b. p. 154—155°/17 mm., $[\alpha]_D -3^\circ$ (*semicarbazone*, m. p. 86—87°), and by methyl-alcoholic alkali into III, $[\alpha]_D -6.6^\circ$; like the free acid, it is sensitive to mineral acids, readily yielding methyl camphene-1-carboxylate.

6-Hydroxycamphane-2-carboxylic acid (A., 1926,

1251), m. p. 221°, $[\alpha]_D +12.2^\circ$, and its *methyl* ester, m. p. 61—62°, $[\alpha]_D^{20} +24.5^\circ$, are not converted into a ketonic acid by methyl-alcoholic alkali; they are very sensitive to mineral acids, yielding camphene-2-carboxylic acid.

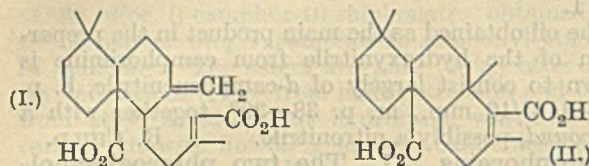
It has not been found possible to convert *dl*-bromocamphane-1-nitrile, m. p. 150—151° (by addition of hydrogen bromide to 2-camphene-1-nitrile; see above), into I.

The oil obtained as the main product in the preparation of the hydroxynitrile from camphorimine is shown to consist largely of *d*-camphenenitrile, b. p. 108—112°/10 mm., m. p. 38—39°, together with a compound, possibly a nitronitrile. R. CHILD.

Camphoreins. II. The two phloroglucinolcamphoreins. V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1930, 18, 164—171; cf. A., 1930, 783).—The isomerism of α -phloroglucinolcamphorein, m. p. above 290° (Sircar and Dutt, J.C.S., 1922, 121, 1283) and β -phloroglucinolcamphorein, m. p. 214—218° (Singh, Rai, and Lal, *ibid.*, 1421), may be attributed to condensation with different carbonyl groups of camphoric anhydride. Neither is convertible into the other by way of the acyl derivatives. α -Phloroglucinolcamphorein yields deeply-coloured sodium and disodium salts of quinonoid structure, and a colourless *tetra*-acetyl derivative, m. p. 136° (decomp.), and pale yellow *tetrabenzoyl* derivative, m. p. 205° (decomp.), of lactone structure. β -Phloroglucinolcamphorein yields deeply-coloured sodium and disodium salts and a colourless *tetra*-acetyl derivative, m. p. 152° (decomp.). R. K. CALLOW.

Higher terpene compounds. XLIII. Bouveault reduction of the esters of agathic- and *iso*-agathic-dicarboxylic acids. Conversion of the last-named ester into a new methylpimanthrene. L. RUZICKA and J. R. HOSKING (Helv. Chim. Acta, 1931, 14, 203—219).—Dimethyl agathiedicarboxylate (one ester group only is hydrolysed by short treatment with alcoholic sodium hydroxide) is treated with sodium and alcohol, the resultant product hydrolysed and separated into neutral (30%) and acidic (70%) fractions. The neutral part consists mainly of *methyl hydroxydihydroagathate*, $C_{18}H_{30}(\text{CH}_2\cdot\text{OH})\cdot\text{CO}_2\text{Me}$, b. p. 193—195°/0.2 mm., d_4^{20} 1.026, n_D^{20} 1.5076, together with a small amount of *dihydroxydihydroagathene*, $C_{18}H_{30}(\text{CH}_2\cdot\text{OH})_2$, m. p. 112—113°, which is reduced catalytically (Adams) in ethyl acetate to *dihydroxytetrahydroagathene*, m. p. 107—108°. Distillation of the acidic fraction in a high vacuum causes elimination of carbon dioxide with the production of *methyl noragathate*, b. p. 146—148°/0.1 mm., d_4^{20} 1.002, n_D^{20} 1.5082 (cf. A., 1929, 572), which is practically unaffected by treatment with sodium and alcohol; *methyl hydrogen dihydroagathiedicarboxylate*, b. p. 210—212°/0.1 mm., is also isolated from the distillate. Reduction of dimethyl *iso*agathiedicarboxylate (this vol., 232) with sodium and alcohol gives a mixture of *methyl hydroxyisoagathate*, b. p. 203—205°/0.3 mm., m. p. 125—126°, and *dihydroxyisoagathene*, $C_{18}H_{28}(\text{CH}_2\cdot\text{OH})_2$, m. p. 172—173°, both of which are unsaturated (yellow colorations with tetranitromethane). The former of these is converted by hot 99% formic acid into a mixture of (probably) *methyl dehydroisoagathate* and *isoagathate*, dehydrogenated

by selenium at 260—340° to a *methylpimanthrene*, m. p. 142—143° [*picrate*, m. p. 161—163°; *quinone*, m. p. 194° (*quinoxaline*, m. p. 131—132°, from *o*-phenylenediamine)]. Crystallographic data [by NANNINGA] are given for tetrahydronoragathic acid (A., 1929, 572). The various transformations of agathidicarboxylic acid are readily explicable when the acid is formulated as I (evidence for this from



ozonolysis experiments to be published later). *iso*-Agathidicarboxylic acid is represented as II. The building of the carbon skeleton (I) from four isoprene units is discussed. H. BURTON.

Higher terpene compounds. XLIV. Constitution of pimanthrene. L. RUZICKA, G. B. R. DE GRAAFF, and J. R. HOSKING (Helv. Chim. Acta, 1931, 14, 233—239).—Oxidation of retenequinone (1-methyl-7-isopropylphenanthraquinone) with potassium permanganate in aqueous pyridine (cf. Bucher, A., 1910, i, 239) affords a mixture of 4- β -hydroxyisopropylidiphenyl-2:2':3'-tricarboxylic acid, m. p. 188° (cf. *loc. cit.*), and amorphous products, separable owing to the ready solubility of the latter in acetone. The tricarboxylic acid is oxidised by chromic and acetic acids to diphenyl-2:4:2':3'-tetracarboxylic acid (*methyl ester*, m. p. 153—154°), whilst the amorphous products are oxidised by nitric acid (*d* 1.5) to hemimellitic and trimellitic acids. Oxidation of retene with alkaline potassium ferricyanide gives a mixture of the above tetracarboxylic acid and phenanthrene-1:7-dicarboxylic acid (*methyl ester*, m. p. 151—152°), separable owing to their differing solubilities in methyl alcohol. The dicarboxylic acid is also formed by similar oxidation of pimanthrene. Pimanthrenequinone is oxidised as retenequinone to the above tetracarboxylic acid and amorphous products (oxidised by nitric acid to hemimellitic acid and the tetracarboxylic acid). Pimanthrene is 1:7-dimethylphenanthrene.

The formation of a dimethylphenanthrene, m. p. 45°, from retene by Meyer's method (Z. angew. Chem., 1924, 37, 796) could not be confirmed.

H. BURTON.

Fokienol, a new monocyclic sesquiterpene alcohol. L. S. GLITCH (Compt. rend., 1930, 191, 1457—1460).—From the essential oil, *d*²⁰ 0.909—0.938, [α]_D +10.75° to 15°, *n*_D²⁰ 1.495—1.505, obtained by distillation of the stems of *Fokienia Hodginsii*, a new tertiary, monocyclic sesquiterpene alcohol, *fokienol*, C₁₅H₂₆O, b. p. 125—126°/2 mm. (corr.), *d*²⁰ 0.9236, [α]_D +18.6°, *n*_D²⁰ 1.4975, is isolated and purified through its *formate*, b. p. 126(166)—170°/2 mm. (corr.), *d*²⁰ 0.9785, [α]_D +16.5°, *n*_D²⁰ 1.4970, some racemisation probably occurring during isolation. The corresponding acetate and benzoate decompose on distillation even under reduced pressure. Fokienol contains two double linkings and is readily dehydrated by the usual acid reagents to a bicyclic sesquiterpene *isofokienene*, b. p. 96—99°/3 mm., *d*²⁰ 0.9076, [α]_D²⁰

+14.6°, *n*_D²⁰ 1.5055 (the constants varying slightly with the conditions of dehydration), but dehydration with metaphosphoric acid gives the monocyclic sesquiterpene *fokienene*, b. p. 112—114°/7 mm., *d*²⁰ 0.8802, [α]_D¹⁶ +16.9°, *n*_D¹⁶ 1.49594, in 15—20% yield. All these compounds yield cadalene on catalytic dehydrogenation with sulphur. J. W. BAKER.

Bitter substances from the elecampane root. K. F. W. HANSEN (Ber., 1931, 64, [B], 67—71).—Technical "helenin" is distilled in a high vacuum and the solution of the distillate in alcohol is saturated with ammonia whereby a mixture of *isoalantolamide*, m. p. 235—240°, and *alantolamide* is precipitated, whereas *dihydroisoalantolactone*, C₁₅H₂₂O₂, m. p. 174°, remains unaffected. When heated at 210° or 240° and then distilled the amides lose ammonia and pass into *isoalantolactone*, m. p. 112°, and *alantolactone*, m. p. 76°, respectively. Reduction of *isoalantolactone* with sodium amalgam and water gives *dihydroisoalantolactone* identical with the natural product. Dehydrogenation of the three lactones by selenium at 260—320° gives 1-methyl-7-ethylnaphthalene, identified as the *picrate*, m. p. 101°, and *styphnate*, m. p. 126°, and oxidised by potassium ferricyanide to naphthalene-1:7-dicarboxylic acid. Complete hydrogenation of the lactones in presence of glacial acetic acid and spongy platinum followed by dehydrogenation of the product with selenium affords 1-methyl-7-ethylnaphthalene in considerably better yield, so that it is very improbable that the second carbon atom removed under the action of selenium is present in a methylene group. The lactones belong to the sesquiterpene series and are of the same type as *cudesmol*. H. WREN.

Velocity measurements on the opening of the furan ring in hydroxymethylfurfuraldehyde. II. H. P. TEUNISSEN.—See this vol., 316.

γ -Nitro- β -furylbutyrophenones. N. L. DRAKE and H. W. GILBERT (J. Amer. Chem. Soc., 1930, 52, 4965—4967).—Furfurylideneacetophenone, b. p. 176°/17 mm., m. p. 26°, reacts with sodionitromethane in methyl alcohol forming *γ -nitro- β -furylbutyrophenone*, m. p. 49.5—50°; *γ -nitro- γ -phenyl- β -furylbutyrophenone*, m. p. 153—153.5°, is prepared similarly, using phenylnitromethane. *Furfurylidene-p-bromoacetophenone*, m. p. 80—81°, gives similarly *p-bromo- γ -nitro- β -furyl-* and *p-bromo- γ -nitro- γ -phenyl- β -furylbutyrophenones*, m. p. 72—73° and 87—88.5°, respectively. H. BURTON.

Absorption spectra of γ -pyrones and pyroxonium salts. R. C. GIBBS, J. R. JOHNSON, and E. C. HUGHES (J. Amer. Chem. Soc., 1930, 52, 4895—4904).—The ultra-violet absorption spectra of γ -pyrone, 2:6-dimethyl- γ -pyrone, benzo- γ -pyrone, and xanthone in alcoholic hydrogen chloride are similar to the spectra in alcoholic solution; there is a slight shift of the bands towards the red in the acid solutions. The formation of the oxonium salts does not appear to cause any appreciable change in the structure of the pyrone ring. The absorption spectrum of the dimethylpyrone in alcoholic sodium ethoxide is the same as in alcohol (cf. Baly, Collie, and Watson, J.C.S., 1909, 95, 144); the pyrone does not exist in

benzenoid-quinonoid equilibrium in solution (cf. Heilbron, Barnes, and Morton, J.C.S., 1923, 123, 2559). The spectrum of the dimethylpyrone also resembles that of 1:2:6-trimethyl-4-pyridone, but differs from that of 4-methoxy-2:6-dimethylpyridine. The absorption spectrum of xanthhydrol in alcoholic hydrogen chloride is identical with that of xanthene in alcohol (or alcoholic hydrogen chloride), but differs from that of xanthone; xanthhydrol exhibits a different spectrum in sulphuric acid. The salts of pyrones are best represented as $O \left\langle \begin{smallmatrix} CH:CH \\ CH:CH \end{smallmatrix} \right\rangle C^{\oplus}OH \left\{ X^{\ominus} \right\}$;

such a formula explains the failure of Gibson and Simonsen to resolve pyrone salts (A., 1928, 1254). The coloured compounds obtained from dimethylpyrone and organic acids by Kendall (A., 1914, i, 858) cannot be prepared with the pure pyrone.

H. BURTON.

Brazilin and hæmatoxylin. XI. Hydroxybenzylchromanones. P. PFEIFFER, E. BREITH, and H. HOYER (J. pr. Chem., 1931, [ii], 129, 31—54; cf. A., 1930, 1041).—By interaction of appropriate derivatives of benzaldehyde with chromanone and 7-methoxy-, 7-hydroxy-, and 7:8-dihydroxy-chromanones in absolute alcohol under the influence of hydrogen chloride, the following are prepared: 4'-methoxy-, m. p. 134°; 3':4'-dimethoxy-, m. p. 117°; 3':4'-methylenedioxy-, m. p. 134.5—137°; 4'-hydroxy-3'-methoxy-, m. p. 126—129° (acetyl derivative, m. p. 160°); 3':4'-dihydroxy-, m. p. 224—225° (sinters 205°) (diacetyl derivative, m. p. 166°); 3'-hydroxy-7:4'-dimethoxy-, m. p. 153—154° (acetyl derivative, m. p. 139—140°); 7-hydroxy-4'-methoxy- (cf. A., 1925, i, 1303); 7-hydroxy-3':4'-dimethoxy-, m. p. 245—249° (acetyl derivative, m. p. 151—152°); 7-hydroxy-3':4'-methylenedioxy-, m. p. 234—236° (acetyl derivative, m. p. 132.5—134°); 7:4'-dihydroxy-3'-methoxy-, m. p. 230—231.5° (sinters at 215°) (purified through the diacetyl derivative, m. p. 151—152.5°); 7:3':4'-trihydroxy-, m. p. 250—253° (sinters 215—217°) (purified through triacetyl derivative, m. p. 132—134°); 7:8-dihydroxy-4'-methoxy-, m. p. 192° (diacetyl derivative, m. p. 140°); 7:8-dihydroxy-3':4'-dimethoxy-, m. p. 174—175° (+1H₂O), m. p. 123—126° (diacetyl derivative, m. p. 183°); 7:8:4'-trihydroxy-3'-methoxy- (+1H₂O), m. p. 206—207° (triacetyl derivative, m. p. 180—181°), and 7:8:3':4'-tetrahydroxy-benzylidenechromanone, decomp. 220—265° (tetra-acetyl derivative, m. p. 166—167°). 7:8-Dihydroxychromanone, m. p. 188—188.5° (+1H₂O, lost at 110—120°) [diacetyl derivative, m. p. 111°; semicarlazone, m. p. 224—225° (decomp.)], is obtained by demethylation of 7:8-dimethoxychromanone (*loc. cit.*) by aluminium bromide in boiling benzene or, better, by boiling, concentrated, aqueous hydrobromic acid. 7-Hydroxychromanone (*loc. cit.*) is also obtained by demethylation of the methoxy-compound by the first method. By hydrogenation in presence of platinum of acetoxy-derivatives of the corresponding benzylidenechromanones 3'-hydroxy-7:4'-dimethoxy-, m. p. 123—124° [acetyl derivative, m. p. 90—91° (oxime, m. p. 160—161°)], 7:3':4'-trihydroxy-, m. p. 201—202° (triacetyl derivative, m. p. 117°), 7:8-dihydroxy-3':4'-dimethoxy-, m. p. 177° (dibenzoyl derivative, m. p. 177.5—178°), and

7:8:3':4'-tetrahydroxy-benzylchromanone, decomp. above 200° (tetra-acetyl derivative, m. p. 107—108°), are obtained. The colours of the solutions of these substances in concentrated sulphuric acid are described.

H. A. PIGGOTT.

Condensation of benzilic and anisilic acids and xanthhydrol with thiophen and thionaphthen. J. ANCÍZAR-SORDO and A. BISTRZYCKI (Helv. Chim. Acta, 1931, 14, 141—153).—Benzilic acid and thiophen condense in presence of acetic and sulphuric acids at the ordinary temperature giving *diphenylthienylacetic acid*, m. p. 217—218° (silver salt; methyl ester, m. p. 149—150°), brominated in acetic acid to a *diphenyldibromothienylacetic acid*, m. p. 213—214° (decomp.). Treatment of the acid with sulphuric acid containing a little acetic acid below 35° affords *diphenylthienylcarbinol*, m. p. 129—130° (lit. 125—131°), whilst potassium hydroxide solution at 180° converts it into *diphenylthienylmethane*, m. p. 63—64°. Pure products could not be obtained from anisilic acid and thiophen. Xanthhydrol and thiophen react in presence of phosphoric oxide and ether forming *9-thienylxanthen*, m. p. 150—151°. Benzilic acid and thionaphthen afford *diphenylthionaphthenylacetic acid*, m. p. 244—245° (decomp.) (sodium salt; methyl ester, m. p. 151—152°), convertible as above into *diphenylbromothionaphthenylacetic acid*, m. p. 223—224° (slight decomp.) (also converted into *diphenylbromothionaphthenylcarbinol*, m. p. 166—167°), *diphenylthionaphthenylcarbinol*, m. p. 125—126°, and *diphenylthionaphthenylmethane*, m. p. 104—105°. Anisilic acid and thionaphthen give *dianisylthionaphthenylacetic acid*, m. p. 245—246° (decomp.) (barium salt; methyl ester, m. p. 166—167°). *9-Thionaphthenylxanthen*, m. p. 172—173°, is prepared similarly to the thienyl analogue.

H. BURTON.

Behaviour of pyrrolidine during catalytic dehydrogenation. N. D. ZELINSKI and J. K. JURJEV (Ber., 1931, 64, [B], 101—103; cf. A., 1929, 1461).—Pyrrole is hydrogenated in presence of palladised asbestos at 160° or, preferably, of rhodium on asbestos at 100° to pyrrolidine, also obtained from pyrroline in presence of palladised asbestos at 135°. The constants, b. p. 85.5—86.5°/741 mm., d_4^{25} 0.8533, n_D^{25} 1.4423, are recorded. At 300°, pyrrolidine is readily dehydrogenated to pyrrole in presence of palladised asbestos.

H. WREN.

Synthesis of compounds in the pyrrole and pyrrolidine series. L. C. CRAIG [with R. M. HIXON] (J. Amer. Chem. Soc., 1931, 53, 187—190).—1-*n*-Butylpyrrole, obtained together with 1-*n*-butylpyrrole-2-carboxy-*n*-butylamide, m. p. 57° [free acid, an oil (*amide*, m. p. 108°)], when mucic acid is treated with *n*-butylamine (cf. Reichstein, A., 1927, 573), is reduced smoothly to 1-*n*-butylpyrrolidine (*chloroaurate*, m. p. 78°) by hydrogen in presence of platinum oxide and an equivalent amount of alcoholic hydrochloric acid. 1-Methylpyrrolidine is prepared by similar reduction of 1-methylpyrrole. Tetra-methylene chloride and *p*-toluidine react at 100°, forming 1-*p*-tolylpyrrolidine, b. p. 120°/8 mm., m. p. 42.5° (*chloroplatinate*, decomp. 175°). H. BURTON.

Preparation of hydroxyproline. H. K. KLABUNDE (J. Biol. Chem., 1931, 90, 293—295).—In

the isolation of proline from the hydrolysis products of gelatin by fractionation of their copper salts (cf. Town, A., 1928, 1148), *l*-hydroxyproline is found in the fraction containing proline, and may be separated by extraction with absolute alcohol, in which it is insoluble, and purified by means of its picrate (cf. Cox and King, A., 1930, 73). H. A. PICCOTT.

Pyrrole-2-aldehyde. B. EMMERT and K. DIEHL (Ber., 1931, 64, [B], 130—132).—The hypothesis that pyrrole-2-aldehyde is in equilibrium dependent on the solvent with a more complex form (cf. A., 1929, 1083) is supported by the observation that it is transformed by benzoyl chloride and powdered potassium hydroxide in light petroleum into a mixture of 1-benzoylpyrrole-2-aldehyde, m. p. 90° (also derived from the sodium derivative of pyrrole-2-aldehyde and benzoyl chloride; phenylhydrazone, m. p. 154°), and the dimeric benzoyl derivative, $\text{CH} \begin{array}{c} \text{CH:C-CH(Obz) \cdot N-CH} \\ \text{CH \cdot N-CH(Obz) \cdot C:CH} \end{array} \text{CH}$, m. p. 178°. 1-*p*-Toluylopyrrole-2-aldehyde, m. p. 79—80° (phenylhydrazone, m. p. 146°), and the dimeric product, $\text{C}_{26}\text{H}_{22}\text{O}_4\text{N}_2$, m. p. 167—168°, are analogously prepared. H. WREN.

Stereochemistry of *N*-phenylpyrroles. Preparation and resolution of *N*-*o*-carboxyphenyl-2:5-dimethylpyrrole-3-carboxylic acid. XIII. L. H. BOCK and R. ADAMS (J. Amer. Chem. Soc., 1931, 53, 374—376).—Ethyl acetonylacetoacetate and anthranilic acid in alcohol give, after alkaline hydrolysis, *N*-*o*-carboxyphenyl-2:5-dimethylpyrrole-3-carboxylic acid, m. p. 224.5—225.5°, resolved by brucine into the *d*-, $[\alpha]_D^{25} + 27^\circ$ in alcohol [brucine salt, m. p. 175—180° (decomp.), $[\alpha]_D^{25} + 13.5^\circ$ in chloroform], and *l*-isomerides, $[\alpha]_D^{25} - 27.2^\circ$ in alcohol [brucine salt, m. p. 231—232° (decomp.), $[\alpha]_D^{25} - 44.9^\circ$ in chloroform]. The active acids racemise when boiled with 0.1*N*-sodium hydroxide for 24 hrs.

H. BURTON.

Resolution of 1- α -piperidinobenzyl- β -naphthol. W. R. BRODE and J. B. LITTMAN (J. Amer. Chem. Soc., 1930, 52, 5056—5058).—*dl*-1- α -Piperidinobenzyl- β -naphthol (A., 1930, 775) is resolved by *d*-camphorsulphonic acid into the *d*-, m. p. 199—200°, $[\alpha]_D^{25} + 189^\circ$ in benzene, and *l*-forms, m. p. 201—202°, $[\alpha]_D^{25} - 211^\circ$ in benzene [*d*-camphorsulphonate, m. p. 184—185° (decomp.), $[\alpha]_D^{25} + 4.7^\circ$ in chloroform]. All m. p. are corr.

H. BURTON.

Hydrogenation of pyridine with hydrogen under pressure by the Bergius process. H. THIATE (Rec. trav. chim., 1931, 50, 77—90).—The products obtained by hydrogenation of pyridine at 500°/50—100 atm. have been investigated qualitatively and quantitatively. In the absence of a catalyst absorption of hydrogen begins at 450°. Analysis of the gaseous products after removal of ammonia shows the presence of hydrogen (67.9%), carbon monoxide (1.2%), nitrogen (1.2%), methane (13.8%), ethane (7.4%), propane (4.7%), butane (2.0%), butane+pentane (1.0%), ethylene+propylene (0.5%), and propylene+butylene (0.4%), the hydrocarbons being formed by cracking of the pentane originally formed. Steam-distillation from an acid solution of the liquid products (1.2%) affords pentane,

valeronitrile, an unsaturated hydrocarbon $\text{C}_{10}\text{H}_{11}$ (formed only when 1% of aluminium or ferric chloride is added as catalyst), and nitriles, b. p. 220—260°. Steam-distillation from an alkaline medium affords primary amines (containing *n*-amylamine), unchanged pyridine, 3- and 3:5-alkylated piperidines, 2:2'-dipyridyl, and, probably, 2:4-dipyridyl. The solid product consists of carbon and ammonium cyanide. The relative proportions of (1) hydrocarbons, (2) nitriles, and (3) secondary and tertiary amines formed varies with the conditions of hydrogenation. Thus at 500°/50 atm. for 1 and 4 hrs., proportions are, respectively, (1) 16, (2) + (3), 2.5%; and (1) 29, (2) + (3), 2.5%, whilst at 500°/100 atm. for 1 hr. they are (1) 25%, (2) 4.6%, and (3) traces only. Since similar products are obtained by hydrogenation of piperidine, the mechanism of the hydrogenation of pyridine is considered to be primarily reduction to piperidine which subsequently breaks down to the products enumerated above, and a scheme of the formation of these is given. A summary of investigations on the hydrogenation of both aromatic and aliphatic compounds is given. J. W. BAKER.

2:4-Substituted derivatives of pyridine. R. GRAF [with E. LEDERER-PONZER and L. FREIBERG] (Ber., 1931, 64, [B], 21—26).—Pyridine-2-carboxylic acid is converted by protracted treatment with boiling thionyl chloride into 4-chloropyridine-2-carboxyl chloride hydrochloride, transformed by water into 4-chloropyridine-2-carboxylic acid, m. p. 180—181°, in 50—55% yield. When treated with hydrazine hydrate in benzene it affords *di*-4-chloropyridine-2-carboxyhydrazide, $\text{C}_{12}\text{H}_8\text{N}_6\text{Cl}_2$, m. p. 269—271° (decomp.). 4-Chloropyridine-2-carboxyl chloride is converted into the methyl ester hydrochloride, which is treated successively with sodium methoxide and hydrazine hydrate, thereby giving 4-chloropyridine-2-carboxyhydrazide, m. p. 167—168° (benzylidene derivative, m. p. 178°). Treatment of the hydrazide in *N*-hydrochloric acid with potassium nitrite affords the azide, m. p. 92°, converted by warm, dilute acetic acid into nitrogen, carbon dioxide, and 4-chloro-2-aminopyridine, m. p. 130—131° (picrate, m. p. 243—244°). 4-Chloro-2-carbethoxyaminopyridine, m. p. 161°, from the azide and boiling ethyl alcohol, is transformed by boiling hydriodic acid into 4-chloro-2-aminopyridine hydriodide, m. p. 206—207° (decomp.). Treatment of the amine with an excess of benzoyl chloride and potassium hydroxide yields 4-chloro-2-dibenzoylamino pyridine, m. p. 165—166°, converted by boiling ethyl alcohol into ethyl benzoate and 4-chloro-2-benzamidopyridine, m. p. 120—121°. 4-Chloro-2-acetamidopyridine, m. p. 115—116°, is described. 4-Chloro-2-hydroxypyridine has m. p. 184°. 2:4-Dichloropyridine, b. p. 184°, m. p. 0° (additive compound with mercuric chloride), is prepared in the usual manner. 4-Iodopyridine-2-carboxylic acid, m. p. 169° (decomp.), prepared from the chloro-acid, hydriodic acid (*d* 1.7), and red phosphorus, is converted by methyl alcohol and sulphuric acid (1:1) into the methyl ester, from which the corresponding amide, m. p. 158°, and hydrazide, m. p. 160—161° (benzylidene derivative, m. p. 207—208°), are obtained. The hydrazide is converted

successively into the azide, m. p. 89° (decomp.), and 4-iodo-2-aminopyridine, m. p. 163—164° (picrate, m. p. 253—254°). 4-Iodo-2-carbethoxyaminopyridine, m. p. 167°, very slowly hydrolysed by boiling hydriodic acid, 4-iodo-2-dibenzoylamino-pyridine, m. p. 176—177°, 4-iodo-2-benzamidopyridine, m. p. 167—168°, 4-iodo-2-acetamidopyridine, m. p. 150°, and 4-iodo-2-hydroxypyridine, m. p. 195°, are described.

H. WREN.

Condensation of pyridine- and quinoline-carboxylic acids with amino-acids. H. MEYER and R. GRAF (Biochem. Z., 1930, 229, 154—163).—Molecular proportions of the chlorides (or, less satisfactorily, of the anhydrides) of the pyridinemono-carboxylic acids as well as of those of quinaldinic and cinchoninic acids and of that of 2-phenylquinoline-4-carboxylic acid react in chloroform solution with aliphatic and aromatic amino-acids to give esters of *N*-substituted amino-acids. The free acids, obtained from the esters by alkaline hydrolysis, are sparingly soluble in water but readily soluble in dilute acids and alkalis. The following substances were prepared: picolinuric acid, m. p. 184—185° (cf. Cohn, A., 1893, ii, 544); nicotinuric acid, m. p. 237—238° (cf. Ackermann, A., 1912, ii, 967) (methyl ester, m. p. 67—68°; amide, m. p. 193—195°); isonicotinuric acid, m. p. 221—222° (ethyl ester, m. p. 89—90°; amide, m. p. 227—228°); quinaldinic acid, m. p. 183—184° (methyl ester, m. p. 100°; amide, m. p. 231—232°); cinchonuric acid, m. p. 244—246° (ethyl ester, m. p. about 120°; amide, m. p. 226—227°); *N*-2-phenyl-4-quinolylglycine, m. p. 216° (ethyl ester, m. p. 140—141°; amide, m. p. 213°); *N*-nicotinylglycylglycine, m. p. 232° (ethyl ester, m. p. 144—145°); *N*-nicotinylanthranilic acid, m. p. 258—259° (methyl ester, m. p. 127°); *N*-picolinylanthranilic acid, m. p. 171—172° (methyl ester, m. p. 84—85°); *N*-nicotinylanthranilanthranilic acid (cf. Meyer, A., 1907, i, 317), m. p. 222° (methyl ester, m. p. 181°).

W. MCCARTNEY.

Anhydrides of pyridine- and quinoline-mono-carboxylic acids. R. GRAF (Biochem. Z., 1930, 229, 164—168; cf. A., 1928, 1379).—The anhydrides can be prepared by the action of a benzene solution of the acid chloride on the sodium salt. The method cannot be used, however, for the preparation of the 2-carboxylic acids. The anhydrides behave like those of the aromatic acids. They are stable towards moisture, have m. p. lower than those of the corresponding acids, and do not sublime. Their b. p. are higher than those of the corresponding acids. Substances previously described (A., 1925, i, 836) contained only traces of the anhydrides. Nicotinic anhydride, m. p. 122—124°, b. p. 200°/1 mm., isonicotinic anhydride, m. p. 103—104°, and cinchoninic anhydride, m. p. 215°, b. p. 240—250°/1 mm. (corresponding amide, m. p. 178—179°), were prepared.

W. MCCARTNEY.

Preparation of isatin from oximinoacetanilide by Sandmeyer's method. J. P. WIBAUT and M. C. GEERLING (Rec. trav. chim., 1931, 50, 41—43).—Oximinoacetanilide is hydrolysed at the ordinary temperature by dilute sulphuric acid to aniline, formaldehyde, and hydroxylamine:

$$\text{NHPh}\cdot\text{CO}\cdot\text{CH}:\text{N}\cdot\text{OH} + \text{H}_2\text{O} \longrightarrow \text{NH}_2\cdot\text{OH} +$$

$\text{NHPh}\cdot\text{CO}\cdot\text{CHO} \xrightarrow{\text{H}_2\text{O}} \text{NH}_2\text{Ph} + \text{CO}_2 + \text{CH}_2\text{O}$. Such hydrolysis explains the observed separation of isatinmonoxime from the acidic mother-liquor in the preparation of isatin by Sandmeyer's method (A., 1919, i, 318), the hydroxylamine formed from the unchanged anilide reacting with the isatin remaining in solution.

J. W. BAKER.

Synthesis of indolylbutyric acid and its derivatives. R. W. JACKSON and R. H. MANSKE (J. Amer. Chem. Soc. 1930, 52, 5029—5035).—Ethyl cyclohexanone-2-carboxylate and benzenediazonium chloride react in presence of ice and alkali hydroxide, forming the phenylhydrazone, m. p. 142—143° (all m. p. are corr.), of ethyl hydrogen α -ketopimelate. Treatment of this with alcoholic sulphuric acid gives ethyl γ -2-carbethoxy-3-indolylbutyrate, b. p. 235°/7 mm., m. p. 76° (corresponding dimethyl ester, m. p. 64°); a small amount of *s*-diphenylcarbamide is isolated during the distillation of these esters. The corresponding dicarboxylic acid, m. p. 193—194° (decomp.), is decomposed by heat to a mixture of 1-keto-1:2:3:4-tetrahydrocarbazole (small amount) and γ -3-indolylbutyric acid, m. p. 124°, when purified through its methyl ester, m. p. 73—74°. γ -3-Indolylbutyrylhydrazide, m. p. 112°, is converted by the usual method into the azide and thence, by treatment with water or methyl alcohol, into *s*-di-(γ -3-indolylpropyl)-carbamide, m. p. 124°, or methyl γ -3-indolylpropylcarbamate, respectively. Both these compounds react with phthalic anhydride at 230°, forming γ -3-indolylpropylphthalimide, m. p. 132°, hydrolysed by aqueous-alcoholic hydrazine to γ -3-indolylpropylamine.

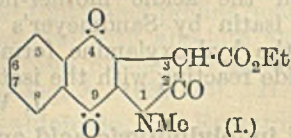
Reduction of methyl β -3-indolylpropionate with sodium and alcohol gives γ -3-indolylpropyl alcohol, solidifies at 0° (picrate, m. p. 101°; phenylcarbamide derivative, m. p. 94°). δ -3-Indolylbutyl alcohol, m. p. 32—33° (picrate, m. p. 192°; phenylcarbamide derivative, m. p. 88°), is prepared similarly from methyl γ -3-indolylbutyrate. When γ -3-indolylbutyrazide is first decomposed in warm benzene and the resultant product treated with hydrogen chloride, about 5% of 2-keto-2:3:4:5-tetrahydrohomo-3-carboline, m. p. 220°, is produced (cf. A., 1927, 256). δ -3-Indolylbutylmalonic acid, m. p. 177°, is produced together with much tetrahydrocarbazole from ethyl sodio-malonate and δ -3-indolylbutyl *p*-toluenesulphonate (cf. Peacock and Tha, A., 1928, 1115).

The formation of the above carbazole derivatives emphasises the reactivity of the 2-hydrogen atom in indole.

H. BURTON.

Synthesis of hydroxy-*N*-methylnaphthindole-quinone and *N*-methylnaphthisatinquinone. Z. KITASATO and C. SONE (Bull. Chem. Soc. Japan, 1930, 5, 348—354).—Ethyl 3-bromo-1:4-naphthaquinonyl-3-malonate (Liebermann, A., 1899, i, 373, 522) and alcoholic methylamine give a mixture of 3-bromo-1:4-naphthaquinonyl-2-acetmethylamide, m. p. 165°, and ethyl 2-keto-1-methyl-2:3-dihydronaphthindole-4:9-quinone-3-carboxylate (I), yellow, decomp. about 220° after turning bluish-violet at 190°. When I is boiled with alkali in air, 2-hydroxy-1-methylnaphthindole-4:9-quinone, deep blue, not melted at 300°, is produced. This is oxidised by nitric and sulphuric acids to 1-methylnaphthisatin-4:9-quinone, m. p. 268°.

Various reactions of indigotin, nandazurin (cf. A., 1927, 1094), and the above hydroxyindole are compared.

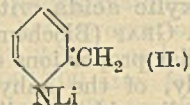
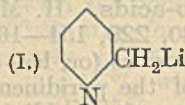


Ethyl 6-bromo-3:4-dimethoxycinnamate, m. p. 114—115° (the free acid, m. p. 244°, is prepared by the usual method from 6-bromoveratraldehyde), and *ethyl 3-bromo-1:4-naphthaquinone-2-carboxylate*, m. p. 119°, prepared from 2:3-dibromo-1:4-naphthaquinone and ethyl formate in presence of alcoholic sodium ethoxide, are converted by alcoholic methylamine into *6-bromo-3:4-dimethoxycinnam-methylamide*, m. p. 183°, and *3-bromo-1:4-naphthaquinone-2-carboxylamide*, m. p. 164—165°, respectively.

H. BURTON.

Organo-alkali compounds. VIII. Reactions between lithium alkyls, pyridine, and condensed pyridine systems. K. ZIEGLER and H. ZEISER (Annalen, 1930, 485, 174—192).—The preparation of pyridine derivatives by the primary addition of lithium alkyls and aryls (A., 1930, 1191) has been extended to various substituted pyridines and condensed pyridine systems such as quinoline, isoquinoline, and acridine. Decomposition of the additive product of quinoline and lithium butyl (in benzene solution) with water affords a 90% yield of *2-butyl-1:2-dihydroquinoline*, b. p. 160—162°/14 mm., 128°/0.06 mm., d_4^{20} 0.9961, n_D^{20} 1.56959, converted by heating in nitrobenzene into *2-butylquinoline*, b. p. 153°/14 mm., d_4^{12} 1.0018, n_D^{12} 1.56932 (*picrate*, m. p. 162—163°). The latter is also obtained (50—60% yield) by thermal decomposition of the *N*-lithium 2-butyldihydroquinoline in an atmosphere of nitrogen, and in this case fractional crystallisation of the *picrate* affords a small quantity of an isomeric *picrate*, m. p. 145°, indicating that a small amount of 1:4-addition of the lithium butyl occurs. Thermal decomposition of the crystalline additive compound of lithium phenyl and quinoline causes decomposition of the expected product, but decomposition with water affords a mixture of 2-phenylquinoline and its 1:2-dihydro-derivative, converted completely into the former by heating in nitrobenzene. The lithium derivatives obtained with isoquinoline are more stable to heat; that from lithium butyl is decomposed by water in an atmosphere of nitrogen to 1-butyldihydroisoquinoline, b. p. about 135°/0.4 mm., which is autoxidisable and is converted directly by heating in nitrobenzene into 1-butyliisoquinoline, b. p. 154—157°/14 mm. (*picrate*, m. p. 185.5°). Decomposition of the product obtained from isoquinoline and lithium phenyl with water causes a large amount of dehydrogenation of the dihydro-compound, and heating with nitrobenzene gives 1-phenyliisoquinoline, m. p. 97° (lit. m. p. 87—88°: the specimen, m. p. 80°, obtained by Bergmann and others, A., 1930, 1596, is impure). 9-Butyl-9:10-dihydroacridine, obtained similarly, has m. p. 105° (lit. m. p. 98—100°). Dehydrogenation of alkylidihydroacridines to the acridine derivative occurs smoothly when they are heated with a slight

excess of mercuric oxide in boiling alcohol. Thermal decomposition, in a sealed tube at 100°, of the product obtained by the action of lithium butyl in benzene on 2-butylpyridine affords, mainly, 2:5(?)*-dibutylpyridine*, b. p. 243—244° [*chloroplatinate*, m. p. 192.5—193° (decomp.)]. The reaction between lithium alkyls and 2-substituted pyridine or quinoline derivatives yields lithium derivatives of these substances, the structure of which may be either type I or II. With alkyl halides they behave as if they



possessed structure I. Thus the lithium compound obtained from lithium phenyl and quinaldine reacts with propyl bromide, benzyl chloride, and allyl chloride to give, respectively, 2-butylquinoline, 2- β -phenylethylquinoline, m. p. 28° (lit. m. p. about 30°), and 2- Δ^7 -butenylquinoline, b. p. 152.5—154°/14 mm., d_4^{14} 1.0255, n_D^{14} 1.58647 (*picrate*, m. p. 143°), whilst with benzophenone is obtained α -diphenyl- β -(2-quinolyl)-ethyl alcohol, $C_9H_6N \cdot CH_2 \cdot CPh_2 \cdot OH$, m. p. 165°, dehydrated by concentrated sulphuric and acetic acids to 2-(β -phenylstyryl)quinoline, m. p. 103—103.5°. Similarly, lithium methyl converts α -picoline, with evolution of methane, into its lithium derivative, which reacts with benzyl chloride to give 2-(β -phenylethyl)quinoline (*picrate*, m. p. 127°). On the other hand, with carbon dioxide these lithium derivatives react according to the structure II, the products being the parent bases, presumably derived from an intermediate *N*-carboxylic acid. Decomposition of the reaction product of 9-methylacridine and lithium phenyl with water affords only the original base.

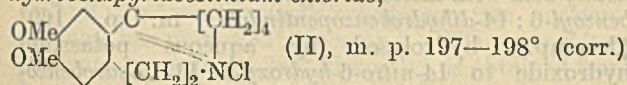
J. W. BAKER.

Synthesis of quinoline compounds. VI. Preparation of acylamido-derivatives of 8-hydroxyquinoline. K. MATSUMURA and C. SONE (J. Amer. Chem. Soc., 1931, 53, 177—179).—The following acetamidohydroxyquinolines are obtained when the appropriate aminohydroxyquinolines (1 mol.) are treated with acetic anhydride (1.1 mols.) in presence of ether and sodium acetate at the ordinary temperature for 3 days: 7-iodo-5-acetamido-8-hydroxy-, m. p. 212° [*hydrochloride*, m. p. 196° (decomp.)]; 5-acetamido-8-hydroxy-, m. p. 218—219° [*hydrogen sulphate*, m. p. 263° (decomp.)]; 5-acetamido-6-hydroxy-, m. p. 278° (decomp.) (*hydrogen sulphate*); 7-acetamido-8-hydroxy-5-methyl-, m. p. 203—204° (*sulphate*, m. p. 180°). 7-Amino-8-hydroxy-5-methylquinoline, m. p. 141—142° [*picrate*, decomp. 215—220°; ON-di-acetyl derivative, m. p. 222° (*hydrogen sulphate*, m. p. 183°); ON-dibenzoyl derivative, m. p. 181°, prepared by a method similar to the above using benzoyl chloride in place of acetic anhydride], is obtained when 7-nitroso-8-hydroxy-5-methylquinoline is reduced with stannous chloride and hydrochloric and acetic acids. 5-Benzamido-8-hydroxyquinoline, m. p. 237—238° [*hydrogen sulphate*, m. p. 225—227° (decomp.)], is prepared by the pyridine method in the cold. Methylation of 8-hydroxy-5-methylquinoline with methyl iodide and methyl-alcoholic potassium hydroxide gives 8-methoxy-5-methylquinoline, b. p. 298—302°/773

mm. [*picrate*, m. p. 180—181°; *chloroplatinate*, m. p. 224° (decomp.)].

H. BURTON.

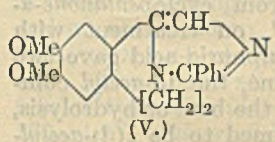
1- ω -Halogenoalkylisoquinolines and their derivatives. R. CHILD and F. L. PYMAN (J.C.S., 1931, 36—49).—**8-Chlorovalero- β -veratrylethylamide**, m. p. 60—62° (corr.), was converted by phosphorus oxychloride into **6:7-dimethoxy-1- δ -chlorobutyl-3:4-dihydroisoquinoline (I)** [*hydrochloride*, m. p. 172—173° (corr.)], isolated as its *picrate*, m. p. 156—157° (corr.). The same substance was also obtained together with a little of the *picrate* of II from **8-bromovalero- β -veratrylethylamide**, m. p. 70—72° (corr.). Cyclisation of I to **5:14-dehydro-10:11-dimethoxy-1:2:3:4:6:7-hexahydrobenzpyridocolinium chloride**,



(air-dried salt, +HCl, 2H₂O, effervesces at 103° after softening at 90°), isolated as the *picrate*, m. p. 185—186° (corr.), was effected by warming. The iodide has m. p. 210—212°. Reduction of II gave **10:11-dimethoxy-1:2:3:4:6:7-hexahydrobenzpyridocoline**, m. p. 54°, b. p. 225°/15 mm. [*hydrochloride*, m. p. 235—237° (corr., decomp.); *picrate*, m. p. 172—174° (corr.)]; α -methiodide, m. p. 228° (corr.); β -methiodide, m. p. 244—245° (corr.). Partial conversion $\alpha \rightarrow \beta$ at 250°. **γ -Bromobutyro- β -veratrylethylamide**, m. p. 65° (corr.), which readily decomposes into butyrolactone and **β -veratrylethylamine hydrobromide**, m. p. 179—180° (corr.), with phosphorus oxychloride gave, after treatment of the product with picric acid, a mixture of **6:7-dimethoxy-1- γ -chloropropyl-3:4-dihydroisoquinoline picrate** (crude), m. p. 163—164°, and **4:13-dihydro-9:10-dimethoxy-1:2:3:5:6:13-hexahydrobenzpyrrocolinium picrate**, m. p. 201—202° (corr.). The corresponding *chloride* (III), m. p. 120—122° (corr.) (+2H₂O), m. p. of anhydrous material 204—205°, on reduction with tin and hydrochloric acid in alcohol gave **9:10-dimethoxy-1:2:3:5:6:13-hexahydrobenzpyrrocoline**, m. p. 88—89° (corr.) [*hydrobromide*, m. p. 186° (corr.); *picrate*, m. p. 187° (corr., decomp.)]. The relatively greater tendency to form the five-membered ring in III than the six-membered ring in II is emphasised. By similar reactions, **chloroaceto- β -veratrylethylamide**, m. p. 96° (corr.), and **bromoaceto- β -veratrylethylamide**, m. p. 115° (corr.), with phosphorus oxychloride gave **6:7-dimethoxy-1-chloromethyl-3:4-dihydroisoquinoline hydrochloride**, darkens at 210°, effervesces at 217° [*picrate*, m. p. 196° (corr., decomp.)], which with aqueous potassium cyanide yielded **1-cyano-6:7-dimethoxy-1-chloromethyltetrahydroisoquinoline**, softens at 122°, m. p. 125° (corr., decomp.). With aqueous-alcoholic potassium cyanide the latter yielded **6:7-dimethoxy-1-cyanomethyl-3:4-dihydroisoquinoline (IV)**, m. p. 173° (corr.) [*hydrochloride*, m. p. 205—206° (corr.); *picrate*, m. p. 225° (decomp.)], also obtained from **cynoaceto- β -veratrylethylamide**, m. p. 115° (corr.), 127—128° after resolidification, and phosphorus oxychloride. Reduction of IV with sodium and alcohol gave, after treatment of the crude base with picric acid, **6:7-dimethoxy-1- β -aminoethyltetrahydroisoquinoline dipicrate** (40% yield), m. p. 205° (corr.); it crystallises from alcohol with EtOH [*dihydrochloride* + H₂O, m. p. 276—277° with

effervescence (corr.)]. **Bromoaceto- β -veratrylethylamide** with phosphorus pentoxide in xylene led to **6:7-dimethoxy-1-bromomethyl-3:4-dihydroisoquinoline picrate**, m. p. 190—191° (decomp., corr.), **chloroaceto- β -m-methoxyphenylethylamide**, m. p. 56—57° (corr.), with phosphorus oxychloride gave **6-methoxy-1-chloromethyl-3:4-dihydroisoquinoline picrate**, m. p. 169—170° (uncorr.), and **chloroaceto- β -piperonylethylamide**, m. p. 72° (corr.), with the same reagent gave **6:7-methylenedioxy-1-chloromethyl-3:4-dihydroisoquinoline picrate**, m. p. 179—180° (corr., decomp.), but with **β -chloropropiono- β -veratrylethylamide**, m. p. 102—103° (corr.), it gave no isolable product.

An attempt to prepare **6:7-dimethoxy-1-amino-methyl-3:4-dihydroisoquinoline** from **hippuro- β -veratrylethylamide** (+H₂O), m. p. 85—95°, by dehydration with phosphorus oxychloride followed by hydrolysis, led unexpectedly to what is considered to be **9:10-dimethoxy-3-phenyl-5:6-dihydrobenzglyoxalocoline (V)**, m. p. 187° (corr.) [*hydrochloride*, m. p. 286—287° (corr., decomp.); *hydrobromide*, m. p. 293° (corr.); *methiodide*, m. p. 255° (corr.); *picrate*, m. p. 226—



227° (corr.); *mononitro*-derivative, m. p. 202° (corr.)]. Demethylation of V yielded **9:10-dihydroxy-3-phenyl-5:6-dihydrobenzglyoxalocoline hydrochloride** (+3H₂O), m. p. 293° (corr.). **Hippuro- β -phenylethylamide** has m. p. 161° (corr.).

None of a number of these substances possessed marked amebicidal, antimalarial, or trypanocidal activity.

J. D. A. JOHNSON.

Preparation of brominated cinchophens [2-phenylcinchoninic acids]. H. G. LINDWALL, J. BANDES, and I. WEINBERG (J. Amer. Chem. Soc., 1931, 53, 317—319).—Isatin reacts with *p*-methoxy- and *p*-bromo-acetophenones in aqueous-alcoholic potassium hydroxide forming **2-anisyl-**, m. p. 216°, and **2-*p*-bromophenyl-cinchoninic acids**, m. p. 293°, respectively. Similarly, **5:7-dibromoisatin** (conveniently prepared by brominating isatin in 95% alcohol) reacts with acetophenone and *p*-methoxyacetophenone to give **6:8-dibromo-2-phenyl-**, m. p. 270—271°, and **6:8-dibromo-2-anisyl-cinchoninic acids**, m. p. 263—264°, respectively.

H. BURTON.

Derivatives of pyrrole. I. Synthesis of 3-keto-4:5-dihydrodi-(1:2)-pyrrole and 8-keto-5:6:7:8-tetrahydropyrrocoline. G. R. CLEMO and G. R. RAMAGE (J.C.S., 1931, 49—55).—Potassium pyrrole and ethyl chloroacetate in benzene gave **ethyl 1-pyrrolylacetate**, b. p. 112°/20 mm., hydrolysed to **1-pyrrolylacetic acid**, m. p. 91° (*amide*, m. p. 169°). **Ethyl β -1-pyrrolylpropionate**, b. p. 122°/23 mm., and **β -1-pyrrolylpropionic acid**, m. p. 62° (*amide*, m. p. 81°), were prepared similarly. Cyclisation of **succino-*n*-butylimide**, b. p. 140°/17 mm. (from potassium succinimide and *n*-butyl bromide; 80% yield), to a derivative of **5:6:7:8-tetrahydropyrrocoline** could not be effected. Potassium pyrrole with β -chloroethyl, β -cyanoethyl, and γ -chloropropyl toluene-*p*-sulphonates yielded **1- β -chloroethylpyrrole**, b. p. 84°/20 mm., **1- β -cyanoethylpyrrole**, b. p. 140°/20 mm., and **1- γ -chloropropylpyrrole**, b. p. 87°/15 mm., respectively.

Cyclisation of 1- β -cyanoethylpyrrole to 3-keto-4:5-dihydrodi-(1:2)-pyrrole, m. p. 54° (piperonylidene derivative, m. p. 194°), was effected by treatment with hydrogen chloride in dry ether in presence of zinc chloride, the product being isolated as its semicarbazone, m. p. 211°. γ -Bromobutyronitrile and potassium pyrrole gave γ -1-pyrrolylbutyronitrile, b. p. 152°/23 mm., cyclised to 8-keto-5:6:7:8-tetrahydro-pyrrocoline, m. p. 34° (semicarbazone, m. p. 193°; piperonylidene derivative, m. p. 136°). Ethyl β -1-pyrrolylpropionate, m. p. 50°, b. p. 162°/22 mm., and β -1-pyrroylethyl methyl ketone, b. p. 148°/16 mm. (phenylhydrazones, m. p. 131°; semicarbazone, m. p. 190°), are also described. J. D. A. JOHNSON.

Action of nitric acid on polycyclic indole derivatives. IX. S. A. BRYANT and S. G. P. PLANT (J.C.S., 1931, 93—105).—7:8-Dihydro- $\alpha\beta$ -naphthapentindole (I), m. p. 167° [picrate, m. p. 167° (decomp.)], prepared from cyclopentanone- α -naphthylhydrazones, m. p. 95°, on treatment with acetic anhydride containing sulphuric acid gave two isomeric acetyl derivatives; one, the 10-acetyl compound, m. p. 157°, reverted to the base on hydrolysis, the other (m. p. 215°) is presumed to be 1(?)-acetyl-7:8-dihydro- $\alpha\beta$ -naphthapentindole, since it cannot be hydrolysed, and it forms an oxime, m. p. 236° (decomp.). cyclopentanone- β -naphthylhydrazones, m. p. 77°, similarly gave 9:10-dihydro- $\alpha\beta$ -naphthapentindole (II), m. p. 103° [picrate, m. p. 189° (decomp.)]; benzoyl derivative, m. p. 196°; carbethoxy-derivative, m. p. 160°. This product could also be an isomeric substance the formation of which would involve fusion of the indole and naphthalene nuclei through the $\beta\beta'$ -positions of the latter. This constitution is considered improbable, since the analogous cyclisation of cyclohexanone- β -naphthylhydrazones has been shown to lead to the $\alpha\beta$ -derivative (Oakshott and Plant, A., 1928, 1023). Acetylation of II with acetyl chloride in acetone in presence of alkali gave 7-acetyl-9:10-dihydro- $\alpha\beta$ -naphthapentindole, m. p. 170° (readily hydrolysed to the base), which with acetic anhydride in presence of concentrated sulphuric acid gave 5(?) : 7-diacetyl-9:10-dihydro- $\alpha\beta$ -naphthapentindole (III), m. p. 234°. Hydrolysis of the latter gave 5(?)-acetyl-9:10-dihydro- $\alpha\beta$ -naphthapentindole, m. p. 239°, which could be reacylated to III and gave a benzoyl derivative, m. p. 163°. Nitration of the 7-acetyl, 7-benzoyl, and 7-carbethoxy-derivatives of II gave 5(?)-nitro-7-acetyl-, m. p. 247°, 5(?)-nitro-7-benzoyl-, m. p. 259°, and 5(?)-nitro-7-carbethoxy-, m. p. 202°, 9:10-dihydro- $\alpha\beta$ -naphthapentindoles, each of which on hydrolysis yielded 5(?)-nitro-9:10-dihydro- $\alpha\beta$ -naphthapentindole, m. p. 228°. From the carbethoxy-derivative a dinitro-compound, m. p. 220° (decomp.), was also obtained.

Cyclisation of 2-methylcyclohexanone- β -naphthylhydrazones gave two products, IV, m. p. 115° [picrate, m. p. 201° (decomp.)], and V, m. p. 92° (picrate, m. p. 166°), the former of which was shown to be 8-methyl-8:9:10:11-tetrahydro- $\alpha\beta'$ -naphthacarbazole, since dehydrogenation led to 8-methyl- $\alpha\beta'$ -naphthacarbazole, m. p. 144°, rationally synthesised from 2-hydroxy-3-naphthoic acid and *o*-tolylhydrazine through 8-methyl- $\alpha\beta'$ -naphthacarb-

azole-6-carboxylic acid, m. p. 320°, by decarboxylation of the latter. By analogy, to product V the constitution of 12-methyl-8:9:10:11-tetrahydro- $\alpha\beta'$ -naphthacarbazoline is assigned. The constitutions given to IV and V by Cecchetti and Ghigi (A., 1930, 787) are therefore incorrect.

Treatment of 5:6-dihydro- $\alpha\beta$ -naphthacarbazole with acetic anhydride containing a little sulphuric acid gave the 1(?)-acetyl derivative, m. p. 253°, b. p. about 370°/40 mm., not hydrolysed by alcoholic potassium hydroxide, and forming an oxime, m. p. 292° (decomp.).

Benzoylation of benzopentindole gave the 7-benzoyl derivative, m. p. 187°, which, treated in acetic acid with nitric acid, gave 14-nitro-6-hydroxy-7-benzoyl-6:14-dihydrobenzopentindole, m. p. 169° (decomp.), hydrolysed by aqueous potassium hydroxide to 14-nitro-6-hydroxy-6:14-dihydrobenzopentindole [not pure, m. p. 200° (decomp.)].

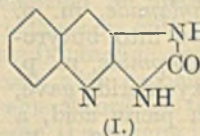
J. D. A. JOHNSON.

Condensation of hydantoin with *o*-nitrobenzaldehyde. J. KOZAK and L. MUSIÅ (Bull. Acad. Polonaise, 1930, A, 432—438).—Hydantoin and *o*-nitrobenzaldehyde condense in presence of zinc chloride at 100—110°, forming 5-*o*-nitrobenzylidene-hydantoin, m. p. 278—280° (decomp.), reduced by red phosphorus and hydriodic acid to the quinoline derivative (I), m. p. 348—349°.

Nitration of 5-*o*-nitrobenzylidene-hydantoin affords the 1-nitro-derivative, m. p. 224—226° (decomp.), whilst bromination and chlorination in acetic acid gives the 1-bromo-, m. p. 247—248°, and the 1:3-dichloro-derivatives, m. p. 180—182° (decomp.), respectively. Oxidation of the nitrobenzylidenehydantoin with ozone in acetic acid affords *o*-nitrobenzaldehyde and parabanic acid, whilst oxidation of its 1-nitro- and halogeno-derivatives with alkaline potassium permanganate gives *o*-nitrobenzoic acid. H. BURTON.

New product derived from pyrimidone. R. CHARONNAT and R. DELABY (Bull. Sci. pharmacol., 1930, 37, 7—27, 75—89; Chem. Zentr., 1930, ii, 1988—1989; cf. A., 1930, 223, 329, 351).—The preparation of dioxypyrimidone, and its solubility relationships with pyrimidone and antipyrine, are described. Colour reactions for distinguishing the substances are described. Dioxypyrimidone is stable towards oxidising agents, halogens, acid dyes, tannin, mercury and silver compounds, alkaloidal salts, and phenols. Partial hydrolysis affords α -acetyl- β -phenyl- α -methylhydrazine and (with barium hydroxide) barium dimethylloxamate. A. A. ELDRIDGE.

Relation of quinoxaline to the ammonia system. F. W. BERGSTROM and R. A. OGG, jun., (J. Amer. Chem. Soc., 1931, 53, 245—251).—Quinoxaline [additive compound (1:2) with sodium hydrogen sulphite] reacts with ethereal magnesium phenyl bromide in nitrogen forming *dl*-2:3-diphenyl-1:2:3:4-tetrahydroquinoxaline (the corresponding 2:3-dimethyl derivative is prepared similarly, using magnesium methyl iodide), and with alcoholic hydrogen cyanide at 100° giving about 30% of 2:3-dicyano-1:2:3:4-tetrahydroquinoxaline, m. p. 168.5° (corr.)



[diacetyl derivative, m. p. 93.5° (corr.)]. Oxidation of quinoxaline with aqueous ammonium persulphate affords 2:3-dihydroxyquinoxaline, whilst treatment with two equivalents of potassamide in liquid ammonia gives the dipotassium salt of fluorubin (Hinsberg and Schwantes, A., 1904, i, 198) and tar. The above reactions are in accordance with the behaviour of quinoxaline as an ammonoglyoxal. Pyrazine does not undergo any of the above reactions.

H. BURTON.

ψ -Bases. I. *N*-Methylpyrazinium salts and their corresponding bases. J. G. ASTON (J. Amer. Chem. Soc., 1930, 52, 5254—5262).—Mainly a more detailed account of work previously reviewed (A., 1930, 1597). The following is new. 6-Hydroxy-1:2:2:5:5-pentamethyltetrahydropyrazine chloroplatinate has m. p. 282° (decomp.). The same chloroplatinate, m. p. about 285° (decomp.), is obtained from 1:2:2:3:5:5-hexamethyl-6-methylenetetrahydropyrazine and 1:2:2:3:5:5:6-heptamethyldihydropyrazinium iodide (after treatment with silver chloride).

H. BURTON.

Spectrochemical study of amino-acid anhydrides. IV. Light absorption of azlactones, diketopiperazines, hydantoin, and thiohydantoin. T. ASAHINA (Bull. Chem. Soc. Japan, 1930, 5, 354—365).—In continuance of previous work (A., 1926, 659; 1928, 218; 1929, 1362), solutions (usually alcoholic) of the following substances were examined spectroscopically: the azlactones of *o*-, m. p. 158.6° (lit. 137—138°), *m*-, and *p*-acetoxy-, m. p. 177.5° (lit. 172—173°), and *o*-, m. p. 161°, *m*-, and *p*-methoxybenzylidenehippuric acids; α -benzamidocinnamic acid; α -benzamido-*o*-, m. p. 199.5° (decomp.; lit. 185.5°), *m*-, and *p*-hydroxycinnamic acids; α -benzamido-*o*-, m. p. 208°, *m*-, and *p*-methoxycinnamic acids; 3:6-dibenzylidene- and 3:6-difurfurylidene-2:5-diketopiperazines; 5-benzylidene- and 5-furfurylidene-hydantoin; 2-thiohydantoin [1-acetyl, 1-benzoyl, 5-benzylidene, and 5-furfurylidene, m. p. 255° (decomp.), derivatives]; 2-thio-5-benzylhydantoin (1-acetyl derivative), and 2-thio-5-*p*-hydroxybenzylhydantoin. The α -benzamido-acids are less bathochromic than the corresponding azlactones, whilst the thiohydantoin is more bathochromic than the corresponding hydantoin.

H. BURTON.

Pyrimidines. CXIX. Determination of constitution of alkylation products of phenyluracil and phenylhydrouracil. J. EVANS and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 4993—5005).—Treatment of 6-phenyluracil with methyl iodide in methyl-alcoholic sodium methoxide gives a mixture of 6-phenyl-3-methyl-, m. p. 228—230°, and 6-phenyl-1:3-dimethyl-uracil, m. p. 122—122.5°; the former of these is also obtained when its 5:6-dihydro-derivative is heated with bromine in acetic acid. Ethyl chloroacetate and 6-phenyluracil (potassium salt, not melted at 300°) in alcoholic sodium ethoxide affords ethyl 6-phenyluracil-3-acetate, m. p. 205—206° [free acid, m. p. 304—305°, converted by methyl sulphate into 6-phenyl-1-methyluracil-3-acetic acid, m. p. 261—263° (methyl ester, m. p. 157—157.5°; ethyl ester, m. p. 109—110°), which could not be reduced]. Benzalde-

hyde, malonic acid, and ammonium acetate react in boiling alcohol to give cinnamic and β -amino- β -phenylpropionic acids, m. p. 215—216° (lit. 228—231°). The amino-acid and potassium cyanate afford the corresponding carbamide, which when heated with 10% hydrochloric acid, passes into 6-phenyl-5:6-dihydrouracil. Treatment of the sodium derivative of this with methyl iodide in alcohol gives 6-phenyl-3-methyl-5:6-dihydrouracil, m. p. 149—150.5°, hydrolysed by barium hydroxide and aqueous methyl alcohol to β -(γ -methylcarbamido)- β -phenylpropionic acid, m. p. 178° (decomp.). The sodium salt of the phenyldihydrouracil and ethyl chloroacetate afford mainly ethyl 6-phenyl-5:6-dihydrouracil-3-acetate, m. p. 154.5—156° [5-bromo-derivative, m. p. 259—261° (decomp.)], hydrolysed to a mixture of the corresponding acid, m. p. 228—231°, and an acid, m. p. 170—180° (ethyl ester, m. p. 132—135°).

Benzylidenemethylamine reacts with malonic acid in alcohol, forming, by way of α -methylaminobenzylmalonic acid, decomp. 147°, a mixture of cinnamic and β -methylamino- β -phenylpropionic acids, m. p. 168.5—169°. The amino-acid and potassium cyanate give β -(α -methylcarbamido)- β -phenylpropionic acid, m. p. 165—167°, converted by hot 10% hydrochloric acid into 6-phenyl-1-methyl-5:6-dihydrouracil, m. p. 158—159.5° [5-bromo-derivative, m. p. 214—215° (decomp.)], which when heated passes into 6-phenyl-1-methyluracil. Treatment of the sodium derivatives of 6-phenyl-1-methyluracil and its 5:6-dihydro-derivative with ethyl chloroacetate gives ethyl 6-phenyl-1-methyluracil-3-acetate and its 5:6-dihydro-derivative, m. p. 70—71°, respectively. H. BURTON.

Azo-compounds from ketotrimethylmethylene-pyrazine. VII. E. PRINCIVALLE (Gazzetta, 1930, 60, 963—966; cf. A., 1928, 1027; 1929, 196, 197; 1930, 223, 929).—6-Keto-1:2:4-trimethyl-5-methylene-1:4:5:6-tetrahydropyrazine (1 mol.) reacts with (1) phenylhydrazine (1 mol.) or benzenediazonium chloride, giving 6-keto-1:2:4-trimethyl-5-benzeneazomethylene-1:4:5:6-tetrahydropyrazine,

$$\text{NPh:N:CH:C} \begin{array}{c} \text{CO-NMe} \\ \text{NMe-CH} \end{array} \text{CMe, m. p. 201° (decomp.),}$$
which forms a hydriodide, m. p. 228° (decomp.), and (2) *p*-toluenediazonium chloride, giving 6-keto-1:2:4-trimethyl-5-*p*-tolueniazomethylene-1:4:5:6-tetrahydropyrazine, m. p. 214° (decomp.), which forms a hydrochloride, m. p. 205° (decomp.), and a hydriodide, m. p. 226° (decomp.). T. H. POPE.

neoNicotine and isomeric pyridylpiperidines. C. R. SMITH (J. Amer. Chem. Soc., 1931, 53, 277—283).—neoNicotine [2-(3'-pyridyl)piperidine], b. p. 280—281°/775 mm. [picrate, m. p. 213° (corr.)], is also formed when pyridine is treated with sodium under the conditions previously described (A., 1924, i, 558); it is reduced catalytically (Adams) to 2:3'-dipiperidyl. Reduction of 2:3'-dipiperidyl with tin and hydrochloric acid gives isoneonicotine [3-(2'-pyridyl)piperidine], b. p. 282° (slight decomp.)/760 mm. [picrate, m. p. 217—218° (corr.)]. Similar reduction of 2:2', 4:4', 3:3', and 3:4'-dipiperidyls affords varying amounts of 2-(2'-pyridyl)piperidine, b. p. 265—266°/756 mm. (picrate, m. p. 187°), 4-(4'-pyridyl)piperidine [isonicotine], 3-(3'-

pyridyl)piperidine [nicotidine], and 4-(3'-pyridyl)-piperidine (*picrate*, m. p. 240° with slight darkening). Nicotimine (Pictet and Rotschy, A., 1901, i, 339) is probably not 2-(3'-pyridyl)piperidine.

H. BURTON.

γ -Triazines: synthesis of thiolamino-ethyl- and -propyl-triazines and new data on thiolimino-methyltriazine. A. OSTROGOVICH and V. GALEA (*Atti R. Accad. Lincei*, 1930, [vi], 11, 1012—1019; cf. A., 1912, i, 320).—2-Amino-6-thiol-4-ethyl-1:3:5-triazine, m. p. 257—258° (decomp.), forms a *picrate*, m. p. 188—189° (decomp.), and a *silver salt*. 2-Amino-6-thiol-4-propyl-1:2:3-triazine, m. p. 262—263° (decomp.), forms a *picrate*, m. p. 153° (decomp.), and a *silver salt*. 2-Amino-6-thiol-4-methyl-1:2:3-triazine (*loc. cit.*) forms anhydrous crystals from hot solutions and hydrated (H_2O) from cold solutions, and gives a *picrate*, m. p. 196—197° (decomp.), and a *silver salt*.

T. H. POPE.

γ -Triazines: synthesis of two aralkylamino-thioltriazines. A. OSTROGOVICH and V. GALEA (*Atti R. Accad. Lincei*, 1931, [vi], 12, 162—165; cf. A., 1930, 1449; this vol., 239).—2-Amino-4-thiol-6-benzyl-1:3:5-triazine, m. p. 270—271° (decomp.), prepared under the conditions employed for obtaining the corresponding alkyl derivatives, forms *silver* and *copper* ($+0.5\text{H}_2\text{O}$) salts and a *picrate*, m. p. 187—188° (decomp.). 2-Amino-4-thiol-6-styryl-1:3:5-triazine, m. p. 284—285° (decomp.), prepared in the cold, forms a *copper salt* and a *picrate*, m. p. 221—222° (decomp.).

T. H. POPE.

Pyrrole compounds with amino-groups and unsaturated side-chains. H. FISCHER and K. ZEILE (*Annalen*, 1930, 483, 251—271; cf. A., 1930, 1298).—Ethyl 3-amino-2:4-dimethylpyrrole-5-carboxylate (I) (*acetyl* compound, m. p. 201°) is better prepared by nitrosation of ethyl 2:4-dimethylpyrrole-5-carboxylate, followed by reduction, than by reduction of the nitropyrrole (cf. Fischer and Stern, A., 1926, 303); the *diazonium chloride* (from I and *isoamyl nitrite*), decomp. 175°, is not convertible in the usual way into a hydroxy-compound, nitrogen being eliminated with formation of ethyl 2:4-dimethylpyrrole-5-carboxylate, m. p. 125°. 3-Amino-2:4-dimethylpyrrole-5-carboxylic acid (by hydrolysis of I) (*acetyl* derivative, m. p. 203°) is converted at 75°, with loss of carbon dioxide, into 3-amino-2:4-dimethylpyrrole, m. p. 127° (*acetyl* derivative, m. p. 205°); the last-named is unstable, readily losing ammonia, and cannot be diazotised. Attempts to obtain a pyrrole substituted by an $\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ grouping by interaction of I and chloroacetic acid were unsuccessful.

The action of hydrobromic and formic acids on I (the corresponding acid or its *acetyl* compound) affords (3-amino-2:4-dimethylpyrrol)-(3'-amino-2':4'-dimethylpyrrolenyl)methene hydrobromide (II), decomp. above 280°; sodium acetate causes elimination of 2 mols. of hydrogen bromide from II, yielding the *monohydrobromide*, m. p. 234°; the free methene could not be crystallised. Attempts to synthesise porphyrins from II by the succinic acid fusion method (cf. A., 1928, 1384) were successful.

Bromination of the *acetyl* derivative of I gives an

unstable bromo-compound, converted by boiling water into ethyl di-(3-acetamido-4-methyl-2-pyrrolyl)methane-5:5'-dicarboxylate, m. p. 251° (after sintering) (corresponding 5:5'-dicarboxylic acid, m. p. 214°). The latter, when boiled with formic acid in the presence of iron powder, affords traces of impure 1:4:5:8-tetramethyl-2:3:6:7-tetra-acetylaminoporphin, which shows absorption bands at 598.9, 578.4, and 552.8 μ .

Bromination of ethyl 2:4-dimethyl-3-(β -dicyanovinyl)pyrrole-5-carboxylate (III) (A., 1924, i, 543) affords a perbromide, converted by hydrogen sulphites into a monobromo-derivative, probably ethyl 2-bromomethyl-4-methyl-3-(β -dicyanovinyl)pyrrole-5-carboxylate, m. p. 258°, which, like the bromo-derivative of ethyl 3-chloroacetyl-2:4-dimethylpyrrole-5-carboxylate (A., 1930, 1298), is unreactive. Bromination of the same compound in methyl alcohol yields ethyl 2-carbomethoxy-4-methyl-3-(β -dicyanovinyl)pyrrole-5-carboxylate, m. p. 187°, hydrolysed to 4-methylpyrrole-3-aldehyde-2:5-dicarboxylic acid, m. p. above 360°; the methyl ester of the latter has m. p. 180° (*oxime*, m. p. 221°; *semicarbazone*, m. p. 247°). 5-Carbomethoxy-4-methyl-3-(β -dicyanovinyl)pyrrole-2-carboxylic acid, m. p. above 360°, results from the action of sulphuryl chloride on III.

Hydrolysis of III affords ethyl 2:4-dimethyl-3-(β -carboxyvinyl)pyrrole-5-carboxylate (*methyl ester*, m. p. 150°); carbon dioxide could not be eliminated from this compound without loss of the vinyl and carbomethoxyl side-chains, the products obtained by vacuum distillation being 2:4-dimethylpyrrole and the corresponding methene (hydrobromide; *picrate*, m. p. 215°). The action of sulphuryl chloride on the acrylic acid above yields 5-carbomethoxy-4-methyl-3-chlorovinylpyrrole-2-carboxylic acid, m. p. 241° (corresponding 2:5-dicarboxylic acid, does not melt); the same reagent converts ethyl 2:4-dimethylpyrrole-3-aldehyde-5-carboxylate into 3-chloro-5-carbomethoxy-4-methylpyrrole-2-carboxylic acid, m. p. 260°.

Condensation of 2:4-dimethylpyrrole-3:5-dialdehyde with cryptopyrrole and 2:4-dimethyl-3-pyrrolyl methyl ketone, respectively, in presence of hydrobromic acid affords 4'-aldehyde-3:3':5:5'-tetramethyl-4-ethylpyrromethene hydrobromide and (3-aldehyde-2:4-dimethylpyrrolyl)-(3'-acetyl-2':4'-dimethylpyrrolenyl)methene hydrobromide, m. p. 210°.

A molecular compound of ethyl 2:4-dimethyl-3- β -nitrovinylpyrrole-5-carboxylate (A., 1924, i, 543) with nitromethane is described.

[With G. LECHNER.] The action of sulphuryl chloride on ethyl 2:4-dimethylpyrrole-3-thioaldehyde-5-carboxylate (A., 1926, 303), an improved preparation of which is described, leads to 5-carbomethoxy-4-methylpyrrole-3-aldehyde-2-carboxylic acid, m. p. 169° (*anil*, m. p. 225°; *phenylhydrazone*, m. p. 235°).

R. CHILD.

Chlorophyll series. IV. Degradation of chlorophyll and allomerised chlorophyll to simple chlorins. J. B. CONANT, J. F. HYDE, W. W. MOYER, and E. M. DIETZ (J. Amer. Chem. Soc., 1931, 53, 359—373).—Pyrochlorin e, $\text{C}_{35}\text{H}_{36}\text{O}_2\text{N}_4\cdot\text{H}_2\text{O}$ (cf. A., 1930, 225), obtained in improved yield when a 1% solution in diphenyl is boiled for 5 min., affords a *methyl ester*, m. p. 184° (*copper salt*), apparently isomeric with phylloporphyr-

rin methyl ester. Reduction of pyrochlorin *e*, catalytically or with hydriodic acid in acetic acid, and oxidation of the resultant product with air gives phylloporphyrin in good yield; a phyllochlorin is also produced which affords a methyl ester, $C_{33}H_{40}O_2N_4$, m. p. 150°, differing from the phyllochlorin ester of Treibs and Wiedemann (A., 1929, 941). Pyrochlorin *e* is considered to be a normal degradation product of chlorophyll. "Pyrochlorin *e*-porphyrin" (*loc. cit.*), identical with the chloroporphyrin e_3 of Fischer and Moldenbauer (A., 1930, 482), is separable by fractionation with ether and hydrochloric acid into phylloporphyrin and *pyrochloroporphyrin* (methyl ester, $C_{33}H_{38}O_2N_4$, m. p. 226—237°). The last-named porphyrin is converted into phylloporphyrin by reduction and re-oxidation as above.

Treatment of crude phaeophytin (*a+b*) with propyl-alcoholic potassium hydroxide in ethereal pyridine, and methylation of the resultant product with ethereal diazomethane gives the dimethyl derivative of phaeopurpurin 7 (A., 1930, 1299). When phaeopurpurin 7 is heated with diphenyl, carbon monoxide and dioxide are evolved and a mixture of small amounts of pyroporphyrins (acid numbers 6 and 8) and 15—16% of *chlorin f monomethyl ester* [methylated further to the dimethyl ester, m. p. (block) 182°] is produced. Hydrolysis of phaeopurpurin 7 with propyl-alcoholic potassium hydroxide gives potassium oxalate, porphyrins, and *chlorin f*, $C_{32}H_{38}O_4N_4$, indicating that it is an α -keto-acid. When *chlorin f* is heated, a considerable amount of pyroporphyrin is produced. Rhodoporphyrin is formed when *chlorin f* methyl ester is treated with alcoholic potassium hydroxide in presence of pyridine and magnesium oxide and when the dimethyl ester is reduced with hydriodic and acetic acids.

When chlorophyll *a* is allomerised by keeping in alcohol for 24—48 hrs. and the resultant product hydrolysed with alcoholic potassium hydroxide, phaeopurpurin 7 (isolated as its dimethyl derivative after treatment with diazomethane) is obtained. Formulæ are suggested for *chlorin f* and pyrochlorin *e*.

H. BURTON.

ψ -Bases in the isooxazole series. III. E. P. KOHLER and C. L. BICKEL (J. Amer. Chem. Soc., 1930, 52, 4943—4949).—5-*p*-Chlorobenzoyl-3:4-diphenylisooxazole, m. p. 165—166° (A., 1930, 786) (improved preparation given), is treated with ethyl sulphate at 125—130°, the product hydrolysed with diluted (1:1) hydrochloric acid, and the solution treated with ferric chloride whereby 5-*p*-chlorobenzoyl-3:4-diphenyl-2-ethylisooxazolinium ferrichloride, two forms, m. p. 130.5° and 139° (the corresponding hydrogen sulphate, m. p. 192—193°, separates from the hydrolysed solution), is produced. Treatment of the ferrichloride with aqueous sodium hydrogen carbonate in ether gives the ψ -base,

$(\text{CPh} \text{---} \text{C}(\text{OH}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Cl})_2$, m. p. about 128° (decomp.), which when kept decomposes to *p*-chlorobenzoic acid and 3:4-diphenyl-2-ethylisooxazolone, m. p. 145—146°; the isooxazolone is also prepared by Kohler and Blatt's method (A., 1928, 430). Attempted preparation of the methyl ether of the ψ -base results in the formation of *p*-chlorobenzoic

acid and methyl β -ethylamino- α -phenylcinnamate, m. p. 101—102° (ozonolysis products benzoic acid and benzethylamide). Hydrolysis of this ester with hydrochloric acid at the ordinary temperature gives methyl benzoylphenylacetate and deoxybenzoin. 3:4-Diphenyl-2-ethylisooxazolinium ferrichloride, m. p. 75—76°, is converted by aqueous alkali into the ether, $(\text{CPh} \text{---} \text{CH} \cdot \text{O})_2$, m. p. 148°, which with methyl-alcoholic sodium hydroxide affords the above cinnamate.

H. BURTON.

Constitution of indophenine. G. HELLER (Chem.-Ztg., 1930, 55, 985).—In support of his own quinonoid formula (Z. angew. Chem., 1924, 37, 1017) for indophenine and criticism of the more recent one of Steinkopf and Roch (this vol., 104) the author briefly reviews previous work and refers *inter alia* to Schotten's isatin-blue, which must be quinonoid, and to the inability of the formula of Steinkopf and Roch to explain the colour of mesoxyphenine.

L. J. HOOLEY.

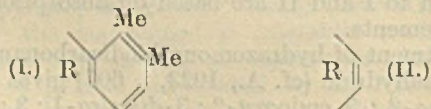
Constitution of the so-called dithiourazole of Freund. IV. Isomerism of hydrazodithiodicarbonamides, iminothiolthiodiazoles, and iminothiodiazolones. S. L. JANNIAH and P. C. GUHA (J. Amer. Chem. Soc., 1930, 52, 4860—4866).—Short treatment of hydrazodithiodicarbonamide, $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{SH}$, m. p. 223° (absorption curve shows one band), with boiling 2*N*-hydrochloric acid gives an isomeride, $[\text{SH} \cdot \text{C}(\text{NH}) \cdot \text{NH}]_2$, m. p. 203° (absorption curve shows two bands), also obtained when the original substance is dissolved in 2*N*-sodium hydroxide, the solution kept for 24 hrs., and then acidified. When the more fusible form is heated at 120° for 24 hrs., it passes into the less fusible modification. Both isomerides give the same derivatives and are converted by short treatment with hydrochloric acid (*d* 1.19) into 2-imino-5-thiol-2:3-dihydro-1:3:4-thiodiazole (I), m. p. 234°. The acetyl derivative, m. p. 303°, obtained from this is hydrolysed by 2*N*-hydrochloric acid to 2:5-endoimino-2-thiol-2:3-dihydro-1:3:4-thiodiazole (II), m. p. 244° (also acetylated to the acetyl derivative of m. p. 303°), also formed when I and the isomeric hydrazodithiodicarbonamides are heated with 5*N*-hydrochloric acid; II is identical with the dithiourazole of Freund (A., 1895, i, 400). The structures assigned to I and II are based on absorption spectra measurements.

Treatment of hydrazomonothiodicarbonamide with acetic anhydride (cf. A., 1923, i, 607) gives probably 2-amino-2:5-endoxy-2:3-dihydro-1:3:4-thiodiazole, m. p. 235°.

H. BURTON.

Yohimbine. II. F. MENDIK and J. P. WIBAUT (Rec. trav. chim., 1931, 50, 91—111; cf. A., 1929, 335).—Dehydrogenation of yohimbine or yohimboic acid with selenium at 300° affords yobyne, $\text{C}_{19}\text{H}_{18}\text{N}_2$, m. p. 217° (*loc. cit.* described as a substance $\text{C}_{18}\text{H}_{16}\text{N}_2$, m. p. 212—213°) (hydrochloride, m. p. 300°; methiodide), dihydroyobyne, $\text{C}_{19}\text{H}_{20}\text{N}_2$, m. p. 170° (methiodide), and ketoyobyne, $\text{C}_{20}\text{H}_{16}\text{ON}_2$, m. p. 328° (*loc. cit.*, m. p. 326°), the nomenclature being based on the hypothetical substance yobine, $\text{C}_{19}\text{H}_{24}\text{N}_2$, derived from yohimbine, $\text{C}_{19}\text{H}_{22}\text{N}_2(\text{OH}) \cdot \text{CO}_2\text{Me}$, by replace-

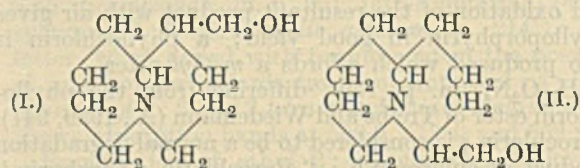
ment of the hydroxyl and carbomethoxy-groups by hydrogen. Yobyryne is probably identical with the substance, m. p. 211°, obtained by Hahn and Schuch (A., 1930, 1194) by heating yohimboic acid with selenium and soda-lime in a high vacuum at 300–350°, but the ether structure, $(C_{18}H_{12}N_2)O_2$, assigned by these investigators is considered improbable. Similar dehydrogenation of diacetylyohimbine (Hahn and Schuch, *loc. cit.*; cf. Schomer, A., 1927, 1097) affords yobyryne and dihydroyobyryne, but no ketoyobyryne, whilst a small quantity of an oil, b. p. 135° (approximately), possibly selenoacetic acid, $AcSeH$, was also isolated. When the *methosulphate* of yobyryne is treated with potassium hydroxide in boiling aqueous solution, a substance, m. p. 192–195°, is obtained which, although the analytical data agree best with $C_{20}H_{18}ON_2$, is probably the methoxy-compound, $C_{20}H_{20}ON_2$, obtained by simultaneous oxidation and reduction in accordance with the known behaviour of quinolinium and acridinium bases. Fusion of ketoyobyryne with potassium hydroxide at 345–350° affords a basic substance, $C_{11}H_{10}O_2N_2$, m. p. 258°, and 1:2-dimethylbenzoic acid (hemellitic acid), m. p. 142–144°, identical with a specimen synthesised by the action of mercury fulminate on *o*-xylene in carbon disulphide in the presence of aluminium chloride and separation of the resulting 2:3- and 3:4-dimethylbenzonitriles or of the benzoic acids obtained on hydrolysis. The solubility of the calcium salt of hemellitic acid decreases with rise of temperature. By the usual Fischer indole synthesis from the *o*-, *m*-, and *p*-tolylhydrazones of propaldehyde are obtained, respectively, 3:7-, b. p. 281–282° (*picrate*, m. p. 142–143°), 3:6-, m. p. 116–117° (*picrate*, m. p. 179–180°), and 3:5-, b. p. 277–278°, m. p. 74.5° (*picrate*, m. p. 179–180°), -dimethylindole, but none of these is identical with the supposed dimethylindole (*picrate*, m. p. 156–157°) obtained by heating yohimbine hydrochloride with alkali and superheated steam or by distillation of yohimbine with zinc dust (Winterstein and Walter, A., 1927, 1208). If the latter is a dimethylindole it can only be the 3:4-derivative. The significance of these results and others in the literature in relation to the structure of yohimbine is discussed, and it is suggested that the relationship of yobyryne, $C_{19}H_{18}N_2$ (I), to the base $C_{13}H_{12}N_2$ (II) obtained by Winterstein and Walter (*loc. cit.*) is probably represented thus:



The bases $C_{13}H_{12}N_2$ and $C_{12}H_{10}N_2$ (1 methyl group lost by reduction) probably contain the benzene ring which is isolated as isoquinoline (Winterstein and Walter, *loc. cit.*) and not as the dimethylindole, that in the latter being the one isolated as 1:2-dimethylbenzoic acid. On this hypothesis yohimbine contains a reduced benzene nucleus and not a tetrahydroisoquinoline or a tetrahydroquinoline ring as suggested by Hahn and Schuch (*loc. cit.*) and by Schomer (*loc. cit.*), respectively. J. W. BAKER.

Constitution of lupinine. I. K. WINTERFELD and F. W. HOLSCHNEIDER (Ber., 1931, 64, [B], 137—

150; cf. Schöpf, A., 1928, 1144).—Examination of lupinine confirms the structure I suggested by Karrer



and others (A., 1929, 200) and shows the presence of a structural isomeride (II), for which the name *allolupinine* is suggested.

Lupinine, m. p. 68–69°, is converted by treatment with acetic and sulphuric acids at 180° into anhydrolupinine, which is hydrogenated in presence of palladised calcium carbonate to lupinane, $C_{10}H_{19}N$, b. p. 82–83°/13 mm. Treatment of the last-named compound with cyanogen bromide in boiling benzene produces *bromolupinanecyanoamide*, $C_{11}H_{19}N_2Br$, which does not yield crystalline salts. Replacement of the bromine atom by hydrogen is effected with difficulty, but *lupinanecyanoamide*, $C_{11}H_{20}N_2$, is obtained in 85% yield by treatment with potassium hydroxide in methyl alcohol and then with hydrogen in presence of palladised calcium carbonate. As by-product, a base, $C_{11}H_{21}N_2$, is isolated as the *chloroplatinate*, $(C_{11}H_{21}N_2)_2 \cdot H_2PtCl_6$, m. p. 217–218° (decomp.), and *mercury salt*. Hydrolysis of lupinanecyanoamide with aqueous-alcoholic hydrochloric acid at 95–98° give a secondary base, $C_{10}H_{21}N$, b. p. 101–102°/11 mm. (*hydrochloride*, m. p. 151–153°; *hydriodide*; *hydrobromide*, m. p. 168–170°; non-crystalline *benzoyl*, *p*-nitrobenzoyl, and *acetyl* derivatives; β -*naphthalenesulphonyl* compound, m. p. 86–87°). Treatment of the hydrochloride with potassium cyanate affords a viscous oil transformed by benzoyl chloride into a *dibenzoyl* derivative of half-hydrolysed lupinanecyanoamide, $C_{10}H_{20}N \cdot CO \cdot NBz_2$, m. p. 169–170°; this compound can also be isolated from the product of the moderated hydrolysis of lupinanecyanoamide with alcoholic hydrochloric acid at 85°. An acid, b. p. 130–132°/9 mm., is obtained by hydrolysis of lupinanecyanoamide with aqueous sulphuric acid. Hydrogenation of lupinanecyanoamide in presence of palladised calcium carbonate gives the base $C_{11}H_{21}N_2$, yielding a chloroplatinate, m. p. 216–217° (decomp.), identical with that described above.

Treatment of the secondary base with silver acetate in acetic acid at 180° gives the tertiary pyridine base, $C_{10}H_{15}N$, b. p. 110–112°/39–40 mm. (*chloroplatinate*, long, orange-red crystal aggregates or coarse, yellowish-red crystals, m. p. 190–191°, decomp. 192–194°; *chloroaurate*, m. p. 46–47°). The base $C_{10}H_{15}N$ is shown to be a mixture of 3-methyl- and 6-methyl-2-*n*-butylpyridine, since when oxidised by potassium permanganate under varied conditions it affords the four pyridinecarboxylic acids: 2-*n*-butylpyridine-6-carboxylic acid, isolated as the *copper salt* and *chloroplatinate*, $(C_{10}H_{13}O_2N)_2PtCl_4$, m. p. 154–155° (decomp.); 2-methylpyridine-6-carboxylic acid, m. p. 95–96°, isolated as the *copper salt*, m. p. 253–255° (decomp.) [yielding 2-methylpyridine when subjected to dry distillation], and *hydrochloride*, m. p. 202.5–203.5° (decomp.) (also

prepared by oxidation of 2:6-dimethylpyridine); pyridine-2:3-dicarboxylic acid; 3-methylpyridine-2-carboxylic acid.

H. WREN.

Lupanine. K. WINTERFELD and A. KNEUER (Ber., 1931, 64, [B], 150—158).—Lupanine is converted by hydriodic acid (*d* 2.0) and red phosphorus at 240—245° into β -lupanine, b. p. 85—86°/15 mm. (*chloroaurate*, m. p. 143—144°; *picrate*, m. p. 165—166°; *chloroplatinate*, decomp. 217°) [identical with the product obtained by Schöpf (A., 1928, 1144) and with that derived from matrine by Kondō and Satō (A., 1921, i, 882)], and a fraction, b. p. 145—147°/12—13 mm., from which crystalline salts could not be obtained but gives a well-marked pyrrole reaction. It is suggested that lupanine is constituted by the union of a lupinane ring with a pyrrolidine complex. Treatment of lupanine with cyanogen bromide in boiling benzene in the absence of moisture affords *bromolupaninecyanoamide*, $C_{15}H_{21}ON_2CNBr$, $[\alpha]_D^{25} +82.86^\circ$ in 90% alcohol, which does not yield salts and is reduced by zinc dust in boiling 80—85% acetic acid to the non-crystalline *lupaninecyanoamide*. The last-named compound is hydrolysed by sulphuric acid to a non-crystalline, secondary base, $C_{15}H_{26}ON_2$, characterised by the *chloroaurate*, m. p. 153°, *picrate*, m. p. 93—94°, *hexahydrated chloroplatinate*, and *benzoyl derivative*, m. p. 195° (*chloroaurate*, m. p. 206°). Fission of the benzoyl compound could not be effected with phosphorus pentabromide or pentachloride. The base is transformed by methyl iodide into a *methiodide*, m. p. 277—278° from which *N-methyl-lupanine* [*chloroaurate*, m. p. 140° (decomp.)] is derived. Attempts to degrade *N-methyl-lupanine* are impeded by the poor yields.

H. WREN.

Optical rotation of quinine alkaloids. R. DIETZEL and K. SÖLLNER (Arch. Pharm., 1930, 268, 629—636).—The values of $[\alpha]_D^{25}$ for 0.0285*M*-aqueous solutions of the monohydrochlorides of quinine, quinidine, and cinchonidine are changed by the addition of 1 equivalent of hydrochloric acid from -175.4° , $+224.2^\circ$, and $+213.2^\circ$ to -277.9° , $+312.3^\circ$, and $+271.4^\circ$, respectively, and by a further 0.4 equivalent of acid to -280.7° , $+310.0^\circ$, and $+271.1^\circ$. The changes are connected with the passage of the quinoline nitrogen atom into the ionised state. Similarly, $[\alpha]_D^{25}$ for 0.25*M*-aqueous sodium tartrate is changed from $+34.1^\circ$ to $+13.1^\circ$ by the addition of 1 equivalent of sulphuric acid and to $+10.2^\circ$ by 3.2 equivalents, and $[\alpha]_D^{25}$ for 0.25*M*-aqueous tartaric acid is changed from $+15.1^\circ$ to $+13.5^\circ$ by 0.80 equivalent of sulphuric acid and to $+41.2^\circ$ by 1.6 equivalents of sodium hydroxide.

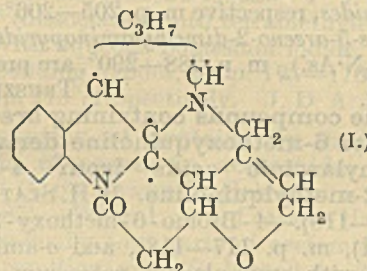
H. E. F. NOTTON.

Cinchona alkaloids. VII. Sulphonation of quinine and hydroquinine. G. GIEMSA and M. OESTERLIN (Ber., 1931, 64, [B], 57—61; cf. A., 1925, i, 291).—The readiness of reaction between hydroquinine and sulphuric acid and the easy hydrolysis of the product appear to indicate that the supposed sulphonic acids are hydrogen sulphates. Reaction does not take place unless an alcoholic hydroxyl group is present. If the latter group is acetylated either hydrolysis and "sulphonation" take place or there is no change. Hydroquinine chloride and

deoxyhydroquinine do not yield "sulphonic acids," whereas acetyl- and benzoyl-hydroquinine undergo exchange esterification. It is not possible to obtain the corresponding "acylsulphonic acids" from "hydroquininesulphonic acid" and acetyl chloride or chloroformic esters. Diazotised 5-aminohydroquinine-sulphonic acid, like diazotised 5-aminohydroquinine, is reduced to methylhydrocuprean. In consequence of the possibility of isomerisation to the *iso*-base, quinine does not afford a homogeneous reaction product with concentrated sulphuric acid. Isomerisation is avoided by the use of acetic anhydride as solvent, whereby *quininesulphonic acid*, decomp. 237° after darkening at 230°, $[\alpha]_D^{25} +88.86^\circ$ in *N*-sodium hydroxide [*hydrochloride* ($+5H_2O$), m. p. 205°], is produced. It is quantitatively hydrolysed by 25% hydrochloric acid to quinine and, with bromine in glacial acetic acid, gives *quininesulphonic acid dibromide*, m. p. 232° after darkening at 218°, hydrolysed to quinine dibromide, m. p. 218—220°. Potassium permanganate oxidises quininesulphonic acid to *chiteninesulphonic acid*, m. p. 221—225°, hydrolysed by boiling hydrochloric acid to chitenine, m. p. 280°. Acetylquinine in acetic anhydride is scarcely affected by sulphuric acid. Treatment of quinine with concentrated sulphuric acid at 0° yields mainly hydroxyhydroquinine-sulphonic acid, which is almost certainly a mixture of isomerides; small amounts of *iso*quininesulphonic acid and *niquinesulphonic acid* are also produced.

H. WREN.

Molecular structure of strychnine and brucine. R. ROBINSON (Proc. Roy. Soc., 1931, A, 130, 431—452).—The Bakerian lecture for 1930. The work of Tafel, Leuchs, Perkin, and Robinson is summarised and the partial structure I assigned to strychnine. Brucine contains methoxyl groups in the 6- and



7-positions of the quinoline fragment. Methyl- ψ -strychnidine has been found to be isomeric with strychnidine; it is re-named *neostrychnidine*.

H. BURTON.

Determination of morphine in aqueous solution. H. BAGGESGAARD-RASMUSSEN and S. A. SCHOU (Arch. Pharm., 1930, 268, 673—680).—A mixture of chloroform (3 vols.) and *isopropyl alcohol* (1 vol.) is superior to the solvents previously suggested for the extraction of morphine (solubility, 0.785% wt./vol.) from its aqueous suspension. The aqueous solution, concentrated, if necessary, to contain 0.1—0.2 g. of morphine in 20 c.c., is treated with 5 c.c. of 4% sodium carbonate solution and extracted as rapidly as possible with four quantities of 25 c.c. of solvent. The extract is filtered through a small dry paper, evaporated to dryness, and the residual morphine determined acidimetrically. The application of the

method to micro-determinations and to more dilute solutions is described. H. E. F. NOTTON.

Germanochlorides of alkaloids. A. TCHAKIRIAN.—See this vol., 322.

Arseno-organic compounds. I. Phenyl- α -naphthylarsine derivatives. J. KLIPPEL (Rocz. Chem., 1930, 10, 777—783).—*Phenyl- α -naphthylcyanoarsine*, m. p. 99.5—100°, is prepared by treating phenyl- α -naphthylmethylarsine with cyanogen bromide, and the corresponding *chloroarsine*, m. p. 46—46.5°, by the action of chlorine. Both products yield *phenyl- α -naphthylarsine oxide*, m. p. 116.5—117.5°, on alkaline hydrolysis, and this oxide gives, on further hydrolysis, *phenyl- α -naphthylarsinic acid*, m. p. 189—189.5°. R. TRUSZKOWSKI.

Arsenopyridine compounds. E. PEŁAZEK (Rocz. Chem., 1930, 10, 751—760).—*3-Arsinopyridine-2-carboxylic acid* (I), m. p. 280—300° (decomp.), is prepared by the action of arsenious oxide on 3-diazopyridine-2-carboxylic acid; decarboxylation of this acid cannot be effected by any of the reactions ordinarily used for this purpose. Its *oxide*, m. p. 316° (decomp.), is prepared by the action of sulphur dioxide on its aqueous solution, and this oxide is converted by hot hydrochloric acid into 3-dichloroarsinopyridine-2-carboxylic acid *hydrochloride*. The acid I reacts with sodium hypophosphite and potassium iodide to yield *bis-3-arsenopyridine-2-carboxylic acid* ($\text{CO}_2\text{H}\cdot\text{C}_5\text{H}_3\text{N}\cdot\text{As}$)₂. The *mono-* and *di-sulphides* of acid I (decomp. 250° and 231°) are prepared by the action of hydrogen sulphide respectively on the oxide and the acid. *2-Dimethylaminopyridine-5-arsinic acid*, m. p. above 300° (decomp.), is prepared by the action of arsenic trichloride on 2-dimethylaminopyridine. The corresponding *oxide*, m. p. 265°, *mono-* and *di-sulphides*, respective m. p. 205—206° and 118—120°, and *bis-5-arseno-2-dimethylaminopyridine*, ($\text{NMe}_2\cdot\text{C}_5\text{H}_3\text{N}\cdot\text{As}$)₂, m. p. 288—290°, are prepared. R. TRUSZKOWSKI.

Quinoline compounds containing arsenic. II. Synthesis of 6-methoxyquinoline derivatives of aminophenylarsinic acids from 4-bromo-6-methoxy-2-methylquinoline. R. H. SLATER (J.C.S., 1931, 107—118).—4-Bromo-6-methoxy-2-methylquinoline (I), m. p. 117—118°, and *o*-aminophenylarsinic acid with amyl alcohol, potassium carbonate, and traces of copper bronze and iodine furnish in moderate yield *o*-6'-methoxy-2'-methyl-4'-quinolylaminophenylarsinic acid (II), m. p. 302—303° (decomp.) (*salts* described), which on reduction in alcoholic hydrochloric acid solution containing a trace of iodine, by means of sulphur dioxide, gives 12-chloro-7-methoxy-11-methyl-5:12-dihydroquinbenzarsazine, darkens 235°, m. p. 245—247° (decomp.), oxidised by hydrogen peroxide in acetic acid solution to 7-methoxy-11-methylquinbenzarsazinic acid, unmelted at 310° (*salts* described). With phosphorus oxychloride II furnishes 7-methoxy-11-methylquinbenzarsazinyl chloride, darkens 150°, m. p. 165—167°. *o*-Tolidine and I when heated at 140—150° for 9 hrs. give 4-*o*-tolidino-6-methoxy-2-methylquinoline, m. p. 199—200° (*acetyl* derivative, m. p. 182—183°), which by the Bart reaction yields 4':6'-methoxy-2'-methyl-4'-quinolylamino-3:3'-dimethyldiphenylarsinic acid, m. p. 304—

305° (decomp.) (*salts* described). *o*-Dianisidine and I similarly yield 4-*o*-dianisidino-6-methoxy-2-methylquinoline, m. p. 195—196° [*acetyl* derivative, m. p. 140° (loss of water), m. p. 200—201°], from which 4':6'-methoxy-2'-methyl-4'-quinolylamino-3:3'-dimethoxydiphenylarsinic acid, m. p. 243—245° (decomp.) (*salts* described), is obtained by the Bart reaction. From I and *pp'*-diaminodiphenylmethane, *p*-6-methoxy-2-methyl-4-quinolylamino-*p'*-aminodiphenylmethane, m. p. 135—145° (loss of water), and *p*-6-methoxy-2-methyl-4-quinolylaminodiphenylmethane-*p'*-arsinic acid, chars at 300° after darkening, are prepared in an analogous manner. From aniline and 4-chloro-6-methoxy-2-methylquinoline, 4-anilino-6-methoxy-2-methylquinoline, m. p. 208—209° (*hydrochloride*, unmelted at 310°), was obtained. J. D. A. JOHNSON.

Constitution of phenarsazine chloride. C. P. A. KAPPELMEIER (Rec. trav. chim., 1931, 50, 44—50).—Polemical against Gibson, Johnson, and Vining (A., 1930, 1601). J. W. BAKER.

Reaction between dichloroarsines and secondary aromatic arsines. C. S. GIBSON (J. Amer. Chem. Soc., 1931, 53, 376—377).—Lewis and Stiegler's observation (A., 1930, 1601) that 6- β -chlorovinylphenarsazine and 7- β -chlorovinyl-7:12-dihydrobenzophenarsazine are 10-chloro-5:10-dihydrophenarsazine and 7-chloro-7:12-dihydrobenzophenarsazine, respectively, was first shown by Burton and Gibson (A., 1926, 419) and confirmed by Seide and Gorski (A., 1929, 1321). H. BURTON.

Oxidation of heterocyclic arsenic compounds by iodine. G. A. RAZUBAIEV and V. S. MALINOVSKI (Ber., 1931, 64, [B], 120—130).—The oxidation of alkyl and aryl derivatives of dihydrophenarsazine by iodine in aqueous-alcoholic solution takes place according to the scheme $\text{NH}\langle\text{C}_6\text{H}_4\rangle\text{AsR} + \text{I}_2 +$

$2\text{H}_2\text{O} \rightarrow 2\text{HI} + \text{NH}\langle\text{C}_6\text{H}_4\rangle\text{AsR}(\text{OH})_2$, whereas with the chloro-derivatives and oxides the equations are $\text{NH}\langle\text{C}_6\text{H}_4\rangle\text{AsCl} + \text{I}_2 + 2\text{H}_2\text{O} = \text{NH}\langle\text{C}_6\text{H}_4\rangle\text{AsO}\cdot\text{OH} + 2\text{HI} + \text{HCl}$ and $(\text{NH}\langle\text{C}_6\text{H}_4\rangle\text{As})_2\text{O} + 2\text{I}_2 + 3\text{H}_2\text{O} = 2\text{NH}\langle\text{C}_6\text{H}_4\rangle\text{AsO}\cdot\text{OH} + 4\text{HI}$. The compound under investigation is dissolved in alcohol and the solution is diluted with water until a turbidity is produced. Alcoholic iodine is added until a bright yellow colour is produced. In course of the titration water is added in two or three portions. Initially the colour of the iodine disappears immediately on shaking, but towards the end of the titration 10—30 seconds are required. The yellow colour caused by a slight excess of iodine should persist for 24—48 hrs. In certain cases it is preferable to add immediately about three fourths of the necessary iodine and, after the precipitated oxide has dissolved, to treat the mixture with sufficient aqueous sodium hydrogen carbonate to neutralise the liberated hydrogen iodide. The titration is subsequently finished in the usual manner. For the isolation of the products of the reactions it is necessary to neutralise the liberated hydrogen iodide either by titration with standard

sodium hydroxide or by addition of an excess of freshly-precipitated silver oxide. In the majority of cases the oxides and dihydroxides separate from the concentrated solutions with hygroscopic moisture or water of crystallisation, which is readily lost in a vacuum over phosphoric oxide at the ordinary temperature. Transition of dihydroxide to oxide occurs at a higher temperature.

The following new compounds are incidentally described: 10-methyl-5:10-dihydrophenarsazine dihydroxide, m. p. (indef.) 201–205°, and the corresponding oxide, decomp. 256–257°; 10-ethyl-5:10-dihydrophenarsazine dihydroxide, m. p. (hydrated) 141–143°, (anhydrous) 141–183° (indef.), and the oxide, m. p. 239°; 10-propyl-5:10-dihydrophenarsazine, m. p. 81–82°, from the 10-chloro-compound and magnesium propyl iodide, its dihydroxide, m. p. 93°, and oxide, m. p. 111–112°; 10-isoamyl-5:10-dihydrophenarsazine, m. p. 76–78° (dihydroxide, m. p. 95–96°; oxide, m. p. 101–102°); 10-phenyl-5:10-dihydrophenarsazine oxide, decomp. 280–300°.

H. WREN.

Preparation of aromatic mercuric chlorides from aromatic diazonium chlorides. R. E. McCURE and A. LOWY (J. Amer. Chem. Soc., 1931, 53, 319–321).—When benzenediazonium chloride is treated with mercury (in a finely-divided state produced by stirring), mercury phenyl chloride is obtained in 45% yield: $\text{Ph}\cdot\text{N}_2\text{Cl} + \text{Hg} \rightarrow \text{Ph}\cdot\text{HgCl} + \text{N}_2$. Mercury *o*-tolyl (72%), *p*-tolyl (52%), *p*-xylyl (64%), and α -naphthyl chlorides (20%) are prepared similarly (percentage yields given in parentheses) from the appropriate amines.

H. BURTON.

Influence of acid chlorides and pyrrole on the colour test for reactive organometallic compounds. Constitution of magnesium pyrrol halides. H. GILMAN and L. L. HECK (J. Amer. Chem. Soc., 1930, 52, 4949–4954).—The colour test for the detection of an excess of a Grignard reagent (A., 1925, ii, 1011; 1928, 160; 1930, 778) in a reaction mixture is interfered with by acetyl, benzoyl, carbonyl, and oxalyl chlorides, phosphorus pentachloride, and thionyl chloride, but is unaffected by the presence of many other chlorides. When pyrrole is treated with magnesium methyl iodide in di-*n*-butyl ether at 29°, only 1 mol. of methane is evolved, indicating the presence of one active hydrogen atom. It is concluded from this that magnesium pyrrol halides contain the group $\text{N}\cdot\text{MgX}$.

H. BURTON.

Heterocyclic systems containing selenium.
IV. **cycloSelenohexane.** G. T. MORGAN and F. H. BURSTALL (J.C.S., 1931, 173–180; cf. A., 1930, 1051).— α -Hexamethylene dibromide and alcoholic sodium selenide yield cyclo selenohexane (I), b. p. 105–106°/68 mm., 188–190°/756 mm., n_D^{20} 1.5470, d_4^{20} 1.353, parachor 302.1, in small yield, together with a dimeride (II), m. p. 92°, and a polymeride (III), m. p. 36–37°. With bromine I, II, and III furnish dibromides, m. p. 118–119°, 145° (decomp.), and 94–95° (decomp.), respectively, reducible to the original selenohydrocarbons. The dichloride, m. p. 78°, di-iodide, m. p. 82°, methiodide, decomp. 149–150°, and mercurichloride, m. p. 193–194° (decomp.),

of I are described. Depolymerisation of II and III at 220° yields 2-methylcycloselenopentane (IV), b. p. 90°/65 mm., 169–171°/764 mm., n_D^{18} 1.5205, d_4^{18} 1.287 [mercurichloride, m. p. 112°; methiodide, m. p. 164° (decomp.)], the dibromide (dichloride, dibromide, and di-iodide are gums) of which on distillation under diminished pressure gives β -methylpentamethylene dibromide. Hexamethylene- α -diselenocyanate (V) (an oil), from potassium selenocyanate and α -hexamethylene dibromide, on alkaline hydrolysis gives cyclohexamethylene 1:8-diselenide (VI), m. p. indef. about 40°, which at 250° decomposes into selenium and IV. Hexamethylenediselenious acid, decomp. 147°, is formed by oxidising V and VI with nitric acid.

J. D. A. JOHNSON.

cycloTellurobutane (tetrahydrotellurophen). G. T. MORGAN and F. H. BURSTALL (J.C.S., 1931, 180–184).—Amorphous tellurium dissolves in α -tetramethylene di-iodide at 130° to give cyclotelluributane 1:1-di-iodide (two forms; both m. p. 149–150°), which is reduced in aqueous suspension by sulphur dioxide to cyclotellurobutane (I), b. p. 105–106°/122 mm., 166–167°/761 mm. (Siwoloboff method), n_D^{18} 1.6175 (mercurichloride, m. p. 146–147° after sintering at 140°; a methiodide, darkens 200°, unmelted at 240°). The dibromide, m. p. 130°, and dichloride, m. p. 111–112°, are obtained from I and the appropriate halogen. cycloTelluributane 1-oxide, m. p. 241° (decomp.), from the dihalides and alkali, or aerial oxidation of I, reacts with the dibromide to give biscyclotelluributane 1:1'-oxydibromide, m. p. 207° (decomp.). Tetramethylene bromide and aluminium telluride at 125° yield 1- δ -bromobutylcyclo-telluributane 1-bromide, m. p. 152–153°, and tetramethylene- α - δ -biscyclotelluributane 1:1'-dibromide, m. p. 225° (dissociation into tetramethylene bromide and I). With aqueous potassium iodide, these yield the corresponding iodides, m. p. 175–176° (decomp.) and decomp. 215°, respectively. J. D. A. JOHNSON.

Disintegration of proteins by amides. Disintegration of casein in acetamide. E. CHERBULIEZ and G. DE MANDROT (Helv. Chim. Acta, 1931, 14, 163–183).—When 1 part of casein (Hammarsten) is added gradually to 5 parts of acetamide at 100–110°, the resulting mixture heated to 200° during several min., and the acetamide removed by distillation at 100–110°/1 mm. and subsequent extraction with acetone, a residue is obtained which is largely soluble in hot water, readily soluble in ammonia or alkali carbonate, gives most of the usual protein colour reactions, and contains slightly less nitrogen than casein. Extraction of the product with alcohol, and purification of the dissolved material by two-fold precipitation with copper acetate and removal of copper as the sulphide, gives a fraction which when analysed by the method previously described (this vol., 245) shows values for the nitrogen distribution and acetylated esters similar to those for casein. Mol. wt. determinations of various products obtained under different conditions of heating show that they all possess approximately the same value of 350 (mean); fractionation with alcohol gives products of the same mol. wt. Determinations of the equivalents of the same products by dissolution in dilute

alkali hydroxide and titrating the excess also show that all the fractions have a similar value (provided the titrations are carried out immediately). Polymerisation occurs under the influence of alkali; this is most marked with the products prepared by short heating with acetamide. Polymerisation does not occur to any appreciable extent in neutral solution. Cyclisation probably occurs during the disintegration.

H. BURTON.

Separation of the digestion products of proteins by the method of differential analysis. S. V. DESAI (Biochem. J., 1930, 24, 1897—1904).—Peptic digests of gelatin, egg-albumin, blood-fibrin, glutelin, and caseinogen and a tryptic digest of gelatin and "bactopeptone" were dialysed through membranes of graded permeability prepared by Pierce's method (A., 1928, 233). Fractions of increasing molecular complexity as shown by determination of free amino- and peptide-nitrogen were obtained. S. S. ZILVA.

Mol. wt. of egg-albumin. II. In presence of electrolytes. J. B. NICHOLS (J. Amer. Chem. Soc., 1930, 52, 5176—5187; cf. A., 1927, 99).—The partial specific volume of crystalline egg-albumin, purified by electrodialysis, does not vary appreciably with p_H (3.6—7.3), except in strongly acid solution. The sedimentation constant in the isoelectric region of the protein has a mean value of 4.06×10^{-13} cm. per sec. at 30°; the diffusion constant is abnormal. The mol. wt. of the protein is approximately 34,500. The molecule is spherical and has a radius of 2.17 $m\mu$. The depression of the sedimentation constant, due to the Donnan effect, is found to be a maximum at about p_H 3 in unbuffered solutions, for the acid side of the isoelectric point. In buffered solutions, the constant has approximately the same value at p_H 3—7. At p_H 1.16, denaturation of the protein occurs; sedimentation is rapid owing to the aggregation of the formed gel into particles containing approximately seven molecules. H. BURTON.

p_H -Stability region of egg-albumin. B. SJÖGREN and T. SVEDBERG (J. Amer. Chem. Soc., 1930, 52, 5187—5192; cf. preceding abstract).—The ultra-violet absorption curve of pure egg-albumin shows a maximum at about 280 $m\mu$ and a minimum at about 254 $m\mu$ for solutions at p_H 2.2, 5.5, and 11.2; the value of the extinction coefficient is lowest at p_H 5.5. Decomposition of the protein into non-centrifugable material occurs above p_H 9 and below p_H 4. The sedimentation constant is independent of p_H in the range 3—11, and has a mean value of 3.54×10^{-13} at 20° as compared with the value of 3.31×10^{-13} calculated from Nichols' results (*loc. cit.*). The mol. wt., sedimentation constant, molar frictional constant, and molecular radius of egg-albumin are identical with the corresponding values for Bence-Jones protein (A., 1930, 233); the isoelectric points of the two proteins differ. H. BURTON.

Denaturation of proteins. VII. N. BOOTH.—See this vol., 316.

Effect of light and salts on gelatin. A. GALINSKY.—See this vol., 319.

Micro-determination of carbon and hydrogen by Pregl's method. A. FRIEDRICH (Mikrochem.,

1931, 9, 20—26).—Errors in carbon determination are generally due to varying composition of the oxygen used and are eliminated by purification of the oxygen. The essential features ensuring correct results for hydrogen are constancy of temperature of the lead peroxide layer and constant conditions of the absorption apparatus. E. S. HEDGES.

Micro-determination of carbon and hydrogen in organic mercury compounds. M. FURTER (Mikrochem., 1931, 9, 27—30).—In the micro-determination of carbon and hydrogen by Pregl's method the presence of mercury compounds causes a high value for hydrogen and a low value for carbon, due to the distillation of small quantities of mercury into the calcium chloride tube and to some reaction between mercury vapour and the lead peroxide-asbestos used for filling, which probably causes incomplete oxidation of the carbon.

E. S. HEDGES.

Micro-analytical determination of methoxyl groups. (Miss) G. M. WARE (Mikrochem., 1930, 8, 352—355).—Micro-Zeisel determinations with compounds containing from one to five methoxyl groups in presence of acetic anhydride and phenol yield results which, after application of the Friedrich correction, are in good agreement with the theoretical values for mono- and di-methoxy-compounds, but are low when a greater number of methoxyl groups are present. In all cases the method is satisfactory if pellets of the substance and hydriodic acid (d 1.96) are employed; the carbon dioxide used should be washed with silver nitrate solution, sulphuric acid, and, finally, with a suspension of red phosphorus in 10% cadmium sulphate solution. H. F. GILLBE.

Determination of fatty acids. II. Determination of mixtures of two fatty acids by partition between ethyl ether and water. C. H. WERKMAN (Iowa State Coll. J. Sci., 1930, 4, 459—464; cf. A., 1930, 1161).—The solution (0.1N, 30 c.c.) is shaken with ether (20 c.c.), and the aqueous phase (25 c.c.) is titrated with 0.1N-alkali. Values of the partition constant have been determined for the pairs of acids: butyric-acetic, -propionic, -lactic; acetic-propionic, -lactic. The composition of mixtures may be determined by reference to the graph.

CHEMICAL ABSTRACTS.

Potentiometric determination of cystine and cysteine. K. YAMAZAKI (J. Biochem., Japan, 1930, 12, 207—222).—Pure cystine and cysteine solutions can be accurately titrated with sodium bromate in presence or absence of bromide ions, but in the presence of other amino-acids titration with sodium iodate in the presence of iodine is more accurate. Temperature and acidity, which determine the extent to which cysteine is oxidised to cystine or cysteinic acid, are important, as also is the rate of titration with iodine. Tryptophan is the only amino-acid which affects the titration of cysteine by sodium iodate, probably owing to its own oxidation in presence of cysteine.

CHEMICAL ABSTRACTS.

Effect of hydrogen-ion concentration on precipitation of certain basic substances by phosphotungstic acid. R. A. PETERS (Biochem. J.,

1930, 24, 1852—1855).—The hydrogen-ion concentration at which phosphotungstate precipitates of certain bases appear depends largely on the constitution of the base. With most of the bases studied the precipitation appears with decreasing alkalinity; with guanidine compounds, this is reversed.

S. S. ZILVA.

Colour reactions of benzene, naphthalene, anthracene, phenanthrene, *p*-benzoquinone, anthraquinone, and quinoline. L. EKKERT (Pharm. Zentr., 1931, 72, 51—53).—Each of the above substances gives brilliant colour reactions when 0.01 g. in ethyl alcohol (1 c.c.) is treated with a 10% solution of *p*-dimethylaminobenzaldehyde in sulphuric acid (5 drops), or with nitroso- β -naphthol (0.001 g.), and first superposed upon, then mixed with sulphuric acid (1 c.c.). The ultra-violet fluorescence colours of the products and of the original alcoholic solutions are also given.

H. E. F. NOTTON.

Determination of cresols. P. DUMONT (J. Pharm. Belg., 1930, 12, 1—4, 21—27, 41—45, 65—67, 87—92; Chem. Zentr., 1930, ii, 98).—By interaction with bromine *o*- and *p*-cresol can be converted into dibromo-derivatives and *m*-cresol into the tribromo-derivative; bromometric titration cannot be used for analysis of the isomerides in solution, but *m*-cresol can thus be determined in a mixture. A colorimetric method for the determination of *o*-cresol in a mixture of isomerides is described. Iodometric titration is not applicable, but *m*-cresol can be determined iodometrically in the absence of its isomerides. The determination of *m*-cresol by Qvist's modification of Raschig's method (gravimetric determination as trinitro-*m*-cresol) is satisfactory. Methods based on distillation with steam or extraction by means of a solvent give good results. A. A. ELDRIDGE.

Differentiation of cyclic monophenols and monoamines from polyphenols and polyamines. A. MARENZI (Ann. Farm. Biochim., 1930, 1, 99—105).—Differentiation is effected by means of phosphotungstic and phosphomolybdic reagents.

CHEMICAL ABSTRACTS.

Determination of piperidine in a mixture with pyridine and its homologues. A. TRAVERS and FRANQUIN (Compt. rend., 1930, 191, 1340—1343).—The piperidine in a mixture with pyridine, α -picoline, 2:6-lutidine, and collidine can be determined by

electrometric titration of the mixture using the hydrogen or quinhydrone electrode.

P. G. MARSHALL.

Detection and determination of cocaine in admixture with novocaine. F. WEISS (Apoth.-Ztg., 1930, 45, 724—726; Chem. Zentr., 1930, ii, 1897).—In dilute alcoholic ethereal (1:2) solution novocaine, but not cocaine, is precipitated by picric acid. Cocaine hydrochloride in 5% admixture with novocaine hydrochloride can be extracted with hot benzene. Determination of methoxyl leads to the determination of cocaine in presence of novocaine.

A. A. ELDRIDGE.

Specificity of the phenol reagent in the determination of tyrosine in proteins. V. CIOCALTEU (Compt. rend. Soc. Biol., 1929, 101, 198—199; Chem. Zentr., 1930, ii, 99).

Effect of precipitates on the proportionality and the development of colour in colorimetric determinations. C. CIOCALTEU (Compt. rend. Soc. Biol., 1929, 101, 216—218; Chem. Zentr., 1930, ii, 99).—The addition of lithium sulphate prevents the formation of disturbing precipitates in the determination of tyrosine according to the Folin-Looney method.

L. S. THEOBALD.

Potentiometric determination of alkaloids by means of potassium mercuri-iodide. II. L. MARICQ (Bull. Soc. chim. Belg., 1930, 39, 496—502).—Atropine, hyoscyamine, pilocarpine, cinchonine, and sparteine can be determined gravimetrically (to within 1—2%) as their mercuri-iodides, by adding potassium mercuri-iodide solution to their dilute acid solutions. Low results obtained with pilocarpine may be remedied by also adding mercuric iodide. J. D. A. JOHNSON.

Sodium alizarinsulphonate as reagent for alkaloids. L. ROSENTHALER (Apoth.-Ztg., 1930, 45, 638—640; Chem. Zentr., 1930, ii, 1742).—Limiting concentrations for the micro-precipitation of alkaloids by sodium alizarinsulphonate are recorded. The reagent is specially suitable for the detection of atropine.

A. A. ELDRIDGE.

Potentiometric titration of alkaloids with bi-metallic electrodes. M. L. HOLT and L. KAHLENBERG (J. Amer. Pharm. Assoc., 1931, 20, 11—15).—Potentiometric methods for the determination of brucine, strychnine, codeine, cocaine, morphine, and cinchonine using various metallic couples are described.

E. H. SHARPLES.

Biochemistry.

Deep respiration tetany. F. HOLTZ (Z. physiol. Chem., 1931, 194, 76—80).—The reactions of a resting human subject to electrical stimuli during deep respiration are described. During this condition, the serum-phosphorus falls to one third of its normal value.

A. COHEN.

Changes in blood-chloride during asphyxiation. I. T. SASO (J. Biochem., Japan, 1930, 12, 161—185).—During acute asphyxia the whole blood- and plasma-chloride diminishes continuously; in slow asphyxia the whole blood-chloride increases despite

diminution in the plasma-chloride. In prolonged asphyxia the plasma-chloride at first decreases, then increases, and finally decreases again. The hæmoglobin content of the blood is unchanged.

CHEMICAL ABSTRACTS.

Peripheral leucocytosis and erythrocytosis. I. Influence of pulmonary ventilation and of p_{r} of blood. P. A. ASHMARIN and I. A. ALEXEEV-BERKMAN. II. Pulmonary ventilation and erythrocytosis. P. A. ASHMARIN and E. A. VLADIMIROVA. III. Effect of the activity of the

gastrointestinal tract on peripheral leucocytosis and erythrocytosis. P. A. ASHMARIN, I. A. ALEXEEV-BERKMAN, and E. A. VLADIMIROVA. IV. Relation of urinary acidity to changes in peripheral leucocytosis. P. A. ASHMARIN and I. A. ALEXEEV-BERKMAN. V. Effect of local cooling and warming on morphological composition of the blood. P. A. ASHMARIN, I. A. ALEXEEV-BERKMAN, and E. A. VLADIMIROVA (Ark. Biol. Nauk, 1929, 29, 273—282, 283—287, 289—298, 299—302, 303—314). CHEMICAL ABSTRACTS.

Fœtal blood. I. Oxygen relationships of umbilical cord blood at birth. N. J. EASTMAN (Bull. Johns Hopkins Hosp., 1930, 47, 221—230).—Fœtal blood exhibits high oxygen capacity and high capillary unsaturation. CHEMICAL ABSTRACTS.

Isolation by cataphoresis of two different oxyhæmoglobins from the blood of some animals. A. GEIGER (Proc. Roy. Soc., 1931, B, 107, 368—380).—By the cataphoresis of oxyhæmoglobin of certain animals such as sheep and ox at a p_H in the neighbourhood of the commonly accepted isoelectric point (6.5—7.0) and in presence of sufficiently low concentrations of phosphate buffer the oxyhæmoglobin from one animal has been separated into two fractions, one migrating to the cathode and the other to the anode. These two oxyhæmoglobins when again subjected to cataphoresis cannot be further fractionated but behaved as homogeneous proteins, the isoelectric points of which differed by 0.3—0.4 p_H unit. The two oxyhæmoglobins from the same blood gave different oxygen dissociation curves, confirming the view that the two fractions represent distinct substances. Sometimes at least, human blood also contains two different oxyhæmoglobins, but their isoelectric points appear to be close together, so that separation is more difficult. Preliminary electro-dialysis of the hæmoglobin solutions facilitates separation.

W. O. KERMACK.

Variation of hæmoglobin content [of blood] and blood-forming function of the liver. S. TATUZAWA (Sei-i-kwai Med. J., 1930, 49, No. 5, 37—62).—The hourly variation for the normal resting rabbit is less than 1%; short exercise reduces the value by 1%. Subcutaneous injection of oxygen increases, and of carbon dioxide decreases, the hæmoglobin content. Liver-juice increases blood formation.

CHEMICAL ABSTRACTS.

Blood pigments. XIII. Preparation of methæmoglobin; fluoro[met]hæmoglobin, fission of hæmoglobin by papain, and the hæmoglobin in pernicious anæmia. F. HAUROWITZ (Z. physiol. Chem., 1931, 194, 98—106).—The method previously described (A., 1924, i, 1127) for the preparation of methæmoglobin is untrustworthy; a more convenient procedure is to suspend oxyhæmoglobin in 5% alcohol and keep the mixture for 6—10 days at 37—40°. The conversion of methæmoglobin into its fluoro-derivative (cf. *loc. cit.*), which shows an absorption maximum at about 606 $m\mu$, is complete only after 30 min. The action of papain—hydrogen cyanide on hæmoglobin at p_H 5 is similar to that of trypsin (A., 1930, 942); the hæmin-proteose produced has properties similar to those of the compound obtained

by the action of sodium hydroxide on hæmoglobin (Waelsch, A., 1927, 893). The hæmoglobin of pernicious and secondary anæmia has the same resistance to sodium hydroxide as that from normal blood.

H. BURTON.

Determination from the optical density and viscosity of a suspension of the number and volume of dispersed particles. (MME.) G. ACHARD (Compt. rend., 1931, 192, 242—244).—The viscosity of a suspension of red blood-corpuscles is related to their number by the formula $\eta/\eta_0 = 1 + 0.0486N^{1/3}$, where η and η_0 are the viscosities of the suspension and excipient, respectively, and N , the number of particles per $mm.^3 \times 10^{-6}$, lies between 0.2 and 10.0. Exponential and hyperbolic equations similar to those of Vles express the relationship between opacity and number of red blood-corpuscles. A. RENFREW.

Proteolytic enzymes in human leucocytes. E. HUSFELDT (Z. physiol. Chem., 1931, 194, 137—165).—Extraction of the leucocytes from the blood of a patient suffering from myeloid leucæmia, which are essentially those from bone-marrow, with 87% glycerol gives an extract containing two proteinases, a cathepsin and a trypsin. The former of these shows hydrolytic action at p_H 3—7; optimum fission of caseinogen and edestin occurs at p_H 4.3 and 5.3, respectively. The activity of the trypsin towards caseinogen increases (from p_H 4) with rise in alkalinity of the medium. The amount of the trypsin isolated from the cells increases with their destruction (by autolysis with chloroform at 37°). Autolysis of the leucocytes (essentially polymorphonuclear) from the exudate of an acute empyema gives a suspension containing mainly trypsin. The fission of caseinogen by this suspension is similar to the hydrolysis by glycerol extracts of the leucocytes from the blood of the horse and dog (Willstätter, Bamann, and Rohdewald, A., 1930, 234). A glycerol extract of the leucocytes from normal blood contains peptidases. The extract hydrolyses alanyl-glycylglycine readily at p_H 7.3; the rate of fission of alanyl-glycine (optimum at p_H 7.2) is three times that of leucyl-glycine (optimum p_H 8.1). The above enzymes are also found in glycerol extracts of granulocytes. H. BURTON.

Phase-rule equilibria of horse serum-globulin. J. W. MCBAIN and E. JAMESON (Trans. Faraday Soc., 1930, 26, 768—769).—Observations have been made on horse serum-globulin to ascertain the various states which it can assume and the conditions under which they can exist. The results obtained have been analysed in a phase diagram. There is great similarity to soap both in respect of the forms of globulin and soap which separate and the shapes of the areas representing the solutions of the two substances. It appears that globulin solution, euglobulin, and pseudoglobulin are three phases of the same substance, dehydrated globulin. A solution of globulin is the ordinary isotropic solution, whilst euglobulin and pseudoglobulin are liquid crystalline phases, or a liquid and glass which are slightly doubly refracting. W. O. KERMACK.

Action of alcohols on the coagulation by heat of protein solutions buffered with acetate. F. TEORELL (Biochem. Z., 1930, 229, 1—15).—Whether

ethyl alcohol is present or not, serum-albumin (horse) is coagulated by heat only between p_H 4.7 and 6.2. Methyl, ethyl, and propyl alcohols, in this order, have increasing inhibitory effects on coagulation by heat provided acetate is present. The effects are more pronounced when the concentration of the acetate is high than when it is low. When the concentration of the alcohol exceeds about 20% (by volume) the coagulated material wholly or partly dissolves when hot, but is re-precipitated on cooling. Coagulation in the cold is promoted in increasing degree by the alcohols in the following order: propyl, ethyl, methyl. Human plasma and horse plasma are affected in the same way as is horse serum, but the coagulation of ovalbumin by heat is not influenced by alcohol-acetate mixtures. W. McCARTNEY.

Composition of ox blood. A. ANDERSON, H. E. GAYLEY, and A. D. PRATT (J. Dairy Sci., 1930, 13, 336—348).—Determinations of hæmoglobin, non-protein-nitrogen, urea-nitrogen, creatinine, sugar, chlorides, phosphorus, calcium, and carbon dioxide-binding capacity have been made.

CHEMICAL ABSTRACTS.

Acetylcholine in ox-blood. F. WREDE and W. KEIL (Z. physiol. Chem., 1931, 194, 229—231).—When ox-blood is treated with alcohol, trichloroacetic acid, and ether as described by Kapfhammer and Bischoff (A., 1930, 1464), the resulting extract contains no acetylcholine. A similar extract from blood to which acetylcholine has been added shows none of the characteristic activity of acetylcholine. H. BURTON.

Determination of cholesterol, phosphorus, and inorganic calcium in one sample of blood-serum. G. H. BARIL and J. LABARRE (Trans. Roy. Soc. Canada, 1930, [iii], 24, V, 185—187).—To 1 c.c. of serum are added 1 c.c. of distilled water and 1 c.c. of potassium oxalate (2%). The calcium oxalate is separated by centrifuging and after washing determined with permanganate in the usual way. The cholesterol in the mother-liquor is extracted with ether after the addition of alcoholic potassium hydroxide and determined by Grigaut's method. The phosphorus is then determined by the method of Benedict and Theis (A., 1924, ii, 700).

W. O. KERMACK.

Precipitation in the determination of unfermentable substances in blood. R. EGE and J. ROCHE (Compt. rend. Soc. Biol., 1929, 102, 703—706; Chem. Zentr., 1930, ii, 100).—Fermentation should not proceed longer than 1—2 hrs. at 37°, the yeast must be practically free from reducing substances, and its amount should not exceed 3—4 mg. of dry substance for 1 c.c. of blood. If 100 mg. are employed the filtrate after precipitation with zinc hydroxide is richer in nitrogen than that obtained after precipitation with sodium tungstate; such a filtrate is unsuitable for the determination of sugar.

A. A. ELDRIDGE.

Colorimetric method of investigating the carbohydrate metabolism of blood and organs. I. Occurrence of hexoses in addition to dextrose in human blood: their production *in vitro*. Z. DISCHE (Biochem. Z., 1930, 229, 169—195).—Differences between the results obtained when the

sugar in a sample of blood is determined by two different methods (diphenylamine-hydrochloric acid and indole-sulphuric acid methods) indicate that, in addition to dextrose, human blood contains two other hexoses, a ketose and an aldose. The amount of these two hexoses in the blood is not increased in alimentary hyperglycæmia. In hypoglycæmia produced by administration of insulin the two hexoses are more rapidly eliminated than is dextrose. In blood kept at 38° for 2 hrs. the greater part of the two hexoses disappears, but when blood is kept at the ordinary temperature, a ketose, probably a constituent of a phosphoric ester and identical with the ketose already mentioned, is produced. This ketose, which disappears from the blood when kept at 37° much more rapidly than does dextrose, is found in the red corpuscles only, whereas the pre-formed hexoses are about equally distributed between plasma and corpuscles. Both the hexoses are produced from dextrose when this is added to blood.

W. McCARTNEY.

Protein-sugar in the blood-plasma of the horse. H. BIERRY (Compt. rend., 1931, 192, 240—241).—In the products of hydrolysis of the protein-sugar obtained from the purified albumin of horse plasma, *d*-mannose, *d*-galactose, and *d*-glucosamine have been detected and determined. The galactose linking is the weakest. The reducing power of the glucosamine is about a quarter of the reducing power of the total protein-sugar.

A. RENTREW.

Blood-sugar level of the ox. E. A. HEWITT (J. Amer. Vet. Med. Assoc., 1930, 77, 362—367).—The blood-sugar of heifers and non-lactating cows is higher than that of lactating cows. A high value may be correlated with œstrus in heifers. Variations in pathogenic conditions are recorded.

CHEMICAL ABSTRACTS.

Distribution of sugar in the blood of fishes. J. E. GRAY and F. G. HALL (J. Elisha Mitchell Sci. Soc., 1929, 45, 142—146).—Whole blood of normal fishes contains about 75 mg. of sugar per 100 c.c. The average ratio of plasma- to corpuscle-sugar is: menhaden 2.12, pickerel 1.75, scup 1.47, silver hake 3.60, shad 3.80, dogfish 1—1.03.

CHEMICAL ABSTRACTS.

Alimentary blood-sugar curve. Changes in the blood-sugar curve during blood-circulation. W. W. OPPEL (Arch. exp. Path. Pharm., 1930, 158, 348—367; cf. A., 1929, 462).—Arterial and venous lævulose and total blood-sugar of dogs are determined at intervals over a period of 3 hrs. after intestinal administration of sucrose (3 g. per kg. body-wt.). The parallel changes exhibited by the lævulose and blood-sugar curves are explained by inversion of sucrose, and it is concluded that absorption of sugar from the intestine, and not glycogen utilisation, is responsible for alimentary blood-sugar.

A. COHEN.

[Determination of] sugar in 0.02 c.c. of blood by the method of Folin and Malmros. J. F. McCLENDON (Proc. Soc. Exp. Biol. Med., 1930, 27, 773—775).—The blood (0.02 c.c.) is blown into tungstic acid solution (2 c.c.), the pipette is rinsed, and the mixture is stirred for 1 min. and centrifuged.

Potassium ferrocyanide solution (0.4 c.c.) and cyanide-carbonate solution (0.2 c.c.) are added to 1 c.c. of the clear liquid and to the standard sugar solution (5 c.c.). The test mixture is boiled for 8 min., cooled in water for 1 min., treated with 1 c.c. of ferric iron-ghatti solution, shaken, kept for 1 min., and then diluted to 5 c.c. Ten colorimetric comparisons are made as rapidly as possible.

CHEMICAL ABSTRACTS.

Micro-determination of blood-sugar. R. B. GIBSON (Proc. Soc. Exp. Biol. Med., 1930, 27, 480—483).—Protein and non-sugar reducing substances are precipitated from 0.2 c.c. of blood with 2.5 times as much sodium tungstate and sulphuric acid as would be required by the original Folin and Wu procedure. The colour developed by the arsenotungstate reagent with formaldehyde (Benedict) is permanent. Venous blood contains 66—122 (average 91) mg. of sugar per 100 c.c.

CHEMICAL ABSTRACTS.

Glycolysis of blood. I. H. K. BARRENSCHEEN and K. HÜBNER (Biochem. Z., 1930, 229, 329—342; cf. A., 1928, 912).—The mathematical equations proposed for representing the mechanism of glycolysis of blood are unsatisfactory and, in particular, fail to allow for the fact that a 15—30 mm. period of induction exists. This period can be suppressed by the addition of sulphate, phosphate, or arsenate ions. Since during glycolysis inorganic phosphate disappears and since this disappearance is accelerated by sulphate ions, the action of the latter may be regarded as an activation of phosphorylation. Administration of large doses of dextrose to fasting persons also suppresses the induction period of the glycolysis and accelerates the disappearance of the inorganic phosphate of their blood. When hexosediphosphate (but not hexosemonophosphate) is added to blood the induction period disappears and glycolysis is accelerated. These results indicate analogy between fermentation by yeast and glycolysis.

W. MCCARTNEY.

Determination of uric acid in blood. R. A. TRELLES and R. FERRAMOLA (Chemia, 1929, 6, 175—180; Chem. Zentr., 1930, ii, 100).—The method of Benedict (A., 1922, ii, 405) is recommended for determining uric acid in blood (plasma and corpuscles), but that of Flatow (A., 1926, 1283) is preferred for plasma or serum alone.

L. S. THEOBALD.

Determination of uric acid in blood. V. V. SAVJALOV and A. VALKOVITSCH (Jahrb. Univ. Sofia Med. Fak., 1928, 7; Chem. Zentr., 1930, ii, 100).—One c.c. of 10% sodium hydroxide solution and 1 c.c. of 5% ammoniacal silver nitrate are covered with the serum (0.5 c.c. in 250 c.c. of water), and after 1 min. a brown ring appears when the blood contains 0.002—0.0025% of uric acid. In a modification of the method, 2 c.c. of sodium hydroxide and ammoniacal silver nitrate are mixed with 1 c.c. of serum and 5 c.c. of water, and the colour obtained is compared with that given by 5 c.c. of a standard solution of uric acid and 1 c.c. of sheep's serum with the same reagents.

L. S. THEOBALD.

Calcium and phosphorus content of blood and the creatinine coefficient of the urine of some inhabitants of Malaya. F. E. BYRON (Bull. Inst.

Med. Res. Malay, 1930, No. 4, 1—4).—The serum-calcium and phosphorus content of the blood of normal tropical inhabitants does not appear to vary from the usual standards, but in natives suffering from tropical ulcers and anæmia the serum-calcium content is sub-normal, whilst the phosphorus determinations are within the normal limits. The urinary excretion of creatinine in native males is comparable with that observed in Europeans, but the values for normal females are lower. The excretion of creatinine in the urine in tropical ulceration and anæmia is considerably reduced. C. C. N. VASS.

Determination of blood-calcium. C. O. GUILLAUMIN (J. Pharm. Chim., 1931, [viii], 13, 65—76).—Plasma or serum (5 c.c.) is digested with 15 c.c. of "nitroperchloric" acid (100 c.c. of perchloric acid, *d* 1.61; 250 c.c. of nitric acid, *d* 1.39), heating gently at first and then vigorously to take to dryness. The colourless residue is dissolved in 5 c.c. of water acidified with hydrochloric acid and washed into a centrifuge tube. After heating for 2—3 min. on the water-bath, 2 c.c. of saturated ammonium oxalate solution are added, followed by ammonia, drop by drop, to give *p_H* 5.0, using methyl-red or cresol-green as indicator. The calcium may then be determined by igniting the oxalate, dissolving in hydrochloric or sulphuric acid, and titrating the excess with carbonate-free sodium hydroxide. Alternatively, the oxalate may be determined by hot permanganate. For the red cells the blood is centrifuged and the cells are treated with 20% trichloroacetic acid. A volume of liquid equivalent to 5 c.c. of original erythrocytes should be evaporated to 3—4 c.c., when ammonium oxalate is added and the determination continued as above.

T. MCLACHLAN.

Micro-determination of copper in blood. F. GRENDL (Pharm. Weekblad, 1930, 67, 1345—1351).—Improvements in the author's method of micro-determination of copper in foods (B., 1930, 1089), which result in greatly increased delicacy, are described. The method permits determination of $3\text{--}5 \times 10^{-3}$ mg. Cu in 3—5 c.c. of blood with an accuracy of 2×10^{-4} mg.

S. I. LEVY.

Silicic acid content of human blood and its variation after ingestion of silicic acid. H. KRAUT (Z. physiol. Chem., 1931, 194, 81—97).—The silica content of the ash from 23 samples of normal blood varies from 1.16 to 3.02%; the average value is about 1.7%. The mean value for 55 samples of blood from subjects with pulmonary tuberculosis is 1.99% (limiting values 1.07 and 4.02%). Administration of "silistren" (a glycol silicate), equivalent to 10 g. of SiO₂ during 4 weeks, to tubercular subjects causes, in about 80% of the cases, an increase in the silica content of the blood; the normal value is reached after 4 weeks. Inhalation of a solution of low-molecular silicic acid (Willstätter, Kraut, and Lobinger, A., 1929, 1251) during 4 weeks (=400 mg. of SiO₂) causes a considerable increase in the silica content of the blood, which is, in many cases, greater than the amount inhaled.

The silica content of the ash (from 5 c.c. of blood) is determined by repeated treatment of the ash with nitric and sulphuric acids, evaporation to dryness, and

incineration of the residue; the difference in weight when this is heated with hydrofluoric and sulphuric acids is determined. H. BURTON.

Toxicity of blood which has been frozen. W. A. OSBORNE (Austral. J. Exp. Biol., 1930, 7, 223—225).—Defibrinated blood taken from a dog produces toxic effects when injected into the same animal after having been twice frozen and thawed. The action is probably due to a protein liberated from the corpuscles and possibly denatured as the result of freezing and thawing. W. O. KERMACK.

Antitrypsin. I. Determination in serum. F. CHROMETZKA and W. KNOKE. **II. Nature.** F. CHROMETZKA (Z. ges. exp. Med., 1930, 69, 656—664, 665—678; Chem. Zentr., 1930, ii, 2143).—The viscosimetric and Willstätter's titration methods are equally good. The effects of reaction time, concentration of enzyme and substrate, and the p_H on the antitryptic action of serum have been investigated. The p_H curve shows in acid as well as in alkaline solutions an antitrypsin decomposition maximum which is independent of the isoelectric point of the serum-colloids, but coincides with a maximal increase in viscosity of the serum. The irreversible decomposition of antitrypsin is regarded as "swelling-denaturation." No change in solubility of the serum components was observed. A. A. ELDRIDGE.

Agglutination of cell suspensions. N. BEUMÉE-NEUWLAND (Chem. Weekblad, 1930, 27, 658—663). S. I. LEVY.

Antigenic properties of collagen and their variations under the influence of radium emanation. J. LOISELEUR and A. URBAIN (Compt. rend. Soc. Biol., 1930, 103, 776—778; Chem. Zentr., 1930, ii, 80).—Collagen from rats' tails, dissolved in dilute acetic acid, shows towards rabbits certain antigenic properties which are weakened by heating or by the action of radon. L. S. THEOBALD.

Toxicity of lungs in foetal life and its accelerating influence on blood coagulation. K. SAKURAI (Sei-i-kwai Med. J., 1930, 49, No. 1, 23—24).—The toxicity to rabbits and the coagulant power for dog's oxalated blood-plasma of a saline extract of foetal dog's lung are parallel, but the toxicity is only one eighth of that of adult lung.

CHEMICAL ABSTRACTS.

Influence of human placental extract on the blood coagulation of the rabbit. E. HORI and K. SAKURAI (Sei-i-kwai Med. J., 1930, 49, No. 2, 21—29).—Changes in the coagulability and composition of rabbit's blood after injection of different quantities of human placental extract are recorded.

CHEMICAL ABSTRACTS.

Toxicity of human placenta for rabbits, and its accelerating influence on coagulation of blood. Chemical nature. K. SAKURAI (Sei-i-kwai Med. J., 1929, 48, No. 12, 52—89).—The toxicity of the placental extract is parallel with its blood-coagulating power. Both activities are weakened or destroyed by oxidation, heat, proteolytic enzymes, and long exposure to air. The active principle is globulin-like in nature, but contains 1.226% P; it is not a

nucleo- or phospho-protein, and is considered to be tissue fibrinogen. CHEMICAL ABSTRACTS.

Determination of the time of coagulation of blood. H. LAMBERT (Münch. med. Woch., 1930, 77, 586—588; Chem. Zentr., 1930, ii, 80).—An alkali-free substance, "Athrombit," which strongly hinders coagulation and is suitable for the manufacture of instruments, is described. L. S. THEOBALD.

Sodium polyanetholesulphonate, a new preventive of blood-coagulation. V. DEMOLE and M. REINERT (Arch. exp. Path. Pharm., 1930, 158, 211—218).—The effect of sodium polyanetholesulphonate on blood-coagulation, blood-pressure, and respiration is described. Blood taken from a rabbit 1 hr. after injection of 15 mg. per kg. body-wt. does not coagulate in 24 hrs. It is suggested that prevention of coagulation is associated with the molecular size rather than with the chemical constitution of the preventive. A. COHEN.

Double refraction of myosin and its relation to the structure of the muscle fibre. A. L. VON MURALT and J. T. EDSALL (Trans. Faraday Soc., 1930, 26, 837—851).—Optical observations on a solution of muscle-globulin undergoing a shearing movement between crossed Nicols indicate that it consists of a monodisperse system of myosin particles of an ellipsoid or rod-like form. Denaturation causes disappearance of double refraction. The extract of muscle-globulin may also be obtained as a thixotropic gel. W. O. KERMACK.

Constituents of muscle extract of aquatic animals. III. Oyster. K. YOSHIMURA and K. NISHIDA (J. Agric. Chem. Soc. Japan, 1930, 6, 618—622).—Fresh oyster contained: water 84.27, crude protein 8.19, protein 5.33, water-soluble crude protein 3.16, water-soluble protein 0.31, crude fat 1.43, crude ash 1.71%. The following nitrogen compounds were isolated from 13 kg. of fresh muscle: trimethylamine chloraurate 1.40, adenine picrate 0.15, arginine nitrate 1.90, betaine hydrochloride 30.70, leucine 4.70, taurine 17.30, ammonium chloride 10.92 g.

CHEMICAL ABSTRACTS.

Choline in the uterus and its relation to labour. E. STRACK and A. LOESCHKE (Z. physiol. Chem., 1931, 194, 269—276).—Non-pregnant human uterus contains 47 mg. of choline per kg. of fresh organ. The uterus of the pig and cow contains about 160 mg. per kg. whether pregnant or non-pregnant. The placenta of the cow, after 5—6 months, contains only 90 mg. per kg. (cf. A., 1929, 1191). There appears to be no relation between the choline content of the uterus and labour.

H. BURTON.

Protein sulphuric ester from the mucous membrane of the stomach. H. MATHIS (Biochem. Z., 1930, 229, 263—264; cf. A., 1930, 945).—The constitution of protein sulphuric esters varies according to the organ from which they are derived. The compound obtained from the anterior part of the pituitary gland has the properties of a globulin, and of the nine sulphur atoms which it contains seven are present in sulphuric acid radicals and none in cystine radicals. None of the properties of a globulin is exhibited by the substance obtained from the liver,

and in this substance two of the three sulphur atoms occur in sulphuric acid radicals, whilst the third is not in a cystine radical. The ester extracted from the mucous membrane of the stomach contains 1.67—1.77% S, all of which forms part of sulphuric acid radicals.

W. MCCARTNEY.

Kephalin from human brain. II. Oxidation and purification of kephalin. I. H. PAGE and M. BÜLOW (Z. physiol. Chem., 1931, 194, 166—190).—Purification of kephalin by Fränkel and Neubauer's method (A., 1909, i, 870) gives an ash-free product; the yield is, however, only 50%. Ether-alcohol precipitation gives a product with a low iodine value, whilst precipitation of an aqueous emulsion with alcohol affords a sample with a higher iodine value. When kephalin is exposed to air for about 30 days, decreases in the carbon, hydrogen, and nitrogen content and the iodine value are found; the neutralisation value increases. These changes are largely obviated when the kephalin is kept under alcohol. The oxidation of solutions or suspensions of kephalin by air is accelerated by the addition of ferrous or ferric salts; the presence of acetic acid is not essential, as is the case with lecithin (cf. Warburg, A., 1913, i, 698).

H. BURTON.

Oxycholesterol and intermediary cholesterol metabolism. G. BISCHOFF (Z. ges. exp. Med., 1930, 70, 83—99; Chem. Zentr., 1930, ii, 2005).—Cholesterol and sitosterol, when heated in air above the m. p., give Lifschütz's oxycholesterol reaction. Cholesteryl oleate gives the reaction without previous hydrolysis. Oxycholesterol is formed when aqueous-alcoholic cholesterol is evaporated in air on a water-bath. Oxycholesterol was not obtained in absence of air from brain, blood, or egg-yolk.

A. A. ELDRIDGE.

Bromides of the highly unsaturated acids of cod-liver oil. I. DENISOV (Masloboino Zhir. Delo, 1929, No. 6, 31—34).—Determinations of the solubility and bromine content of the bromo-compounds indicate that the compounds insoluble in ether probably represent terpinic acid as octabromo-derivative. Linolenic acid is probably not present.

CHEMICAL ABSTRACTS.

Nature of the highly-unsaturated fatty acids in lard from pigs fed on menhaden oil. J. B. BROWN (J. Biol. Chem., 1931, 90, 133—139).—Feeding of pigs on a diet containing about 14% of menhaden oil results in an increase in unsaturation of the lipins and fatty acids of the livers, and the storage of 2.7% of highly-unsaturated acids in the lard. These highly-unsaturated acids, isolated as the polybromides of their methyl esters, are of approximately the same mol. wt., but are less unsaturated than those isolated in a similar manner from the original menhaden oil; the m. p. range of the methyl ester polybromides is similar in the two cases.

H. A. PIGGOTT.

Cystine and cysteine content of human hair. T. TADOKORO and H. UGAMI (J. Biochem., Japan, 1930, 12, 187—193).—The cystine content of the terminal portion of human hair is lower than that of other portions; it diminishes with age, although the cystine : nitrogen ratio remains constant. Black

hair contains more melanin than white; it also has a high cystine and low nitrogen content. The hair of young men contains more glutathione and has a higher cystine : cystine ratio than that of old men.

CHEMICAL ABSTRACTS.

Occurrence of lead in hen's eggs. W. B. S. BISHOP and T. COOKSEY (Med. J. Austral., 1929, 2, 660—662).—Lead (0.052—0.114 mg. per egg) was detected.

CHEMICAL ABSTRACTS.

Geographic location and iodine content of the thyroid gland. F. FENGER, R. H. ANDREW, and J. J. VOLLERTSEN (J. Amer. Chem. Soc., 1931, 53, 237—239).—The (yearly) average iodine content of desiccated, fat-free, pig-thyroid glands from N. Dakota is 0.32% (limits 0.13 and 0.53%), whilst for glands from Texas it is 0.60% (limits 0.44 and 0.78%).

H. BURTON.

Relative amounts of lysozyme present in the tissues of some mammals. H. FLOREY (Brit. J. Exp. Path., 1930, 11, 251—261).—In general the spleen, kidneys, and lungs are rich in lysozyme; skeletal muscle contains little or none. The amount present in the testis and brain is small. Rat tissue has a low content of the enzyme.

CHEMICAL ABSTRACTS.

Chemical nature of protein substances of living cells. O. LOEW (Protoplasma, 1930, 11, 196—209).—Evidence is advanced in support of the theory that protoplasm is built up from labile protein molecules which represent the initial stage of protein synthesis in plants. The labile form may be coagulated and yield the normal reserve protein of the tissues.

A. G. POLLARD.

Isoelectric point of cells and tissues. H. PFEIFFER (Trans. Faraday Soc., 1930, 26, 822—834).—A discussion of the conception of the isoelectric point of cell contents, with a review of methods used for its determination.

W. O. KERMAK.

Osmotic properties of living cells (eggs of *Arbacia punctulata*). M. McCUTCHEON, B. LUCKÉ, and H. K. HARTLINE (J. Gen. Physiol., 1931, 14, 393—403).—The Boyle-van 't Hoff law is followed reasonably accurately over wide variations in osmotic pressure by eggs of *Arbacia punctulata*, if allowance is made for osmotically inactive constituents, and the membrane is truly semipermeable.

P. G. MARSHALL.

Kinetics of osmosis in living cells. B. LUCKÉ, H. K. HARTLINE, and M. McCUTCHEON (J. Gen. Physiol., 1931, 14, 405—419).—The permeability of unfertilised eggs of *Arbacia punctulata* is independent of the osmotic pressure of the solution and is greater during exosmosis than during endosmosis at 15—21°.

P. G. MARSHALL.

"Hyrax," a new mounting medium for diatoms. G. D. HANNA (J. Roy. Microscop. Soc., 1930, 50, 424—426).—The properties of "hyrax," a synthetic naphthalene resin, n_D^{20} 1.82248, are described.

F. O. HOWITT.

The mucus of the gastric juice and its variations. D. R. WEBSTER (Trans. Roy. Soc. Canada, [iii], 1930, V, 24, 199—200).—Gastric juice obtained from dogs with a gastric fistula and oesophagotomy

was neutralised with sodium hydroxide, acidified with acetic acid, and 1–2 volumes of acetone were added, when a precipitate was obtained from which a substance was separated, apparently a monosodium salt of mucitimonosulphonic acid. The content of the mucin-like substance in the gastric juice varied inversely with the acidity, but directly with the concentration of total base and neutral chlorides. It was very scanty in histamine juice, but greatly increased by pilocarpine stimulation.

W. O. KERMACK.

Variations in the composition of the gastric juice under different conditions. B. P. BABKIN (Trans. Roy. Soc. Canada, 1930, [iii], 24, V, 201–205).—Experiments on dogs with a Heidenhain pouch (in which the parasympathetic nerves have been cut) show that “hormonal” stimulation (caused by the presence of food in the stomach and independent of nervous impulse) causes increase in the quantity and acidity of the juice, but not in content of organic substance (mucin-like material) or of enzyme, whilst injection of pilocarpine, which stimulates the parasympathetic, causes the formation of a juice rich in enzymes and organic substance. The quantity and acid content are in this latter case increased only in a minor degree.

W. O. KERMACK.

Gastric secretion in infants and children. A. V. NEALE (Arch. Dis. Childhood, 1930, 5, 137–145).—The effect of injection of histamine on the acidity is described.

CHEMICAL ABSTRACTS.

Acidity and chloride content of gastric juice. G. V. RUDD (Brit. J. Exp. Path., 1930, 11, 240–244).—Responses to meals of gruel and cream have been compared. Variations in composition of the gastric juice are due to changes in the amounts of hydrochloric acid and neutral chloride being secreted; the total chloride content remains approximately constant.

CHEMICAL ABSTRACTS.

Changes in composition of parotid saliva in the dog after section of the sympathetic nerve in the neck and after extirpation of the superior cervical sympathetic ganglion. H. BAXTER (Trans. Roy. Soc. Canada, 1930, [iii], 24, V, 207–211).

Digestive secretions of the larva of the Japanese beetle (*Popillia japonica*, Newm.). M. C. SWINGLE (J. Econ. Entom., 1930, 23, 956–958).—The presence of iron (ferrous), aluminium, calcium, magnesium, potassium, sodium, ammonium, carbonate, chloride, nitrite, and phosphate is recorded.

A. G. POLLARD.

Iron content of milks (human, cow, donkey, and goat). E. LESNÉ, R. CLEMENT, and P. ZIZINE (Bull. Soc. Chim. biol., 1930, 12, 1410–1413).—The milk (500 c.c.) is evaporated to a paste and then incinerated. The iron in the ash is determined by dissolving in hydrochloric acid, adding potassium permanganate solution until pink, and making alkaline with sodium hydroxide solution. After warming to remove traces of ammonia, the solution is made exactly neutral with hydrochloric acid and diluted to 40 c.c. The coloration produced by adding 5 c.c. of a 1% solution of alloxantin is compared with that produced by a standard solution of iron. It is shown

that the iron content is approximately the same in the milks of woman, cow, goat, and donkey.

B. LEVIN.

Determination of acids in urine. F. MAINZER and M. BRUHN (Biochem. Z., 1930, 229, 216–232).—A method is described by which the titratable acidity of urine can be determined while its content of carbon dioxide is kept constant. Although the magnitude of the titratable acidity of the urine is dependent on the pressure of carbon dioxide prevailing during the titration, this method gives satisfactory results with acid urines, and the errors arising in the case of alkaline urines can be corrected by calculation if the carbon dioxide content and its pressure are known. If the titratable acidity and the total carbon dioxide content are determined at the same pressure of carbon dioxide the value (titratable acidity + ammonia – hydrogen carbonate) is independent of the absolute value of the carbon dioxide pressure.

W. MCCARTNEY.

Detection of acetone and acetoacetic acid in urine. H. KAISER and E. WETZEL (Süddeut. Apoth.-Ztg., 1930, 70, 175–180; Chem. Zentr., 1930, ii, 2018–2019).—Normal urine is free from ketonic substances; when present, acetone and acetoacetic acid occur together. The nitroprusside reaction detects both. The Lorber-Fischer-Horkheimer iodoform reaction is the most trustworthy. Gerhardt's ferric chloride reaction is characteristic but insensitive. For the detection of acetoacetic acid Arréguine's improved method is free from objection. Colorimetric methods for the determination of acetone substances are inaccurate.

A. A. ELDRIDGE.

Acetoacetic acid in the organism. H. KAISER, E. WETZEL, and D. BEISCHER (Süddeut. Apoth.-Ztg., 1930, 70, 152–153; Chem. Zentr., 1930, ii, 2018).—Saturation of a solution of sodium acetoacetate (Emden and Michaud) with sodium chloride affords the solid salt, which in solution is much more stable than the free acid. Methods of detection are discussed.

A. A. ELDRIDGE.

Origin of urobilinogen. I. M. RABINOWITCH (Arch. Int. Med., 1930, 46, 1014–1017).—Removal of blood from a human ovarian cyst caused an excessive urobilinogen content of the urine to become normal. Since this blood was sterile, it is suggested that urobilinogen may be formed not only extraintestinally, but also in the absence of reducing bacteria.

A. COHEN.

Urine containing bile pigment. H. SZANCER (Süddeut. Apoth.-Ztg., 1930, 70, 262; Chem. Zentr., 1930, ii, 1895).—The reactions of an icterous urine containing bile pigment and 3% of dextrose are described. Bilirubin appears to be easily oxidisable, a fact which may lead to error owing to the production of a green colour with reagents for protein or aldehyde.

A. A. ELDRIDGE.

Determination of bile acids. **Cholaluria.** C. L. DUCCO and P. T. PANZA (Semana méd., 1930, 37, 1193–1198; Chem. Zentr., 1930, ii, 1893).—The surface tension of a solution, brought to the isoelectric point with 1% phosphoric acid, is determined before and after removal of the bile acids by means

of animal charcoal. The depressant effect on the surface tension of balsamic substances is independent of the acidity; hence these can be distinguished from bile acids by determination of the surface tension before and after acidification. Determinations of bile acids in urine and duodenal juice were made. Salts of bile acids are normally excreted in the urine, which contains 0.10–0.25 g. per litre, calculated as sodium glycocholate. A. A. ELDRIDGE.

Microscopical studies in pernicious anæmia. I. W. E. COOKE and C. F. HILL (J. Roy. Micros. Soc., 1930, 50, 427–432).—An investigation of the histology of the erythroblasts and erythrocytes in pernicious anæmia. F. O. HOWITT.

Effect of muscular exercise in beriberi. III. Oxygen debt, oxygen requirement, and changes in respiratory quotient, respiratory volume, and carbon dioxide output. E. HAYASAKA and R. INAWASHIRO. **IV. Intermediate water exchange. V. Lactic acid metabolism.** E. HAYASAKA (Tôhoku J. Exp. Med., 1930, 14, 53–71, 72–84, 85–92). CHEMICAL ABSTRACTS.

Relation of vitamins to carcinogenesis. W. NAKAHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 15, 32–36).—There is no satisfactory evidence supporting the view that vitamin-A deficiency or excessive administration of vitamin-D is conducive to the development of cancer. W. O. KERMACK.

Effect of testicle extract and normal serum on the growth of a transplantable epithelial tumour of the rabbit. F. D. REYNALS (Science, 1930, 72, 608–609).—Testicle extract inhibited, whilst normal rabbit serum promoted, growth. L. S. THEOBALD.

Mechanism of enhancement of infections by testicle extract. D. C. HOFFMAN and F. D. REYNALS (Science, 1930, 72, 508).—An inert substance such as India ink spreads to a greater extent in the skin of rabbits when mixed with testicle extract and intracutaneously injected. Kidney and spleen extracts also increase spreading, but rat and rabbit sera are without effect on the diffusion of the ink. An increased permeability of the host cells also appears to be an effect of the enhancing extract. The enhancing activity of testicle extract is destroyed by heating at 60° for 30 min. L. S. THEOBALD.

Increase of the blood-phenol and -phenol derivatives and the appearance of free phenol in the blood in cirrhosis of the liver. E. BECHNER (Münch. med. Woch., 1930, 77, 751–752; Chem. Zentr., 1930, ii, 79).—A moderate increase in blood-phenol could be detected in many cases of cirrhosis; the appearance of free phenol is also noteworthy. Disturbances in the detoxication of intestinal poison must take place accordingly in cirrhosis. L. S. THEOBALD.

Acceleration of blood coagulation by eclampsia urine. K. SAKURAI (Sei-i-kwai Med. J., 1930, 49, No. 4, 27–37).—Urea, uric acid, creatinine, and hippuric acid do not accelerate blood coagulation. Urine of eclampsia accelerates coagulation, whilst that of pregnant women excreting a large amount of albumin does not contain a coagulant. CHEMICAL ABSTRACTS.

Urobilin and bilirubin in the blood and urine in leprosy. E. A. MOLINELLI and M. ROYER (Compt. rend. Soc. Biol., 1929, 102, 873; Chem. Zentr., 1930, ii, 79).—Urinary urobilin is normal in leprosy. Blood bilirubin is not increased; urobilin is not present in the blood. L. S. THEOBALD.

Post-operative blood chemistry. E. ANDREWS and K. REUTERSKIÖLD (Ann. Surg., 1930, 92, 786–799).—After operation no significant changes were found in the blood-sugar, -water, -chloride, or -carbon dioxide. The permeability of the skin was increased. Profound changes occur in the mineral salt balance, the potassium:calcium ratio often falling below unity. CHEMICAL ABSTRACTS.

Acid-base equilibrium in man after removal of the stomach. P. A. ASHMARIN and E. E. MARTINSON (Ark. Biol. Nauk, 1928, 28, 399–417).—Abrupt and relatively great changes in the p_H of the urine with changes in the acidity of the diet were observed; they are attributed to retention of bases and to excretion of bases through the intestinal tract. For low p_H values, urinary $A-B=NH_3+F-K$; for all p_H values $A-B=NH_3+R-K$, where A =inorganic acid, B =inorganic bases, F =total titratable acidity, K =organic acids with correction for amino-acids and creatinine, and R =titratable acids less hydrogen carbonate and free carbon dioxide. CHEMICAL ABSTRACTS.

Acid-base equilibrium of peptic ulcer. R. STERN (Arch. exp. Path. Pharm., 1930, 158, 108–115).—Peptic ulcer was treated (orally) with an alkaline preparation on a protein-deficient diet. In a small proportion of cases the urine was readily alkalisied. In most cases, however, a p_H of 7.0 was only temporarily observed after several days of continuous treatment, the response resembling that of cases of acid urine without ulcer. A. COHEN.

Effect of parathyroidectomy on the formation of ethereal sulphates in dogs. V. E. STEFANOVICH (Ark. Biol. Nauk, 1928, 28, 291–295).—Extirpation of parathyroid or thyroid of dogs with gastric fistula resulted in augmented ethereal sulphate conjugation, whilst complete thyroparathyroidectomy caused great diminution in this synthesis. Administration of calcium stimulated indirectly the activity of the liver. Lowering of the blood-calcium did not always diminish ethereal sulphate synthesis. Complete extirpation did not disturb the synthesis in dogs which fasted before and after the operation. CHEMICAL ABSTRACTS.

Parathyroid and fluoro-hypocalcæmia. R. GERSCHMANN (Compt. rend. Soc. Biol., 1930, 104, 411–412; Ann. farm. bioquim., 1930, 1, 77–84; Chem. Zentr., 1930, ii, 1870).—With thyroparathyrectomised dogs the hypocalcæmia following intravenous injection of sodium fluoride sets in more rapidly and remains at the minimal value; with normal dogs the original value was not reached after 24 hrs. A. A. ELDRIDGE.

Parathyroid and hypocalcæmia. R. GERSCHMANN (Compt. rend. Soc. Biol., 1930, 104, 413–414; Ann. farm. bioquim., 1930, 1, 85–88; Chem. Zentr., 1930, ii, 1870).—The blood-calcium curve of thyroparathyrectomised dogs after intravenous injection

of calcium chloride is similar to, but at a lower level than, that of normal dogs given a similar injection.

A. A. ELDRIDGE.

Derangement, during disease, of the mechanism regulating the mineral metabolism of cattle. B. SJÖLEMA and L. SEEKLES (Biochem. Z., 1930, 229, 358—380; cf. A., 1928, 1395).—The mineral content of the blood-serum of cows suffering from parturient paresis or grass staggers has been examined. It has been found that, especially as regards the quantities of magnesium, total calcium, diffusible calcium, and inorganic phosphorus, great differences are exhibited between the diseased and healthy animals and between animals suffering from one disease and those suffering from the other. Differences were also found in the ratios between the different mineral constituents as well as between the different forms in which they were present. Generalisations regarding the connexion between the mineral contents of the blood and the symptoms of the diseases cannot be given, although from knowledge of these contents diagnoses can be made.

W. MCCARTNEY.

Serum-calcium in pneumoconiosis. M. J. SOKOLOFF and A. CANTAROW (Amer. Rev. Tuberculosis, 1930, 22, 449—454).—The serum-calcium (7.98—14.81 mg. per 100 c.c.) was high in 26 of 31 cases; the value is not related to the incidence or activity of the complicating tuberculous process.

CHEMICAL ABSTRACTS.

Serum-proteins in the toxæmias of pregnancy. N. J. EASTMAN (Amer. J. Obstet. Gyn., 1930, 19, 343—351).—Variations in the serum-protein during gestation and the toxæmias of pregnancy tend towards a decrease in total protein, associated with a slight relative increase in globulin in normal pregnancy and a more marked increase in pre-eclampsia and eclampsia. The average albumin:globulin ratio is: normal 1.7, pregnant 1.6, eclampsia and pre-eclampsia 1.3.

CHEMICAL ABSTRACTS.

Gastric juice in pregnancy. F. ARZT (Amer. J. Obstet. Gyn., 1930, 20, 382—385).—In pregnancy the free hydrochloric acid and total acidity of the stomach are low.

CHEMICAL ABSTRACTS.

Relation between phosphorus, chloride, and hydrogen carbonate in the serum of rachitic and normal rabbits. B. HAMILTON, L. KAJDI, and D. MEEKER (Bull. Johns Hopkins Hosp., 1930, 47, 215—220).—In both cases the serum-phosphorus varies in the opposite direction to the sum of chloride and hydrogen carbonate.

CHEMICAL ABSTRACTS.

Absorption spectrum of blood and its relation to rickets. R. SUHRMANN and W. KOLLATH (Naturwiss., 1931, 19, 65—66).—The failure to confirm the work of the authors on a difference in absorption between blood-cell solutions of normal and rachitic rats by Gibbs, Johnson, and Shapiro (A., 1930, 1311) is explained as due to the use of a different diet either normally or during the breeding period.

F. O. HOWITT.

Maize component of a rachitogenic diet. R. S. HARRIS and J. W. M. BUNKER (Science, 1931, 73, 95).—Storage of ground maize meal for six months

ensures the development of a definite rachitic condition in white rats, without unduly restricting growth.

L. S. THEOBALD.

Chloride and water content of striped muscle, liver, and kidney tissue in experimental scurvy. L. RANDOIN and A. MICHAUX (Compt. rend., 1931, 192, 108—110).—The rise in percentage of chloride and water in the liver and kidney tissue of guinea-pigs deprived of vitamin-C, minimal at first, increases as death approaches, although the total amounts of both these constituents remain constant. On the other hand, muscle-chloride may rise from 0.50 g. to 1.67 g. per kg. on a completely vitamin-free diet and may exceed 1 g. per kg. even when the latter is devoid of chloride.

P. G. MARSHALL.

Artificial toothache in rabbits. I. Influence on blood-sugar. T. NAGIRA and S. NOGUCHI. **II. Sedative action of reagents on the pulp.** T. NAGIRA and T. YAO (Folia Pharmacol. Japon., 1930, 9, No. 4, 262—272, 273—281).—Moderate electrical stimulus of the pulp produced an increase in blood-sugar which decreased after double splanchnectomy. Secretion of adrenaline was increased. Sedative action was exhibited, in decreasing degree, by phenol, clove oil, menthol, and cineole.

CHEMICAL ABSTRACTS.

Chemical alterations in the blood of rats infected with pathogenic and non-pathogenic trypanosomes. R. W. LINTON (J. Exp. Med., 1930, 52, 695—700).—Blood of rats infected with *Trypanosoma Lewisii* gives normal values for lipid phosphorus, lecithin, and carbon dioxide-combining capacity; the liver-glycogen also is normal. *T. equiperdum* is injurious to the host.

CHEMICAL ABSTRACTS.

Effect of oral administration of irradiated ergosterol on blood serum-calcium in pulmonary tuberculosis. J. KAMINSKY and D. L. DAVIDSON (Amer. Rev. Tuberculosis, 1930, 22, 48—52).—Ingestion of "viosterol" was followed by a considerable, and sometimes persistent, rise in serum-calcium.

CHEMICAL ABSTRACTS.

Blood-phosphorus in health and disease. V. Composition of the reticulocyte. H. D. KAY (Brit. J. Exp. Path., 1930, 11, 148—152).—In diseases involving a high percentage of reticulocytes small quantities of nucleic acid-phosphorus, approximately proportional to the reticulocytosis, have been detected.

CHEMICAL ABSTRACTS.

Action of ultra-violet radiation on the protein fraction of blood-plasma *in vitro*. L. KOSTYÁL (Biochem. Z., 1930, 229, 100—108).—When blood-plasma taken from persons suffering from various diseases is irradiated with a quartz lamp, alterations, which vary according to the nature of the disease, take place in the rate at which red corpuscles sink in such plasma. An explanation of the changes is suggested.

W. MCCARTNEY.

Structure, behaviour, and physiological characteristics of vertebrate cells cultivated *in vitro*. H. B. FELL and E. N. WILLMER (Trans. Faraday Soc., 1930, 26, 772—778).—A review of the factors determining the uncontrolled growth of tissues *in vitro*.

W. O. KERMAK.

Surface structure in the integration of cell activity. R. A. PETERS (Trans. Faraday Soc., 1930, 26, 797—807).—A general theory of the structure and activity in the living cell is sketched, emphasis being laid on the importance of the molecular constitution and orientation of interfaces.

W. O. KERMACK.

Membrane-phenomena in living matter: equilibrium or steady state. A. V. HILL (Trans. Faraday Soc., 1930, 26, 667—673).—The osmotic pressure of the white and yolk of the hen's egg has been determined by the thermo-vapour pressure method of the author (cf. A., 1930, 1211). The difference of osmotic pressure between the white and the yolk in the one-day-old egg corresponds with 0.26—0.29% sodium chloride and on keeping in air it gradually declines, in agreement with the results of Straub (A., 1929, 264). Very similar results are obtained when the eggs are kept in an atmosphere of hydrogen, so that the energy which is required for the maintenance of the difference of osmotic pressure is presumably not derived from oxidation processes. It is argued that the concentration differences inside and outside living cells and the electric potentials which exist across cell membranes are not equilibrium conditions, but are presumably sustained by chemical reactions proceeding in the cell or at its membrane.

W. O. KERMACK.

Kinetics of living matter. E. FAURÉ-FREMIET (Trans. Faraday Soc., 1930, 26, 779—793).—A discussion of the formation of pseudopodia and the motility of cells and the relation of these to the physico-chemical properties of the protoplasm.

W. O. KERMACK.

Oxidative nature of the nerve impulse. F. O. SCHMITT (Science, 1930, 72, 583—584).—Sodium cyanide can completely inhibit nerve respiration; in 0.001*N*-sodium cyanide inhibition is complete for only an hour or so, and then falls to a residual amount, whilst in 0.1*N*-solution inhibition is practically constant at 80—95%. Nerve respiration can also be inhibited more or less completely by carbon monoxide in the dark, but illumination of the nerve weakens inhibition of the resting metabolism. Action potential is produced by an oxidation of a substance or substances in nerve and a respiratory enzyme containing iron appears to be essential.

L. S. THEOBALD.

Conditions of metabolism affecting change of sex. P. JOYET-LAVERGNE (Compt. rend., 1931, 192, 180—182).—When the germinal cells of the male are subjected to an environment where their fat metabolism is higher, they give rise to ova. Conversely, when female germinal cells are subjected to conditions producing a rise in general metabolism and a lowering of the reducing power of the tissues, they give rise to spermatozoa.

P. G. MARSHALL.

Relationship between electrical differences of potential in the skin and normal basal metabolism. C. PURDY, A. F. JOHNSON, and C. SHEARD (Science, 1931, 73, 46—49).—Electrical potential in the skin of normal persons has been correlated with basal metabolism. Higher basal metabolic rates are accompanied by smaller *P.D.* and *vice versa*.

L. S. THEOBALD.

Relation of the calcium : phosphorus ratio to calcification. R. M. BETHKE, C. H. KICK, and O. H. M. WILDER (Ohio Agric. Exp. Sta. Bull., 1930, No. 446, 147).—Experiments with rats indicate that, within certain limits, the ratio of calcium to phosphorus in the ration is of greater significance in calcification than the concentration of these elements. The degree of calcification is directly proportional to the Ca : P ratio. Wider Ca : P ratios are associated with greater requirements for vitamin-D.

A. G. POLLARD.

Relationship in the hen between the development of ova, blood-calcium, and the antirachitic factor. W. C. RUSSELL, C. H. HOWARD, and A. F. HESS (Science, 1930, 72, 506—507).—The presence of large ova and high blood-calcium does not always indicate active egg production. The antirachitic factor may not be the essential factor in the development of ova or in causing high blood-calcium.

L. S. THEOBALD.

Utilisation of milk and inorganic calcium and phosphorus. M. T. POTTER and M. M. KRAMER (J. Home Econ., 1930, 22, 923—924).—In periods in which milk furnished most of the calcium, or in which chiefly inorganic calcium and phosphorus were administered, the calcium and phosphorus were retained equally well.

CHEMICAL ABSTRACTS.

Relation between ovarian function and mineral content of blood. A. SCHEPETINSKY and M. KAFITIN (Arch. Gynäk., 1929, 136, 397—406; Chem. Zentr., 1930, ii, 1387).—During menstruation the blood-calcium of normal women varies only between 11 and 14 mg. per 100 c.c.; in the premenstrual period the value is slightly high. The blood-potassium, -sodium, and -chlorine diminish during menstruation, whilst the inorganic phosphorus shows little change.

A. A. ELDRIDGE.

Ovarian function and lipid metabolism. I. Relation between cholesterol metabolism and ovarian function. II. Relation between lecithin metabolism and ovarian function. III. Distribution of blood-cholesterol between free and esterified cholesterol in various functional phases of the generative gland. Total blood-fatty acid in regular, irregular, and absence of, ovarian function. C. KAUFMANN and O. MÜHLBOCK (Arch. Gynäk., 1928, 134, 603—625; 1929, 136, 478—502; 1929, 139, 254—277; Chem. Zentr., 1930, ii, 1386—1387).—I. Women's blood-serum normally contains 125 mg. of cholesterol per 100 c.c. During menstruation values down to 41% of the average are observed; this fall is preceded by an increase which may reach 50%. In disturbance of the ovarian function a fall was also observed; it was independent of the loss of blood.

II. The lecithin content is 234 mg. per 100 c.c., and is normally not subject to regular variation during various periods of the cycle.

III. The fall in blood-cholesterol during menstruation is due to a fall in free cholesterol; 85—90% of the cholesterol is then esterified, instead of about 70%. An increase in blood-total fatty acid was observed during normal menstruation.

A. A. ELDRIDGE.

Auriculo-ventricular junctional system of the heart. II. Metabolic activity. III. Phosphatide and cholesterol content. IV. Anaërobic oxidation. K. YAMAZAKI (J. Biochem., Japan, 1930, 12, 223—234).—The junction has a higher dehydrogenase and oxidase activity, but a lower sulphydryl content, than the rest of the heart muscle. The Tawara bundle of the ox heart contains less phosphatide than the heart muscle. It is resistant to cyanide, still consuming oxygen when poisoned with 0.0004*M*-potassium cyanide.

CHEMICAL ABSTRACTS.

Rôle of the spleen in genesis of bilirubin and cholesterol. D. ANTIĆ and D. BORIĆ (Z. ges. exp. Med., 1930, 70, 658—665; Chem. Zentr., 1930, ii, 2153).—With rabbits extirpation of the spleen caused a fall in bilirubin and a rise in cholesterol and erythrocyte number. Similar results were obtained in a case of hæmolytic icterus after splenectomy.

A. A. ELDRIDGE.

Effect of consumption of various foods on the amount of multiply unsaturated acids in the blood. N. BEREND (Biochem. Z., 1930, 229, 323—328).—The amount of multiply unsaturated acids in the blood of dogs first decreases then increases if they are fed on fat. If carbohydrate is given with the fat the initial decrease does not occur. No change takes place in the content of multiply unsaturated acids as a result of feeding with carbohydrate alone or with protein alone.

W. MCCARTNEY.

Protein [feeding] studies. A. E. PERKINS (Ohio Agric. Exp. Sta. Bull., 1930, No. 446, 115—116).—Comparison is made of the composition of the blood, milk, and urine of cows receiving high-protein and low-protein rations. The urea contents of blood and urine during high-protein feeding averaged respectively 15 and 300 times those during low-protein feeding. Little difference was apparent in routine tests of milk in the two cases, but a closer examination of the non-protein-nitrogen showed a close agreement between the proportions of these constituents in the blood and milk of the respective animals. Of the non-protein-nitrogen group of substances only the proportions of urea and ammonia were markedly and consistently affected by differences in the ration.

A. G. POLLARD.

Nutritive value of blood-meal protein for growth. A. R. WINTER (Ohio Agric. Exp. Sta. Bull., 1929, No. 436, 42 pp.).—The palatability of blood-meal is low and in general controls its nutritive value. The digestibility of blood-meal decreases with fall of temperature used in preparation. The biological value of the protein is low. The basic amino-acids occur in approximately the same amounts as in caseinogen. Pig's blood has a greater nutritive value than sheep's blood and the serum a higher value than the clot. Blood-meal is not toxic, and is satisfactorily supplemented by caseinogen or maize gluten.

A. G. POLLARD.

Nutritive value of benniseed (*Sesamum indicum*). W. E. McCULLOCH (Nature, 1931, 127, 199—200).—Analyses of seed grown in the Benue Province gave the following relative percentages: oil 52.6, protein 23.4, ash 4.0, CaO 1.2, P₂O₅ 1.39.

The plant appears to exercise a strong selective absorptive power for calcium. L. S. THEOBALD.

Increase of hepatic proteins with a diet of a mixture of amino-acids, butter-fat, and dextrose. C. GAUTIER (Bull. Soc. Chim. biol., 1930, 12, 1382—1391; cf. A., 1928, 792).—By comparing the weight of the right lobes of the livers removed from frogs with the weight of the left lobes and remaining portions of the liver after feeding the same animals for some weeks on a diet composed of a mixture of amino-acids, butter-fat, dextrose, vitamins, and saline mixture, it is found that the weight of the liver is greatly increased, and the total amount of protein is increased, although the proportion of protein is less. The weight of the liver is increased twice in proportion to that of the total amount of protein.

B. LEVIN.

Tryptophan and histidine are anabolic substances. G. FONTÈS and L. THIVOLLE (Compt. rend., 1931, 192, 63—65).—Subcutaneous injection of 100 mg. of tryptophan per day into dogs fed on a constant diet causes a marked increase in weight. Histidine (200 mg. per day) is without effect, but simultaneous injection of the same quantities of these amino-acids causes a greater increase in weight than tryptophan alone, and a distinct decrease in urinary nitrogen. It is concluded that these amino-acids aid assimilatory processes, particularly those affecting nitrogen metabolism.

A. COHEN.

New function of the stomach. Rôle of this organ in the metabolism of carbamide. R. VLADESCO, D. SIMCI, and M. POPESCO (Compt. rend., 1931, 192, 308—310).—In normal metabolism the stomach removes a portion of the carbamide from the blood and passes this into its contents in the form of ammonia. Carbamide (60 c.c. of a 2.5% solution) was injected into the jugular vein of a dog, previously anæsthetised with chloralose, followed by a histamine injection to increase gastric secretion, and the amount of carbamide in the blood, and of ammonia in the gastric juice, determined at intervals. The former rapidly decreases, a corresponding increase in the ammonia content being observed. Similar results are obtained when a carbamide solution is kept with gastric juice (dog) *in vitro* at 37°. J. W. BAKER.

Nitrogen metabolism of children. J. P. PARSONS (Amer. J. Dis. Children, 1930, 39, 1221—1239).—Normal children, 4—8 yrs. old, and diabetic children receiving insulin may maintain a positive nitrogen balance on 1.1 or 2.2 g. of protein per kg., respectively. An isodynamic equivalent of carbohydrate or fat must replace the protein withdrawn in order to maintain nitrogen balance on a minimum protein intake.

CHEMICAL ABSTRACTS.

Sulphur compounds in the organism of the dog. I. Action and fate of thiophen in the metabolism of the dog. A. A. CHRISTOMANOS (Biochem. Z., 1930, 229, 248—254).—Of the total amount of thiophen subcutaneously administered to dogs up to 12% is excreted in the combined form in the urine and part of the remainder may be converted in the organism into ethyl sulphide. Thiophen has no inhibitory effect on the nitrogen metabolism.

A modification of the process of Fletcher and Hopkins for the determination of lactic acid (A., 1907, ii, 373) can be used for the colorimetric determination of 0.07—7.0 mg. of thiophen. W. McCARTNEY.

Elimination of phosphoric acid from adenylic acid in muscular contraction. G. EMBDEN and M. LEHNARTZ (Klin. Woch., 1930, 9, 937; Chem. Zentr., 1930, ii, 2154).—At the moment of contraction adenylic acid liberates phosphoric acid. The increase in the non-pentose-phosphoric acid observed immediately after fatiguing stimulation is followed by a much greater increase in this pentose fraction after 2 hrs. A. A. ELDRIDGE.

Caloric quotient of lactic acid in muscle. O. MEYERHOF, R. McCULLAGH, and W. SCHULZ (Pflüger's Archiv, 1930, 224, 230—248; Chem. Zentr., 1930, ii, 1722).—The following new determinations ($\pm 10\%$) of the caloric quotient (g.-cal. per g. of lactic acid formed anaerobically in muscle) are recorded: up to the beginning of fatigue 360—395; in progressive anaerobiosis without effusion of lactic acid from muscle 345; during effusion 300; in caffeine rigor 280; in minced muscle up to the formation of 0.5—0.7% of lactic acid 300; with passage of lactic acid into phosphate solution 240. A. A. ELDRIDGE.

Toxicity of *dl*-lactic acid and extent to which it can be assimilated. O. FURTH and P. ENGEL (Biochem. Z., 1930, 229, 381—396).—The most satisfactory method for the determination of lactic acid in urine is that of Ishihara (A., 1913, ii, 536). In man, when *dl*-lactic acid is administered 20—30% of it is excreted in the urine. In rabbits, the toxic effect of the acid, especially when orally administered, is high. The toxicity to mice is not so pronounced, and rats tolerate very large doses. Neither the assimilation of the acid nor its toxic effects are affected by administration of sodium carbonate, adrenaline, phloridzin, or dextrose. In rabbits non-fatal phosphorus poisoning causes excessive excretion of lactic acid, but after recovery the power to assimilate the acid is temporarily increased. In rats to which over-doses of lactate are administered no storage of lactic acid or of its precursors takes place. As regards their catalytic oxidation with active charcoal, there is no difference between *d*- and *l*-lactic acids. It is concluded that *dl*-lactic acid is not a completely assimilable or useful food. W. McCARTNEY.

Lactacidogen in intermediary metabolism. A. Y. KHARIT (Arch. Biol. Nauk, 1929, 29, 443—454).—The blood-lactacidogen of man, dog, and rabbit is of the same order of magnitude as the muscle-lactacidogen. Evidence of lactacidogen synthesis in the intestinal wall and lungs is adduced. Carbohydrate feeding and increased blood-sugar do not raise the blood-lactacidogen. The lactacidogen-phosphorus is found in the acid-soluble fraction of the blood-phosphorus. CHEMICAL ABSTRACTS.

Glycogen storage in the white rat when fed on the roots of *Arctium lappa*. J. C. KRANTZ, jun., and C. J. CARR (J. Pharm. Exp. Ther., 1931, 41, 83—87).—The addition of the dry powdered root of *A. lappa* (containing 50—70% of carbohydrate yielding laevulose on hydrolysis) to the basal diet (cacao

butter) of white rats results in an increase of glycogen in the liver to 5—6 times the amount found in controls. An increase is also caused by the addition to the basal diet of the pure carbohydrate isolated from the roots.

W. O. KERMACK.

Action of maltose on the metabolism and anabolism of infants. M. STEUBER and A. SEIFERT (Arch. Kinderheilkunde, 1930, 87, 192—207; Chem. Zentr., 1930, ii, 85).—The increase in weight of children was always less with successive increased administration of dextrose and equicaloric lowering of fat. The effect of the increased carbohydrate dose on digestion manifested itself only in a slightly lower consumption of nitrogen and mineral substances. The retention of nitrogen and of inorganic material was essentially less, but the heat production per unit area was unaffected. Fat synthesis from dextrose was not detectable. L. S. THEOBALD.

Significance of bile acids in carbohydrate metabolism. VIII. Mechanism of the hypoglycæmic action of bile acids. K. TSUJI (J. Biochem., Japan, 1930, 12, 139—160).—The hypoglycæmic effect of the administration to rabbits of bile acids is probably due to paralysis of the sympathetic. The effect is increased by potassium ions.

CHEMICAL ABSTRACTS.

Morphological basis for certain tissue resistance. W. DEB. MACNIDER (Science, 1931, 73, 103—105).—Subcutaneous injection of a solution of uranium nitrate (2—4 mg. per kg.) results in an initial increase in the formation of urine, which is albuminous, a decrease in elimination of phenolsulphonephthalein, a reduction in reserve alkali of the blood, and an initial retention of blood-carbamide and -non-protein-nitrogen followed by retention of creatinine. The morphological changes are described.

L. S. THEOBALD.

Action of magnesium chloride on the respiration and contractility of the frog ventricle. J. LEIBOWITZ and A. SCHWEITZER (Biochem. Z., 1930, 229, 291—295; A., 1930, 1613).—At the end of the season of the year at which the frog's heart exhibits hypersensitivity towards the action of magnesium salts the gradually decreasing inhibitory effect which these have on the contractility of the organ runs parallel with their inhibitory effect on the respiration of the tissues. The inhibitory effect of low concentrations of magnesium chloride on biological oxidation in the frog can be observed, in summer, in the heart tissue but not in the liver tissue.

W. McCARTNEY.

Action of intracerebral injection of calcium, magnesium, strontium, barium, potassium, and sodium ions. M. CLOETTA and H. FISCHER (Arch. exp. Path. Pharm., 1930, 158, 254—281).—Typical phenomena of sleep may be induced in rats, cats, dogs, and rabbits by injecting 0.05—1.5 mg. of calcium chloride into a sharply-defined area of the infundibular region of the brain. The effect of magnesium is indefinite, but, in higher doses, is similar to that of calcium. Strontium produces non-characteristic symptoms of paralysis and stimulation associated with toxic effects. The barium ion is highly toxic, causing intense stimulation on injection into any part

of the brain. Potassium chloride has a stimulant effect which may be suppressed by calcium chloride. Hypertonic solutions (3—4%) of sodium chloride cause slight stimulation which may not be a specific effect of the sodium ion. A. COHEN.

Deposition of gold and lead in the organism. V. HENRIQUES and H. OKKELS (Pflüger's Archiv, 1930, 225, 364—371; Chem. Zentr., 1930, ii, 1876).—The colloidal metals are selectively deposited in the reticuloendothelial apparatus and complex compounds in the parenchyma cells; differential deposition is observed in the latter case. A. A. ELDRIDGE.

Acute toxicity of glyceryl trinitrate and sodium nitrite in rabbits. T. V. OLTMAN and L. A. CRANDALL, jun. (J. Pharm. Exp. Ther., 1931, 41, 121—126).—The minimum lethal doses of glyceryl trinitrate and of sodium nitrite administered intravenously to adult rabbits are 45 mg. and 80—90 mg. per kg., respectively. Asphyxia is probably one of the main causes of death from lethal doses of these compounds. W. O. KERMAK.

Relative toxicities of some organic salts of triethyl lead hydroxide. H. GILMAN and O. M. GRUHZIT (J. Pharm. Exp. Ther., 1931, 41, 1—4).—The minimum toxic and lethal doses of the triethyl lead hydroxide salts of salicylic, *p*-toluenesulphonic, phenylacetic, furoic, *p*-aminobenzoic, furylacrylic, and phosphoric acids (cf. Gilman and Robinson, A., 1930, 1277) have been determined on rats and rabbits. They are all highly toxic with marked action on the mucous membranes and the nervous system. W. O. KERMAK.

Mercurial chemotherapy. I. Mercurial toxicity, its evaluation, mechanism, and relation to chemical constitution. II. Quantitative evaluation of mercurial diuresis and its relation to chemical constitution. E. FOURNEAU and K. I. MELVILLE (J. Pharm. Exp. Ther., 1931, 41, 21—45, 47—64).—I. The toxic action on rabbits of four groups of mercury compounds injected intravenously has been investigated: (1) inorganic salts of mercury, (2) compounds of the formula $\text{Ar}\cdot\text{Hg}\cdot\text{OH}$, (3) compounds of the formula $\text{R}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{Hg}\cdot\text{OH}$, (4) compounds of the formula $\text{Hg}(\text{S}\cdot\text{CS}\cdot\text{R})_2$. The water intake has a marked influence in decreasing the toxicity of mercury compounds only when administered by the mouth, and not when injected subcutaneously. The "minimum toxic dose" is defined as that weight of substance in g. per kg. of rabbit which, when injected intravenously into animals kept on a "basal water-free diet," leads to progressive emaciation and death in 7—14 days. The toxic action is diminished if the diuresis is controlled by the administration of a posterior pituitary extract. Of the compounds studied those belonging to the first group are the most toxic, the minimal toxic dose varying from 1.5 to 2.1 mg. of mercury. The compounds belonging to group (4) are almost equally toxic, although the mercury in these compounds is not precipitated by hydrogen sulphide. Compounds of group (2) are less toxic, the M.T.D. varying from 6.78 to 9.60 mg. of mercury, whilst compounds of group (3) have a M.T.D. from 3.1 to 4.68 mg. of mercury. D D

II. A method has been elaborated for evaluating the diuretic activity of mercury compounds injected intravenously into rabbits, based on the chemotherapeutic coefficient (*i.e.*, the ratio of minimum dose active diuretically to the minimum toxic dose) and the maximum increase of diuresis produced in rabbits kept under certain specific conditions of water elimination. Solubility appears to play an important rôle in determining the activity. W. O. KERMAK.

Influence of diuretics on calcium excretion. M. RACHMILEWITZ and E. STRANSKY (Arch. exp. Path. Pharm., 1930, 158, 129—153).—The low calcium excretion of normal rabbits fed on oats is not affected by sodium sulphate, sodium acetate, or "salyrgan" given orally, and is slightly diminished by potassium acetate. Drinking water causes a small indefinite increase, and the rise caused by caffeine or sodium chloride (*per os*) is slow and protracted. Simultaneous administration of the last two exerts greater diuretic effect without increasing calcium excretion. Calcium gluconate is without effect on the normal diuresis and on the action of repeated administration of caffeine. A. COHEN.

Appearance of protein in bile. T. MATSUDA (Japan. J. Gastroenterol., 1930, 2, 130—147).—Injury of the liver mechanically, or by carbon tetrachloride, chloroform, tolylenediamine, phosphorus, arsenic, alcohols, or certain organic dyes, causes excretion of protein in the bile.

CHEMICAL ABSTRACTS.

Glucose threshold in kidney. S. IMAGAWA (Proc. Imp. Acad. Tokyo, 1930, 6, 383—384).—Introduction of drugs (phloridzin, mercuric chloride, and potassium cyanide) into the glomerular circulation of the toad results in a glycosuria at low concentrations, whilst that into the capillaries around the tubules has the same effect only at much higher concentrations. This indicates the glomerulus as the seat of the renal sugar-threshold. F. O. HOWITT.

Hyperglycæmia in poisoning. H. JACOBY (Z. ges. exp. Med., 1930, 70, 100—109; Chem. Zentr., 1930, ii, 2008).—High blood-sugar values are frequently observed in acute hypnotic poisoning. The values fall when oxygen is respired; a similar transient effect is observed in diabetes. Radium emanation causes a similar effect. In a case of oral hydrochloric acid poisoning an abnormally low blood-sugar value (30 mg. per 100 c.c.) was observed.

A. A. ELDRIDGE.

"Larocain," a new local anæsthetic. K. FROMHERZ (Arch. exp. Path. Pharm., 1930, 158, 368—380).—An account of the pharmacological properties of "larocain," the monohydrochloride of the base $\text{NET}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2(\text{p})$.

A. COHEN.

Local anæsthetic action of 23 isomeric octyl alcohols. H. SCHROEDER and D. I. MACHET (Arch. exp. Path. Pharm., 1930, 158, 53—64).—The local anæsthetic actions of 23 isomeric octyl alcohols show the same relationships as their general pharmacological properties (cf. A., 1930, 954). The bearing of the phenomenon of synergism on the interpretation of pharmacological data is discussed. A. COHEN.

Significance of reaction of medium in the action of poisons. I. Influence of hydrogen-ion concentration on the action of chloral hydrate and camphor on isolated frog's heart. K. A. SCHMELEV. II. Influence of hydrogen-ion concentration on the action of potassium and calcium ions on frog's heart. N. V. GOLJACHOVSKI (Arch. exp. Path. Pharm., 1930, 158, 65—75, 76—89).—The depression of the pulse-rate of the isolated frog's heart by chloral hydrate (1:1000) and camphor (1:5000) in Ringer solutions of varying p_H is greater and the return to normal more difficult in acid than in alkaline medium. Chloral hydrate exerts greater effect on the contraction amplitude in acid solution, whilst the effects of camphor are most marked in alkaline and acid media, and only slight at p_H values of 6.60 and 7.31.

II. The systolic effects of calcium and potassium on the frog's heart are increased and the diastolic effects decreased by hydrogen ions. Hydroxyl ion has the opposite influence on these effects. Potassium-calcium antagonism is more marked in acid than in alkaline medium. A. COHEN.

Biological assay of analgesics and their mixtures. I. E. HESSE. II. E. HESSE, G. ROESLER, and F. BÜHLER (Arch. exp. Path. Pharm., 1930, 158, 233—246, 247—253).—I. A method is described for assaying analgesics by observing their influence on the reactions of healthy mice to mechanically induced pain. Several drugs have been examined and analgesia is observed with opiates, of which morphine is best, pyrazolones, and derivatives of *p*-aminophenol. Aniline derivatives show little action, and quinoline compounds and salicylates are inactive in contradistinction to clinical experience.

II. A second method of assay, based on the reactions of guinea-pigs to pain caused in an inflamed area of skin, shows that opiates, pyrazolones, salicylates, and the quinoline derivative, "atophan," are active, whilst "hexophan" and *p*-aminophenol derivatives are inactive. It is suggested that, excepting the opiates, the analgesia is due to direct action of the drug on the inflammatory focus. Data are also given for the action of a number of commercial preparations of mixtures of analgesics. A. COHEN.

[Antipyretic action of] sulphur-containing piperazine derivatives. E. HESSE and W. LOCH (Arch. exp. Path. Pharm., 1930, 158, 327—333).—The substances obtained by the condensation of methyl-, ethyl-, *n*-propyl-, *n*-butyl-, allyl-, phenyl-, and *p*-ethoxyphenyl-thiocarbimides with the additive compound of theophylline and piperazine have been examined for antipyretic properties. These are only possessed by the methyl and ethyl derivatives, which are active in a subcutaneous dose of 0.1 g. per kg. rabbit. Since the unsubstituted theophylline-piperazine compound is inactive, it is concluded that antipyretic properties are conferred by the thiocarbamyl group. The diuretic effect of the purine component of these substances is not influenced by the group containing sulphur. A. COHEN.

Thebaine and its derivatives. I. Influence of injection of thebaine and its derivatives on the carbohydrate metabolism. Y. TAKEUCHI (Sci-i-

kwai Med. J., 1930, 49, No. 6, 74—86).—Subcutaneous injection of thebaine hydrochloride into rabbits increased the blood-sugar and inorganic phosphorus. Dihydrothebaine and oxycodone cause similar effects, differences in degree being recorded.

CHEMICAL ABSTRACTS.

Influence of p_H on the adsorptive fixation of cocaine hydrochloride by nerve fibres. J. RÉGNIER and G. VALETTE (Compt. rend., 1931, 192, 114—116).—Agitation of 0.25 g. of almost ash-free charcoal with 50 c.c. of a 0.005*N* solution of cocaine hydrochloride causes the fixation of 0.083 g. at p_H 3 and 0.127 g. at p_H 7.5 per g. of charcoal. When the charcoal is replaced by 10.0 g. of ox vagus the fixation rises from 0.08 mg. at p_H 3 to 0.45 mg. at p_H 7.6 per g. of nerve fibre. P. G. MARSHALL.

Effect of lipins and urine on the diazo-reaction of alkaloids. A. SCHAKIR (Z. Immunität., 1930, 65, 120—124; Chem. Zentr., 1930, ii, 1740).—In certain pathological urines the diazo-reaction of added morphine or heroin is inhibited. The active principle of such urine may be isolated by precipitation with lead acetate. A. A. ELDRIDGE.

[Pharmacological] potential effects. H. PAF-FRATH (Arch. exp. Path. Pharm., 1930, 158, 304—313).—The intensity of the stimulant action of choline, acetylcholine, pilocarpine, trimethylamine, and histamine on the mucous membrane of the small intestines of several mammals is inversely proportional to their diffusibility through the membrane. The results support the theory that poisons act in accordance with a potential gradient between the interior of cells and the external medium, since slow permeation of tissues would tend to maintain the necessary *P.D.* A. COHEN.

Motor reactions of the small intestine to histamine. M. E. MACKEY (Trans. Roy. Soc. Canada, 1930, [iii], 24, V, 197—198).—The administration of histamine to dogs and cats anaesthetised by a mixture of chloralose and urethane markedly increases the motility of the intestine when injected in doses of 0.25—0.5 mg. intravenously, but not when injected subcutaneously or intra-intestinally. Characteristic effects are produced on the duodenum, jejunum, and ileum, respectively. Paralysis of the parasympathetic nervous system by atropine greatly diminishes but does not abolish the action. W. O. KERMACK.

Importance of exact method of preparation of tincture of digitalis and the number of pigeons in the pigeon-emesis method. P. J. HANZLIK, A. B. STOCKTON, and S. S. DAVIS (J. Pharm. Exp. Ther., 1931, 41, 5—10).—Tinctures of digitalis prepared from the same leaves with different percolation times may be of different strengths as determined by the pigeon-emesis method.

W. O. KERMACK.

Use of therapeutic effects as end-points in the biological titration of the digitalis substances. H. GOLD, B. GELFAND, and W. HITZIG (J. Pharm. Exp. Ther., 1931, 41, 89—102).—In the assay of digitalis with the cat as test animal more precise results are obtained when ventricular fibrillation is used as the end-point than when effects within the

therapeutic range of the drug are employed. The pigeon-emesis method of standardisation is criticised.

W. O. KERMACK.

Cell fats. R. DEGWITZ (Klin. Woch., 1929, 8, 2224—2229; Chem. Zentr., 1930, ii, 69).—Highly dispersed sodium oleate, lecithin, triolein, cholesterol, and cholesteryl ester are powerful cellular poisons at concentrations far below physiological. In experiments with *Paramecia* the toxicity is a physical effect, altering the relationship between the hydrophilic and hydrophobic colloids and producing a protoplasmic form incompatible with life.

A. A. ELDRIDGE.

Effects of pimento pepper on poultry. W. L. BROWN (Georgia Agric. Exp. Sta. Bull., 1930, No. 160, 11 pp.).—Addition of pimento to poultry rations increases the pigmentation of the shanks, comb, and wattles, the effect being more pronounced in cockerels than in pullets. Pimento pigment appears in chicks 5—6 days after hatching.

A. G. POLLARD.

Titanium-alloy electrodes as a therapeutic agent. W. B. TROUP (Brit. J. Actinother., 1931, 5, 235).—The titanium-alloy electrodes (98% W, 1.5% Ti, 0.5% Cr) generate a greater proportion of infra-red rays than other electrodes used in artificial light therapy and the radiation in certain regions of the spectrum is more penetrating than that from a pure tungsten arc.

C. C. N. VASS.

Nature of the active radiations in the phenomena of photosensitisation. J. CUZIN (Bull. Soc. Chim. biol. 1930, 12, 1401—1409; cf. A., 1930, 1215).—The action of radiations of various wave-lengths in sensitising eosin, methylene-blue, and hæmatoporphyrin in their action on the isolated intestine of the rabbit is studied. Ultra-violet light increases the amplitude and tone of the intestine; with eosin, the toxic action of light rays of all wave-lengths with the exception of blue light suppresses the depressive action of the dye on the intestine. The action of ultra-violet light on a dilute solution of methylene-blue increases its toxic effect, whilst with a concentrated solution it increases its depressive effect. Light of other wave-lengths has no action. Hæmatoporphyrin exhibits the strongest response. Without irradiation, it has little or no effect. Irradiation with total light and yellow light causes a marked depressive action, whilst, in order of decreasing strength, green, blue, and ultra-violet light have a similar effect.

B. LEVIN.

Metabolic effects of mitogenetic irradiation. A. GURVITSCH (Biochem. Z., 1930, 229, 109—114; cf. Gesenius, A., 1930, 1620).—Results obtained under the experimental conditions used by Gesenius are not to be explained as contradicting those of the author. The possible effects of over-irradiation and the phenomenon of secondary irradiation must be taken into consideration.

W. MCCARTNEY.

Action of X-rays on tissue cultures *in vitro*. L. DOLJANSKI, J. J. TRILLAT, P. L. DU NOÛY, and A. ROGOZINSKI (Compt. rend., 1931, 192, 304—306).—By means of an ionisation chamber the lethal dose of X-rays necessary completely to arrest the growth of a culture of fibroblasts is found to be of the order of 120,000 r (international units), a value of the same

magnitude as that observed with other micro-organisms.

J. W. BAKER.

Biological significance of the physical state of lyophilic colloids. F. F. NORD (Trans. Faraday Soc., 1930, 26, 760—767).—A summary of the work of the author and his collaborators on the activation and protection of enzyme solutions by ethylene and acetylene and on the action of these hydrocarbons on the viscosity and surface tension of lyophilic colloids, e.g., soap solutions and egg-albumin (cf. B., 1929, 994; A., 1930, 1367). The unsaturated hydrocarbons produce an increase in surface tension and a decrease in the viscosity of the lyophilic colloids and of the enzyme solutions, although they have no effect on pure water. It is concluded that they bring about an increase in the dispersion of the colloidal particles correlated with the observed increase in enzyme activity.

W. O. KERMACK.

Apparatus for measuring catalase activity in plant and animal tissues. H. H. BUNZELL (Science, 1930, 72, 505—506).—Descriptive. A unit of catalase activity is defined as that which produces in 5 min. the liberation of 1 γ of oxygen per g. of tissue.

L. S. THEOBALD.

Mechanism of oxidation processes. XXVI. Dehydrogenating enzymes of milk. H. WIELAND and T. F. MACRAE (Annalen. 1930, 483, 217—250; cf. Wieland and Rosenfeld, A., 1930, 248).—In different samples of milk the power of promoting the oxidation of xanthine by methylene-blue is not in constant proportion to the power of promoting the oxidation of aldehydes by methylene-blue. In a sample of fresh milk the xanthine-dehydrogenase activity is relatively low, but slowly increases on keeping. This increase is brought about more rapidly by agitation. Similar although less marked alterations in activity occur in respect of the aldehyde-dehydrogenase. It appears that the union of the fat droplets into larger ones with the resultant decrease in surface at which the enzyme is probably adsorbed and partly inactivated is responsible for this phenomenon. This conclusion is supported by observations on the separated cream. The results obtained confirm the view (cf. Wieland and Rosenfeld, *loc. cit.*) that the xanthine- and aldehyde-dehydrogenases are separate enzymes. The xanthine-dehydrogenase is removed from whey by adsorption on calcium carbonate, leaving the aldehyde-dehydrogenase in solution, but the former is largely inactivated in the process. When the oxidation of aldehydes (acetaldehyde, formaldehyde, benzaldehyde, salicylaldehyde, or anisaldehyde) by oxygen takes place in presence of the dehydrogenase and ceric hydroxide, the hydrogen peroxide formed reacts to form cerium peroxide (cf. *loc. cit.*). The low values (about 60% of the theoretical) previously obtained when the hydrogen peroxide formed was determined are due to an error in the determination. By an improved method results are obtained more nearly approaching the theoretical. The effect of hydrogen cyanide on the oxidation of acetaldehyde, formaldehyde, and benzaldehyde has also been determined. The oxidation of the aldehyde in presence of methylene-blue is inhibited by small quantities of hydrogen peroxide, especially if this reacts with the enzyme in presence

of substrate. Observations have been made on the decolorisation of methylene-blue in presence of the enzyme when more than one substrate is present, e.g., xanthine plus an aldehyde, or two different aldehydes. The enzyme solutions are also able to effect the dismutation of aldehyde (aliphatic or aromatic) into acid and alcohol, the optimum p_H being about 8.3. Evidence is adduced that the same enzyme is responsible for the aerobic and anaerobic oxidation in presence of methylene-blue and for dismutation. The effect of hydrogen cyanide on all three reactions is of the same order of activity.

W. O. KERMACK.

Mechanism of oxidative processes. XXVII. Dehydrogenases of muscle tissue. H. WIELAND and A. LAWSON (*Annalen*, 1931, 485, 193—210).—The retarding influence of hydrogen cyanide on succinic acid dehydrogenase (A., 1930, 168) and catalase is of similar magnitude and hence this anti-catalyst cannot be used to retard the catalase activity preferentially and so detect the formation of hydrogen peroxide. In the presence of ceric hydroxide the activity of catalase is reduced to 10% of its original value and added hydrogen peroxide escapes the attack of this enzyme and is retained quantitatively as cerium peroxide. Hydrogen cyanide (0.002*N*) in the presence of ceric hydroxide has a greater retarding effect on succinate dehydrogenation than has hydrogen cyanide alone, although ceric hydroxide alone has almost no retarding effect. In the presence of ceric hydroxide increasing the concentration of hydrogen cyanide from 0.002—0.01*N* is without effect. At the latter concentration of hydrogen cyanide the reaction velocity is greater in the presence of ceric hydroxide. The enzyme from muscle fibre has also a dehydrogenating action on quinol (p_H 6.8), the velocity decreasing with decreasing concentration of quinol, and in this reaction an initial latent period is observed. Benzoquinone has a strong retarding influence which, however, depends on the quinol concentration. The retarding action of hydrogen cyanide is similar to that in succinate dehydrogenation. In the presence of 0.004—0.001*N*-quinol (p_H 6.8) and succinate the absorption of oxygen is somewhat more rapid than with 0.02*N*-succinate alone, suggesting the simultaneous action of two different enzymes, but with higher concentrations of quinol (0.04—0.02*N*) the reaction is strongly retarded. The ratio of the amounts of oxygen absorbed in 2 hrs. at p_H 6.8 by 0.02*N*-succinate and 0.02*N*-quinol, respectively, varies from 2.2 with a dehydrogenase preparation 4 days old to 0.21 with the same preparation after 17 days. Dehydrogenation of pyrocatechol, *p*-cresol, and tyrosine is also effected by the enzyme, but its activity is only 20, 10, and 2%, respectively, of that with quinol. Dihydroxyphenylalanine is unattacked. The ratio of the activities of the expressed muscle juice and of the tissue (from left ventricle of a horse's heart) is 3:2 for succinate dehydrogenation and 4:1 for dehydrogenation of quinol. Desiccation of the expressed juice over concentrated sulphuric acid in a vacuum destroys its quinol activity, but 50% of its succinate activity is still preserved. The partial separation of the two dehydrogenases which the above results suggest to be present is effected by precipitation of the

centrifuged expressed juice with saturated ammonium sulphate. An aqueous suspension of the centrifuged precipitate retains most of the succinate dehydrogenase, but most of the quinol dehydrogenase remains in solution. Conversely, precipitation with acetone affords a preparation free from succinate dehydrogenase which, however, retains considerable activity towards quinol.

J. W. BAKER.

Peroxidase reagents producing quinoneimide dyes. II. A. CASOLARI (*Biochim. Terap. sperim.*, 1929, 16, 254—266; *Chem. Zentr.*, 1930, ii, 2551).—The use of aromatic bases, or mixtures thereof, which are oxidised by hydrogen peroxide in presence of peroxidase to dyes of the quinone-di-imide series is recommended for the detection of blood and the distinction between fresh and boiled milk. A similar oxidation is effected by other peroxides, e.g., ether containing peroxide or aged oils. The reactions are retarded by mineral acids, and inhibited even by acetic acid in high concentration, but must be carried out in dilute acetic acid solution. The reactions taking place by the use of various reagents are described.

A. A. ELDRIDGE.

Determination of peroxidase activity. J. D. GUTHRIE (*J. Amer. Chem. Soc.*, 1931, 53, 242—244).—The method utilises the formation of indophenol from *p*-phenylenediamine and α -naphthol in presence of a citrate buffer, by treatment with the extract (containing the enzyme) and dilute hydrogen peroxide. The amount of indophenol produced is determined colorimetrically.

H. BURTON.

Autoxidation of leucomethylene-blue. T. F. MACRAE (*Ber.*, 1931, 64, [B], 133—137).—Dissolved methylene-blue is hydrogenated in the presence of milk enzyme and the approximately calculated amount of hypoxanthine in an atmosphere of nitrogen, catalase being added to exclude the production of hydrogen peroxide. After destruction of the enzyme, the absorption of oxygen is measured in the solution with or without addition of ceric hydroxide or catalase. It is shown that the hydrogen peroxide formed has little part in the dehydrogenation of leucomethylene-blue. In the presence of ceric hydroxide, the hydrogen peroxide is almost completely retained and, in the absence of this acceptor, two thirds of the peroxide formed can be identified at p_H 8.0; the remainder is probably consumed by the uric acid arising from the hypoxanthine. Leucomethylene-blue at p_H 8.0 is oxidised about ten times as rapidly by molecular oxygen as by hydrogen peroxide; the autoxidation is not restricted by hydrocyanic acid or carbon monoxide. Addition of iron under the experimental conditions causes a fivefold increase in the rate of oxidation, which is reduced to half by hydrocyanic acid in 125*M* concentration. The rate of oxidation exhibits normal dependence on the temperature.

H. WREN.

Carbohydrate-redoxase. H. VON EULER and R. NILSSON (*Z. physiol. Chem.*, 1931, 194, 260—268).—Aqueous extracts of the seeds of *Corchorus capsularis* contain co-zymase. The co-zymase-free extract does not decolorise methylene-blue in presence of sodium hexosediphosphate (cf. Deuticke, this vol., 122);

decolorisation proceeds rapidly when co-enzyme is added. The decolorisation of methylene-blue by fresh rat-muscle is slightly accelerated by creatine; a dry muscle preparation is not affected. The muscle-juice, diluted with phosphate containing co-enzyme, is without action on methylene-blue. Decolorisation is markedly accelerated by creatine or, better, by sodium creatinephosphate or hexosediphosphate. A dry ox-muscle preparation shows a similar behaviour with the phosphates, but not with creatine. Washed muscle does not cause reduction of methylene-blue either in absence or presence of creatine.

H. BURTON.

Enzymes and light. XVII. Effect of visible and ultra-violet light on the succinodehydrogenase of horse-muscle. L. PINCUSSEN and W. ROMAN (Biochem. Z., 1930, 229, 281–290).—On curves showing the relation between the activity of succinodehydrogenase, in the system succinic acid–fumaric acid in the presence of malic acid, and the reaction of the medium in which it acts, two peaks appear. The peak representing highest activity is at p_H 6.9; the other is at p_H 7.7. In general, the enzyme is more active in the acid zone of hydrogen-ion concentration than in the alkaline. The activity of the enzyme is greatly reduced by exposure for 15 min. to ultra-violet light at p_H 6.0–8.0, but in the acid zone is not completely destroyed. Irradiation for 1 hr. with visible light also causes reduction of the activity, such reduction being greatest at the points corresponding with the peaks on the curves, but when this irradiation lasts for only 0.5 hr. the activity is so increased at weakly acid and weakly alkaline reactions that it surpasses that of the unirradiated enzyme at the same reactions. When the reaction of the medium is neutral the activity of the enzyme is reduced by irradiation of short duration.

W. MCCARTNEY.

Substances protecting amylase. I. Introduction. II. Protective action of proteases. III. Protective action of proteins and digestion products. H. NAKAMURA (J. Soc. Chem. Ind. Japan, 1930, 33, 521–522B, 523–524B, 524–526B).—I. The activity of takadiastase, measured by the formation of reducing sugar from starch under standard conditions, varies little between p_H 4.9 and 5.8. The decrease in activity after preliminary heating at 50° at various values of p_H and different concentrations is determined.

II. The addition of pepsin or papain solution, even after having been heated at 100° for 20 min., prevents heat-inactivation.

III. Peptone prevents heat-inactivation, and gelatin, egg-albumin, and caseinogen exert protective action, decreasing in strength in the order given. The solutions obtained by digestion with pepsin or papain also exert protective action, enhanced in the case of egg-albumin and pepsin. No activation phenomena are observed in any case.

R. K. CALLOW.

Glycogenolysis. H. K. BARRENSCHEEN, J. PANY, and R. BERGER (Biochem. Z., 1930, 229, 196–215).—In the livers of guinea-pigs, rabbits, and dogs post-mortem decomposition of glycogen and the production of inorganic phosphate proceed in such a way that

the curves representing these changes follow parallel courses which take the form of a series of steps. The inorganic phosphate is derived chiefly from that portion of the acid-soluble organic phosphate which is difficultly hydrolysed. Neither the decomposition of the glycogen nor the production of inorganic phosphate is affected *in vitro* by addition of insulin or by temporary poisoning with insulin. As a result of the decomposition of glycogen a *hexosemonophosphoric acid*, $[\alpha]_D^{25} -6.34^\circ$ (osazone, m. p. 177°; barium salt, $[\alpha]_D^{25} -8.4^\circ$), not identical with the other known natural or synthetic substances can be isolated by Neuberg and Leibowitz's modification (A., 1927, 700) of Robison's method (A., 1923, i, 86) from both rabbit and dog livers.

W. MCCARTNEY.

Post-mortal production of lactic acid in the liver. E. FENZ and H. POPPER (Biochem. Z., 1930, 229, 397–426).—The post-mortal lactic acid content of the human liver (and also of that of the guinea-pig) reaches a maximum about 7 hrs. after death. Pathological conditions have no great effect on the maximum amount of lactic acid produced nor does this amount depend on the total carbohydrate content. In human livers kept at 37° in sodium hydrogen carbonate solution or in disodium hydrogen phosphate solution for a period of 10–33 hrs. no further increase in the lactic acid content occurs even if dextrose be added. In guinea-pig livers placed immediately after death in a buffer solution and kept at 37° the power to produce lactic acid decreases in such a way that after about 7 hrs. no more can be detected and additions of dextrose, laevulose, glycogen, or hexosediphosphate usually have no effect on this decrease. The same holds, at least partly, of human livers, and their pathological condition is also without effect on this loss of power to produce lactic acid. As regards post-mortal lactic acid production human kidneys resemble human livers. The lactic acid content of practically all the organs from two human corpses and from two guinea-pigs has been determined.

W. MCCARTNEY.

Production of methylglyoxal and pyruvic acid by yeast under the influence of plasmolytic substances. C. NEUBERG and M. KOBEL (Biochem. Z., 1930, 229, 255–262).—The process in which methylglyoxal and, later, pyruvic acid are produced from magnesium hexosemonophosphate by the action of yeast can be checked and the two compounds allowed to accumulate by the addition of one of many plasmolytic substances, of which toluene and bromobenzene are especially suitable. The substrate itself, if present in sufficient concentration, has the same effect. The dinitrophenylhydrazones of the two compounds can be distinguished from each other by the difference in the colours which they give (methylglyoxal, deep bluish-violet; pyruvic acid, brown then red) with alcoholic potassium hydroxide solution and can be separated by the use of sodium carbonate solution, in which the methylglyoxal compound is insoluble.

W. MCCARTNEY.

Carbohydrate metabolism of higher plants. Production of methylglyoxal by the enzymes of germinated seeds. C. NEUBERG and M. KOBEL (Biochem. Z., 1930, 229, 433–442; cf. A., 1929,

722).—The enzyme which acts on magnesium hexose-diphosphate in such a way as to lead to the production of methylglyoxal is present in germinated peas (*Pisum saccharatum*) and in germinated beans (*Vicia faba*). W. McCARTNEY.

Glyoxalase. F. SAKUMA (J. Biochem., Japan, 1930, 12, 247—279).—The liver is richest in glyoxalase; values for cold-blooded animals are only half as great as those for warm-blooded animals. When the tissues are deprived of sugar the glyoxalase content also diminishes, that of the liver decreasing least rapidly. In germinating soya beans the glyoxalase content at first increases and then decreases after 7—8 days. The extraction of the enzyme is described. Dextrose or polysaccharides containing glucose accelerated the activity of glyoxalase, whereas phosphate inhibited it. Guanine and its derivatives and amino-acids cause a rapid disappearance of methylglyoxal with production of ammonia and carbon dioxide. CHEMICAL ABSTRACTS.

Kinetics of ester hydrolysis by enzymes. III. Influence of the indicator on the activity of esterases. IV. Behaviour of esterases towards lactones. E. BAMANN and M. SCHMELLER (Z. physiol. Chem., 1931, 194, 1—13, 14—20; cf. A., 1930, 956).—III. The retardation of ester hydrolysis caused by small amounts of indicator leads to inaccuracies in the method of Knaffl-Lenz (A., 1923, i, 621) for the titrimetric determination of liver-esterase. Data are presented for the hydrolysis of methyl butyrate by liver enzymes from man, horse, sheep, and rabbit, with varying concentrations of indicator and ester, using phenolphthalein, bromothymol-blue, and bromocresol-purple. The indicator effect decreases as p_H increases, and, in alkaline medium, gives way to an acceleration of the hydrolysis, which may be associated with a change of structure of the phthalein type of indicator. Thus, a 31% inactivation observed with 1 mg. of bromothymol-blue per 100 c.c. of reaction mixture at p_H 7.0 is replaced by an activation of 44% at p_H 8.9.

Bromocresol-purple (0.04 mg. per 100 c.c.) and neutral-red (0.3 mg. per 100 c.c.) have no measurable effect on hydrolysis at p_H 6.8 and 7.3, respectively, and, under these conditions, are regarded as the most suitable indicators.

IV. γ -Butyrolactone, γ -valerolactone, coumarin, and santonin are not appreciably hydrolysed by liver-esterases in solutions buffered at p_H 8.9. It is probable that the intermediate lactone-enzyme complex decomposes slowly, since these lactones inhibit the hydrolysis of methyl butyrate by esterase to a degree which varies inversely with the concentration of ester. A. COHEN.

Substance suitable for use as a model for illustrating the mode of action of the pectases. C. NEUBERG and C. OSTENDORF (Biochem. Z., 1930, 229, 464—466).—The properties of the calcium salt of methyl hydrogen *d*-tartrate (A., 1909, i, 361) make this substance suitable for use as a model in the study of the mode of action of the pectases. These decompose the compound liberating methyl alcohol and causing the precipitation of gelatinous calcium tartrate which eventually crystallises. W. McCARTNEY.

Liberation of tyrosine and tryptophan from caseinogen by papain activated with hydrocyanic acid. T. LEIPERT and I. HÄRNER (Biochem. Z., 1930, 229, 427—432).—Amino-nitrogen equivalent to 47% of its total nitrogen content was liberated from caseinogen as a result of digestion for 12 days with papain which had been activated by treatment with hydrogen cyanide. During this period all of the tyrosine in the caseinogen was set free, but the tryptophan was liberated only partly and at the same rate as were the remaining amino-acids. Activated papain in conjunction with trypsin liberated, in one week, 71% of the total nitrogen of caseinogen as amino-nitrogen, but the liberation of tyrosine and tryptophan was not otherwise affected by this combined action. W. McCARTNEY.

Multiple nature of the enzyme carrier in the hydrolysis of polypeptides by yeast macerates. Production of a protein-free eluate which acts on higher polypeptides only. A. FODOR and L. FRANKENTHAL (Biochem. Z., 1930, 229, 16—27).—When the material precipitated by acid from diluted yeast macerates is adsorbed on kaolin and this is then kept for 2 hrs. at 37° in contact with a 2% solution of glycine the liquid which is obtained when the glycine solution is filtered is free from protein but retains the activity of the original macerate. Since this liquid exhibits specificity with regard to its effects on peptides, some of which it hydrolyses more rapidly than others, the authors' views concerning the anchoring and disconnecting of enzymes and their transference from one carrier to another are confirmed (cf. this vol., 262). W. McCARTNEY.

Hydrolysis of proline-polypeptides by yeast and pancreas extracts and by pancreatin preparations. A. FODOR, M. FRANKEL, and S. KUK (Biochem. Z., 1930, 229, 28—40; cf. preceding abstract).—*dl*-Prolylalanine is readily hydrolysed by the water-insoluble part of dried pancreatin, but only slowly and partly by the water-soluble portion. Hydrolysis is also caused by macerates of fresh pancreatic glands (especially if such macerates are first purified by dialysis) and by the two active constituents of yeast macerates. *dl*-Alanylproline is hydrolysed by yeast macerates, but not by pancreatin. It follows from these results that the enzymic hydrolysis of polypeptides is not directly dependent on the presence in the latter of certain groups such as the free amino- or carboxyl groups. W. McCARTNEY.

Specificity of animal proteases. XX. Mechanism of the enzymic fission of dipeptides. A. K. BALLS and F. KÖHLER. XXI. Causes of steric selection by enzymes. E. WALDSCHMIDT-LEITZ and A. K. BALLS (Ber., 1931, 64, [B], 34—45, 45—48; cf. Waldschmidt-Leitz and others, A., 1929, 723; 1930, 957).—XX. The presence of a free amino-group but not of a free carboxyl group appears essential to the enzymic activity of that component of intestinal erepsin which hydrolyses dipeptides. The apparent minor importance of the second component of the dipeptide is not in harmony with the observed hydrolysis of glycyl-*d*-alanine and non-hydrolysis of glycyl-*l*-alanine by dipeptidase. The apparent contradiction is explained by the hypo-

thesis that the enzyme unites with the substrate by two haptophoric groups, the second of which is regarded as the imino-group of the peptide. Since *p*-nitroaminoacetanilide, *p*-aminoacetamidobenzoic acid, and nitroaminoacetamidobenzoic acid are hydrolysed by dipeptidase, whereas aminoacetanilide, aminoacet-*p*-toluidide, and *o*-aminoacetamidobenzoic acid are unaffected, the influence of the substituent (nitro-group or carboxyl) is ascribed to change in the acidic nature of the imino-group. The restriction of dipeptidase action by substances such as chloroacetyl-tyrosine and aceturic acid confirms the view that the imino-group is the second point of attachment of the enzyme. The following new compounds are described: *aminoacetanilide hydrochloride*, m. p. 170°; *aminoacet-o-toluidide*, m. p. 256°; *o-aminoacetamidobenzoic acid*, m. p. 236°; *m-aminoacetamidobenzoic acid*, m. p. 245°; *nitro-o-aminoacetamidobenzoic acid*, m. p. 245–260° according to the rate of heating (from *o*-aminoacetamidobenzoic acid, sulphuric acid monohydrate, and potassium nitrate at –5° to –10°); *chloroacet-p-toluidide*, m. p. 168–169°, from chloroacetyl chloride and *p*-toluidine in benzene; *aminoacet-p-toluidide*, m. p. 137° after softening at 95°; *chloroacet-p-chloroanilide*, m. p. 173°; *aminoacet-p-chloroanilide*, m. p. 85°; *chloroacet-p-nitroanilide*, m. p. 185°; *aminoacet-p-nitroanilide*, m. p. 165°.

XXI. The preparation of *o*-chloroacetamido-, m. p. 190°, *m*-chloroacetamido-, m. p. 232°, and *p*-chloroacetamido-benzoic acid, m. p. 257° (cf. Tropp, A., 1928, 1025), is described. Of these, only the *meta*-derivative is hydrolysed by carboxypolypeptidase from pancreas. The underlying causes are discussed.

H. WREN.

Nature of proteases. VII. Pepsin in cold- and warm-blooded animals. N. P. PJATNITZKIJ (Z. physiol. Chem., 1931, 194, 43–52; cf. Adova and Smorodincev, A., 1930, 1620).—Frog's gastric juice, obtained by the method of Smirnow, has p_H varying between 1.52 and 3.9. Its hydrolytic activity, referred to egg-albumin, for which the optimum p_H is 1.0–1.4, is 25% greater than that of dog's gastric juice, but only half of that for the dog when estimated on caseinogen. The stomach extract of a frog has smaller hydrolytic activity on egg-albumin than an extract of the mucous membrane of the dog's stomach. Pepsin preparations from cold- and warm-blooded animals appear to be identical.

A. COHEN.

Plant proteases. XVI. Activation of animal and plant proteases by glutathione. W. GRASSMANN, O. VON SCHOENEBECK, and H. EIBELER (Z. physiol. Chem., 1931, 194, 124–136).—Reduced glutathione activates papain, yeast proteinase, and cathepsin, thus resembling cysteine (A., 1930, 500). The oxidised form has no activating power, and neither form has any action on pepsin. Yeast phytokinase (cf. Ambros and Harteneck, A., 1929, 606) is identical with glutathione.

H. BURTON.

Action of proteases on urease preparations. J. ZAKOWSKI (Biochem. Z., 1930, 229, 41–84).—The activity of urease is reduced by as much as 80% by the action, at 30–40° and in media having certain hydrogen-ion concentrations, of papain or trypsin. Results obtained with activated and inactivated

papain and trypsin indicate that it is not impossible, although not probable, that the diminution of activity (which is not caused by the presence of inhibitory substances) may be due to enzymes which attack the urease itself or the material which carries it. Erepsin has no effect on the activity of urease.

W. McCARTNEY.

Action of arginase. VI. S. EDLBACHER and H. BURCHARD (Z. physiol. Chem., 1931, 194, 69–75; cf. A., 1928, 88).—Arginylarginine prepared from clupeine by the method of Kossel and Staudt (A., 1928, 81) is completely hydrolysed by a peptidase-arginase mixture from calf-liver extract. Purified arginase, obtained free from peptidase by adsorption of the latter on aluminium hydroxide, hydrolyses only one guanidyl group in arginylarginine.

A. COHEN.

Respiration and fermentation of top and bottom beer yeasts. K. TRAUTWEIN and J. WASSERMANN (Biochem. Z., 1930, 229, 128–153).—Examination of the behaviour of biologically pure strains of yeast showed that the rates of respiration of top yeasts are on the average 77% greater than are those of bottom yeasts. The difference is related to the racial characteristics of the strains and is traced to adaptation to environment. In both types of yeast increase in rate of respiration is accompanied by increase in the degree of fermenting power, a constant ratio persisting between these two factors. The metabolic energy expended in respiration and fermentation by top yeast is 42% greater than that expended by bottom yeast. The proportion of energy involved in respiration is, for the top yeasts, 40% and for the bottom yeasts 32%. Of the sugar decomposed by the yeasts 2–3% is required for respiration and 98–97% is fermented.

W. McCARTNEY.

Fourth form of cell-free fermentation by yeast. M. KOBEL and M. SCHEUER (Biochem. Z., 1930, 229, 238–247).—The fermentation of yeast maceration juice may proceed in such a way that the fourth type of fermentation only occurs. When the juice is diluted six times and the initial concentration of magnesium hexosediphosphate in the fermenting liquid is 0.9749% 79% of the hexose is liberated and converted entirely into pyruvic acid and glycerol.

W. McCARTNEY.

Hydrolysis of non-phosphorylated sugars by yeast with production of glycerol and pyruvic acid. C. NEUBERG and M. KOBEL (Biochem. Z., 1930, 229, 446–454).—By the action of yeast on dextrose in the presence of magnesium phosphate, magnesium oxide, or disodium hydrogen phosphate glycerol and pyruvic acid can be produced, although the yields obtained are not so high as when salts of hexosephosphoric esters are used.

W. McCARTNEY.

Iodo- and bromo-acetic acid poisoning in carbohydrate degradation. R. NILSSON, K. ZEILE, and H. VON EULER (Z. physiol. Chem., 1931, 194, 53–68; cf. Lundsgaard, A., 1930, 954, 958).—When alcoholic fermentation is inhibited by iodo- or bromo-acetic acid, formation of hexosediphosphate is not observed, and hexosemonophosphate is not detected under conditions which do not prevent its formation in the case of sodium fluoride poisoning. Iodoacetic acid

also prevents acetaldehyde reduction, which is not affected by fluoride. In agreement with Lundsgaard, it is found that over a small range of concentrations of iodoacetic acid (0.001–0.0001*M*) oxygen consumption continues, whilst fermentation is completely inhibited. It is suggested that iodoacetic acid poisoning involves the later stages of the chain of fermentation reactions. A. COHEN.

Order of death of organisms larger than bacteria. O. RAHN (J. Gen. Physiol., 1931, 14, 315–337).—The death of bacteria is brought about by the destruction of only one definite gene-like molecule in the cell. A discussion and criticism of previous work are given, from which it is shown that, of the larger organisms, only *Chlamydomonas* has a similar order of death. The mould, *Botrytis cinerea*, has more than one reacting molecule, and the flagellate *Colpidium*, together with erythrocytes, has two reacting molecules. P. G. MARSHALL.

Variations in the response to light of *Amoeba proteus* with special reference to the effects of salts and of hydrogen-ion concentration. S. O. MAST and H. R. HULPIEU (Protoplasma, 1930, 11, 412–431).—The effect of changing light intensity on the protoplasmic streaming in *A. proteus* is influenced by the presence of dissolved substances in the culture liquid. The reaction time (period between light change and response) is increased by the presence of hydrochloric acid and the chlorides of magnesium, calcium, and potassium and decreased by carbon dioxide. The effect of sodium chloride was irregular. A. G. POLLARD.

Hæmotoxin in *Sarcosporidia*. S. SATO (Kitasato Arch. Exp. Med., 1930, 7, 201–212).—The thermostable hæmolytic principle of sarcosporidiotoxin is negative to protein tests, but the hæmagglutinative principle (destroyed at 85° in 30 min.) is positive. Inhibition or acceleration by serum fractions is recorded. CHEMICAL ABSTRACTS.

Effect of initial reaction of Raulin's medium on the culture of *Aspergillus niger*. C. LOPARDO, J. B. MARGARA, and J. DEL VECCHIO (Ann. farm. biochim., 1930, 1, 111–118).—*Aspergillus niger* cultivated at 37° in Raulin's medium of p_H 1.9–6.7 produces an increasing acidity which is maximal (p_H 1.8) on the third day. CHEMICAL ABSTRACTS.

Effect of ammonium salt on the growth of *Penicillium roqueforti* in cheese. N. S. GOLDING (Trans. Roy. Soc. Canada, 1930, [iii], 24, V, 133–140).—Fresh Wensleydale cheese contains very little ammonia. The addition of ammonium chloride to the curd at salting does not favourably affect the rate or extent of growth of *P. roqueforti* on the cheese, but appears to exert a slight detrimental effect. W. O. KERMACK.

Biochemical transformations of acetic acid by the action of moulds. Chemistry of citric acid production. T. CHRZASZCZ and D. TIUKOV (Biochem. Z., 1930, 229, 343–357; cf. A., 1930, 1218).—By the action of a certain species of *Penicillium* (a typical accumulator of citric acid) on alkaline solutions of the calcium, sodium, or potassium salt of acetic acid, succinic, fumaric, oxalic, *l*-malic, and citric acids

and at least one other unidentified acid are produced. The number and amount of acids produced vary according to the salt used. Production of citric acid and possibly also of oxalic acid is favoured by the use of the alkali salts. The mechanism of the process of conversion is discussed and it is suggested that the production of citric acid from sugars by the action of moulds proceeds by way of the following substances in the order given: pyruvic acid and acetaldehyde, ethyl alcohol, acetic acid, succinic acid, fumaric acid, *l*-malic acid. W. MCCARTNEY.

Significance of aldehyde dismutation in acetic fermentation. A. BERTHO and K. P. BASU (Annalen, 1931, 485, 26–42).—Further work is described in support of the view that aldehyde dismutation plays little part in acetic fermentation (Wieland and Bertho, A., 1929, 219; Bertho, *ibid.*, 1492) contrary to Neuberg and Windisch (A., 1926, 324) and Simon (A., 1930, 1477). It is found that with *B. pastorianum* under fully aerobic conditions the formation of alcohol from acetaldehyde takes place at less than the velocity of anaerobic dismutation. No significant variation in velocity with p_H is observed, contrary to Simon (*loc. cit.*). The alcohol formed is 2–10% of theory on the assumption of exclusive dismutation. Parallel measurements of the consumption of oxygen and of the formation of acetic acid are concordant with the predominance of dehydrogenation of acetaldehyde over dismutation. R. K. CALLOW.

Acids produced by various strains of propionic bacteria. P. W. WILSON, E. B. FRED, and W. H. PETERSON (Biochem. Z., 1930, 229, 271–280).—Experiments with 11 strains of propionic bacteria and pure sugars or mixtures containing sugars show that dextrose, lactose, maltose, and sucrose are partly fermented by pure cultures of the bacteria and practically completely fermented by mixtures of the cultures with those of *Lactobacillus casei*, up to 75% of the sugar consumed being converted into volatile acids. The quantity of volatile acids produced during the fermentation varies with the strain of the bacteria used and those strains which are most effective with pure sugars are also most effective with mixtures. Of the latter molasses and hydrolysed starch are most rapidly fermented. The volatile acids produced consist chiefly of acetic and propionic acids in the molecular proportion 1:2.46. W. MCCARTNEY.

Formation of hydrogen peroxide by lactic acid bacteria. A. BERTHO and H. GLÜCK (Naturwiss., 1931, 19, 88).—Certain facultative anaerobic, catalase-free lactic acid bacteria (*B. Delbrücki*, *B. iugurt*, and *B. acidophilus*) produce hydrogen peroxide in oxidative metabolism. The reaction is not influenced by a 0.0005*M* solution of hydrocyanic acid. The peroxide can be detected by titanium sulphate, and determined either as cerium peroxide or by direct titration. *Streptococcus casei* did not, under similar conditions, produce hydrogen peroxide. W. R. ANGUS.

The *Coccaceæ*. XVI. The genus *Leuconostoc*. G. J. HUCKER and C. S. PEDERSON (N.Y. State Agric. Exp. Sta. Tech. Bull., 1930, No. 167).—The fermentation of sugars by numerous strains of gas-producing, chain-forming cocci isolated from milk

products, fermenting vegetables, etc. indicates their classification as a separate genus, viz., *Leuconostoc*, Van Tieghem. These produce *l*-lactic and acetic acids, carbon dioxide, and ethyl alcohol during the fermentation of carbohydrates. Mannitol and, in most cases, dextran or *l*ävulose are produced from *l*ävulose. Most species require growth accessory factors, e.g., yeast or tomato juice. A. G. POLLARD.

Glycuronic acid, a constituent of the gum of root nodule bacteria. E. W. HOPKINS, W. H. PETERSON, and E. B. FRED (J. Amer. Chem. Soc., 1931, 53, 306—309).—Glycuronic acid has been identified as a constituent of the gum produced by the root nodule bacteria of pea and red clover (A., 1930, 1478). H. BURTON.

Effect of Bordet's bacillus on rabbit's blood. S. TAKAHASHI (Sei-i-kwai Med. J., 1930, 49, No. 1, 116—130).—*B. pertussis* increases the sedimentation velocity of the blood and the colloidal instability of the serum, normal values being reached after 10 days.

CHEMICAL ABSTRACTS.

Gersbach's indole determination [of *B. coli*]. E. L. KRUGERS DAGNEAUX (Chem. Weekblad, 1931, 28, 66—67).—The various methods for rapid identification of *B. coli* are discussed, and it is pointed out that the Gersbach indole method, whilst not a positive test in all cases, is important as a means of detecting recent infection, especially in milk. S. I. LEVY.

Oxybiotic metabolism of bacteria. I. Dependence of respiration of *Bacillus coli* on some physico-chemical and biological factors. T. WOHLFEIL (Zentr. Bakt. Par., 1930, 115, 413—426; Chem. Zentr., 1930, ii, 77).—The respiration of *B. coli* is but little sensitive to p_H between 6.5 and 8.0. Young cultures washed with sodium chloride solution show an increased respiration over older cultures, the young, short bacilli having a relatively larger adsorption surface for oxygen. The temperature coefficient decreases with a rise in temperature and with the age of the culture. The initial process of protein digestion by bacteria is assumed to be a case of adsorption with which enzymic activity is connected.

L. S. THEOBALD.

Peroxidase in relation to bacterial growth with special reference to the influenza bacillus. L. R. ANDERSON (J. Bact., 1930, 20, 371—379).—The production of peroxidase serves to differentiate certain bacteria. The identity of peroxidase with the X factor of Thjotta and Avery is confirmed.

A. G. POLLARD.

Nature of the growth-promoting principle in the potato. Culture of tubercle bacilli. N. UYEI (Amer. Rev. Tuberculosis, 1930, 22, 203—217).—Of the various substances present in the potato, inositol, maltose, and dextrose are metabolic stimulants, stimulating the growth of tubercle bacilli only when these are present in large numbers, whilst soluble starch and dextrin, but not glycogen, are reproductive stimulants, effective when tubercle bacilli are present in any numbers.

CHEMICAL ABSTRACTS.

Preparation of antigenic specific substance from streptococci and pneumococci (type 1). H. B. DAY (Brit. J. Exp. Path., 1930, 11, 164—173).

—Methods of extraction are described; heat is usually desirable, but extraction at 100° is destructive. The antigenic specific substance contains two groups: (1) a stable portion which reacts with immune serum, (2) an unstable antigenic portion which provokes the formation of antibody. The antigenic group resembles an enzyme in some properties. It is possible to obtain an antigenic type-specific substance apart from ordinary bacterial protein.

CHEMICAL ABSTRACTS.

Increase of toxic properties of bacilli and of their toxins through weak fermentation. A. KOMIS (Zentr. Bakt. Par., 1930, 115, 454—457; Chem. Zentr., 1930, ii, 77).—The toxicity of various bacilli is increased by weak fermentation with yeast at 37°. Strong and resistant forms of bacilli can be obtained by this means. L. S. THEOBALD.

Toxin of the gas-gangrene bacillus. II. A. EBEL (Biochem. Z., 1930, 229, 265—268; A., 1930, 1623).—From solutions obtained from cultures by repeated precipitation with alcohol, electrodialysis, and precipitation with lead acetate, the toxin of the gas-gangrene bacillus can be purified and concentrated in ethereal alcohol solution. W. MCCARTNEY.

Relationship between diphtheria toxin and blood-sugar. T. USUI (Sei-i-kwai Med. J., 1930, 49, No. 4, 38—50).—Only in serious cases were markedly high values of blood-sugar observed. Hyperglycæmia in guinea-pigs and rabbits is observed only when the toxin or organism is injected subcutaneously. It is considered that diphtheria antitoxin diminishes the hyperglycæmia to some extent.

CHEMICAL ABSTRACTS.

Diphtheria toxin-antitoxin precipitate. F. MODERN and R. WERNICKE (Anal. Asoc. Quím. Argentina, 1930, 18, 47—56).—Diphtheria toxin-antitoxin precipitate requires a minimum acidity of p_H 3.6 for complete solution. When kept in acid solution the antitoxin is liberated and the toxin is destroyed (cf. Ramon, A., 1924, i, 463, 1149; 1925, i, 339). The recovery of antitoxin is maximal at p_H 3.2—3.6 and 10—15°, and increases with time up to several weeks. The yield increases with increasing dilution, and the ratio of units of activity to protein may be raised to 18 times that of the original serum.

R. K. CALLOW.

Purification of anti-diphtheria serum by adsorption with aluminium hydroxide. R. WERNICKE and F. MODERN (Anal. Asoc. Quím. Argentina, 1930, 18, 98—111).—Dry, powdered aluminium hydroxide has little or no adsorptive power for the proteins or antitoxins. When aluminium hydroxide is precipitated in the serum, however, marked adsorption occurs, particularly at the neutral point. In acid or alkaline solution slight preferential adsorption of inactive proteins is observed. By elutriation of the precipitate at p_H > 8.4 the proteins and antitoxins are recovered quantitatively. No useful concentration of the antitoxins is attained by these methods.

R. K. CALLOW.

Effect of certain oxidation-reduction potential indicators on diphtheria toxin. P. J. MOLONEY and E. M. TAYLOR (Trans. Roy. Soc. Canada, 1930, [iii], 24, V, 127—132).—Certain oxidation-reduction

indicators, especially those which are easily reduced, e.g., chloroindophenol and phenolindophenol, accelerate the detoxification of diphtheria toxin at 36–39°. The indicators are more active in the oxidised than in the reduced form and the action increases with increased concentration of indicator and with increase of p_H between 6.5 and 7.5. The detoxified material retains its antigenic power.

W. O. KERMACK.

Action of formaldehyde on the aggressive substance of blackleg filtrate, bacterin, and aggressin. J. P. SCOTT (J. Infect. Dis., 1930, 46, 460–468).—Formaldehyde (0.5%) increases the anti-serum neutralising potency of *C. chauvei* bacterins and filtrates. It inhibits the agglutininogen, but increases the activity of the protective antigenic complex.

CHEMICAL ABSTRACTS.

Mechanism of bacterial action. J. H. QUASTEL (Trans. Faraday Soc., 1930, 26, 853–861).—A summary of the author's theory of the activity and specificity of cellular enzymes (cf., A., 1927, 1113; 1928, 797).

W. O. KERMACK.

Theories of the bacteriophage. J. BORDET (Proc. Roy. Soc., 1931, B, 107, 398–417).—A review of the work of the author on bacteriophage, the view being expressed that the active principle is probably not a virus but possesses the characters of an enzyme capable of autolysing the bacteria, and itself being reproduced during the process of autolysis.

W. O. KERMACK.

Balanced salt action as manifested in bacteriophage phenomena. F. M. BURNET and M. MCKIE (Austral. J. Exp. Biol., 1930, 7, 183–198).—In presence of an excess of sodium, potassium, or ammonium ions, bacteriophage exhibits an increased susceptibility to the adverse effects of high temperature, but this may be partly or wholly counteracted by a sufficient concentration of calcium, barium, or magnesium ions. Bacteriophage is inactivated by certain dyes, but in presence of calcium salts inactivation does not occur. In the case of one phage, the rate of migration towards the anode in presence of calcium ions is greater than in presence of sodium ions, a result probably due to a shrinkage in the size of the particles in presence of the bivalent ions. In the case of other phages similar changes in cataphoretic velocity were not detected, possibly because of insufficiently accurate experimental methods.

W. O. KERMACK.

Electrical behaviour of bacteriophages. F. M. BURNET and M. MCKIE (Austral. J. Exp. Biol., 1930, 7, 199–209).—Various bacteriophages normally possess a negative charge as shown by experiments on their cataphoretic migration.

W. O. KERMACK.

Immunisation with aluminium hydroxide mixtures of poliomyelitis virus. C. P. RHOADS (Science, 1930, 72, 608).—The virus of poliomyelitis when adsorbed on aluminium hydroxide is incapable of producing the disease, but can induce active immunity in monkeys. Inactivation of the virus is promoted by p_H 5.5 and prevented by p_H 8.8.

L. S. THEOBALD.

Influence of substitution on the colloid-chemical action of derivatives of acetic acid and

phenol, and relationship to disinfective properties. R. LABES and E. JANSEN (Arch. exp. Path. Pharm., 1930, 158, 1–28).—By observing the shift to the acid region of the optimum p_H for flocculation of denatured serum-albumin caused by substituted acetic acids (cf. Michaelis and Rona, A., 1919, i, 358), the influence of the substituents in increasing the affinity of the anions for protein has been arranged in the following series: $\text{Ph} > \text{I} > \text{Br} > \text{Cl} > \text{NO}_2 > \text{Me} > \text{OH}$. In the phenols this colloid-chemical action runs parallel with disinfective activity.

A. COHEN.

Effect of substituted benzoic acids and aromatic sulphonic acids on the flocculation optimum of denatured serum-albumin. R. LABES and T. SCHUSTER (Arch. exp. Path. Pharm., 1930, 158, 29–41).—The greater significance of orientation of substituents in determining the colloid-chemical action of the benzoic acids as compared with the phenols is attributed to the polar character of the former. Both the antiseptic activity and the influence on serum-albumin of iodobenzoic acids increase with the number of substituent iodine atoms, and the colloid-chemical action of sulphonic acids increases with the number of aromatic nuclei.

A. COHEN.

Bacteriostatic action of certain components of commercial peptones as affected by conditions of oxidation and reduction. R. DUBOS (J. Exp. Med., 1930, 52, 331–345).—The substances are bacteriostatic only in the oxidised form; their effect is overcome by the addition of reduced thiol compounds to the media. Commercial peptones differ greatly in their content of bacteriostatic substance, which may be removed by precipitation with acid and acetone.

CHEMICAL ABSTRACTS.

Susceptibility of various bacteria to hydrogen sulphide. R. DOURIS and J. BECK (Ann. Inst. Pasteur, 1931, 46, 73–77).—The bactericidal action of hydrogen sulphide is greater on cocci than on bacilli and is most marked on Gram-positive types. Motile bacteria are usually more resistant than non-motile.

W. O. KERMACK.

Bactericidal action of thiocyanates. I. Hydrothiocyanic acid and sodium thiocyanate in neutral or acid solution. G. LOCKEMANN and W. ULRICH (Z. Hyg., 1930, 111, 387–419; Chem. Zentr., 1930, ii, 1880–1881).—The disinfective action of sodium thiocyanate is much greater than that of the sodium halides; the activity is greatly increased with increase in hydrogen-ion concentration. Free hydrothiocyanic acid is a more efficient bactericide than trichloroacetic acid.

A. A. ELDRIDGE.

Oligodynamic dilutions. J. MEYER (Chem.-Ztg., 1931, 55, 85–86).—It has been claimed that dilutions of lead and silver nitrate down to 1 part in 10^{29} parts of water have an appreciable effect on organisms. This appears impossible, as it would require a very large container to secure the presence of one salt molecule at such dilution. At even rather less dilution the interaction between the salt and the glass would be a preponderating one. It appears likely that the true limit of any real effect is 1 part in 10^{10} in 10^{12} .

C. IRWIN.

Reaction of blood-pressure to adrenaline in parathyroidectomised animals. R. S. ABRAMSON and E. N. SPERANSKA-STEPANOVA (Ark. Biol. Nauk, 1929, 29, 481—491).—In dogs and cats in which the blood-calcium was lowered by means of injection of oxalate, with or without parathyroidectomy, the adrenaline effect was pronounced regardless of the calcium level. CHEMICAL ABSTRACTS.

Biological detection of adrenaline in drugs, especially in presence of local anaesthetics. A. STASIAK and L. RIGÓ (Magyar Gyó. Táro. Ert., 1930, 6, 389—394; Chem. Zentr., 1930, ii, 2552).—Adrenaline inhibits the spontaneous contractions of the surviving mouse-uterus, whence it can be detected in presence of local anaesthetics and posterior pituitary extract. The sensitivity of the uterus towards adrenaline is increased by novocaine and diminished by β -eucaine and stovaine. A. A. ELDRIDGE.

Influence of adrenaline and insulin on the excretion of sugar from the liver through the bile during continued ingestion of sucrose. N. M. IVANOV (Z. ges. exp. Med., 1930, 71, 263—273; Chem. Zentr., 1930, ii, 2540).—Addition of sucrose (200 g.) to the ordinary diet does not markedly increase the bile-sugar of the dog unless adrenaline is administered simultaneously by subcutaneous injection. After injection of insulin the bile-sugar falls in spite of ingestion of sucrose; insulin causes an increase which appears only when large doses (400 g.) of sugar are administered for a long time.

A. A. ELDRIDGE.

Evaluation of insulin. A. STASIAK and B. ZBORAY (Magyar Gyó. Táro. Ert., 1930, 6, 268—274; Chem. Zentr., 1930, ii, 1897—1898).—Marks' cross test has been simplified. Each animal (2 ± 0.3 kg.) receives 1 international unit administered in the same way; three samples of blood are drawn after 1.5, 3, and 5 hrs., respectively. The original and simplified methods are liable to an average error of 10%. Of 16 commercial preparations 14 gave values within 10% of those declared. A. A. ELDRIDGE.

Insulin. S. NIITSU (Sei-i-kwai Med. J., 1930, 49, No. 2, 1—20).—Subcutaneous injection of insulin in large amount causes a rapid decrease in blood-sugar, the minimum value being reached in 3 hrs. Inorganic phosphorus follows approximately the same course, but becomes normal at the seventh hour. Subarachnoid injection causes more gradual changes. Pituitrin introduced hypodermically produces hyperglycaemia, but a decrease in organic phosphorus; subarachnoid injection of pituitrin causes more marked changes.

CHEMICAL ABSTRACTS.

Effect of insulin. V. M. OGAWA (Folia Pharmacol. Japon., 1929, 9, No. 3, 137—149).—Insulin is destroyed in the rabbit's intestine, but a certain amount is resorbed in the intestinal mucosa. Insulin is destroyed more readily in the duodenum and jejunum on account of the alkalinity and the presence of proteolytic enzymes. CHEMICAL ABSTRACTS.

Effect of insulin, synthalin, and glukhorment on cellular fixation of dextrose. E. B. SALÉN and T. NYRÉN (Acta Med. Scand., 1928, 69, 69—98; Chem.

Zentr., 1930, ii, 2201).—The increase in fixation of dextrose was, respectively, 180, 149, and 140%.

A. A. ELDRIDGE.

Action of proteolytic enzymes on crystalline insulin. A. F. CHARLES and D. A. SCOTT (Trans. Roy. Soc. Canada, 1930, [iii], 24, V, 95—99).—When crystalline insulin is acted on by pepsin or trypsin its physiological activity disappears much more rapidly than does the protein present as indicated by precipitation with 3.3% trichloroacetic acid. It does not appear possible by means of these enzymes to hydrolyse insulin into a physiologically active protein of smaller molecular weight. W. O. KERMACK.

Spectroscopic properties of insulin. H. DES B. SMS and D. A. SCOTT (Trans. Roy. Soc. Canada, 1930, [iii], 24, V, 117—119).—Amorphous and crystalline insulin of activities 13 and 25 units per mg., respectively, placed in the copper arc gave no evidence of inorganic material. The ultra-violet absorption spectrum of crystalline insulin dissolved in 0.001N-hydrochloric acid showed absorption bands centred at 2855 and 2740 Å., and another beyond 2340 Å. Satisfactory X-ray spectra were not obtained from insulin crystals. W. O. KERMACK.

Detection of an insular hormone in the duodenum. N. B. LAUGHTON and A. B. MACALLUM (Canad. Med. Assoc. J., 1930, 23, 348).—Extracts of duodenal mucosa, when injected into normal rabbits or dogs prior to administration of dextrose, diminish the hyperglycaemia; they do not contain insulin, since they do not affect the hyperglycaemia of depancreatized dogs. The extracts do not give protein or peptone reactions, and the active principle is not adsorbed on bone charcoal or fuller's earth; they appear to contain a substance which stimulates the islets of Langerhans. The mechanism of insular failure is discussed.

CHEMICAL ABSTRACTS.

Circulatory hormone. V. An internal secretory function of the pancreas. E. K. FREY, H. KRAUT, and F. SCHULTZ (Arch. exp. Path. Pharm., 1930, 158, 334—347; cf. A., 1930, 1624).—The circulatory hormone (callicrein), identical with that from urine, is found in considerable quantity in normal pancreas and in fluid from pancreatic cysts. The hormone content of the urine of the dog is diminished in a few hours to 15% of its original value by extirpation of the pancreas, but is maintained if extirpation is not quite complete. Although callicrein is chemically different from insulin, some functional similarity between them is observed. Splenectomy causes a temporary and non-characteristic loss of the hormone from the urine, but extirpation of other glands has little effect. A. COHEN.

Action of pituitrin, pitressin, and pitocin on the blood-phosphatides. W. RAAB (Endocrinol., 1930, 14, 150—156).—The effects of pitressin and pitocin are irregular but in general are similar to that of pituitrin in depressing the blood-phosphatides. Injection of egg-yolk did not produce lecithinaemia.

CHEMICAL ABSTRACTS.

Physiological properties of the growth-promoting extracts of the anterior pituitary lobe. H. M. TEEL and H. CUSHING (Endocrinol., 1930, 14, 157—163).—Injection into dogs causes a fall in the

urea-, amino-acid-, and "undetermined" nitrogen, approximately in proportion to the respective concentration. Retention of nitrogen and phosphorus, and increased urinary excretion of calcium, were observed.

CHEMICAL ABSTRACTS.

Ovary-stimulating hormone of the placenta. J. B. COLLIP (Canad. Med. Assoc. J., 1930, 22, 761—764).—Methods for obtaining concentrated placental extracts are described. The yield of product is about 1 mg. per kg. Its potency is unaffected by boiling for 5 min. with dilute acetic acid or by treatment with pepsin or trypsin. In addition to "emmenin," the active fraction contains another hormone or hormones, apparently of protein-like nature.

CHEMICAL ABSTRACTS.

Isolation of the male sexual hormone in a water-soluble crystalline state. B. FRATTINI and M. MAINO (Arch. Ist. Biochim. Ital., 1930, 2, 639—668).—Testes are extracted with boiling 1% acetic acid and the filtrate is treated with magnesium sulphate. The precipitate is extracted with 95% alcohol and the oil obtained by evaporation is emulsified in boiling water (p_H 5) and the mixture filtered. The turbid filtrate is treated with 4% of sodium hydroxide and filtered. The solution, which contains the hormone as a sodium salt, is treated with 1% of copper sulphate and the resultant precipitate, suspended in water, is decomposed with hydrogen sulphide. The ethereal extract of the solution when evaporated deposits the hormone in feathery aggregates of needles, soluble in organic solvents and in water containing a little alkali. The substance contains no nitrogen.

The crystalline substance promotes the growth of the comb and wattles of capons, and causes development of the seminal vesicles in immature or castrated rats. It also causes œstrus in ovariectomised rats and development of the uterus in immature rats. Parallel tests of the crystalline follicular hormone (A., 1930, 505) show that this promotes development of the genital tract in the male. The two hormones thus have in common the power of influencing the genital tract of both sexes, but differ in their effect on secondary sexual characteristics, for the promotion of comb-growth is specific to the male hormone. The œstrogenic action of the testes and urine of males is due to the male hormone, and the presence of the female hormone need not be assumed.

R. K. CALLOW.

Androkinin (male sexual hormone) in male blood. S. LOEWE, F. ROTHSCHILD, W. RAUTENBUSCH, and H. E. VOSS (Klin. Woch., 1930, 9, 1407; Chem. Zentr., 1930, ii, 1868).—Bull's blood contains 1—2 mouse-units of androkinin per litre; with improved methods higher values would probably be obtained.

A. A. ELDRIDGE.

Diazo-reaction of thyroxine and its inhibition by blood-constituents. W. KOMANT (Arch. exp. Path. Pharm., 1930, 158, 116—128).—Thyroxine (and its methyl or ethyl ester), when treated with diazotised sulphanilic acid at p_H 9—10, gives a dark red colour which behaves as an indicator towards acid and alkali. A rose colour is developed at a dilution of 1 in 10^5 . The reaction is not given by the bromine

analogue of thyroxine, nor by 3:5-dichloro- and 3:5-dibromo-tyrosine; 3:5-di-iodotyrosine gives a slight positive reaction. The reaction is inhibited by serum-protein, uric acid, and, to a smaller extent, by some amino-acids. Urine destroys the colour after it has appeared. Additive compound formation between inhibitor and thyroxine is suggested as the cause of inhibition. Simultaneous intravenous injection of thyroxine and serum or glycine into rabbits does not influence the increased oxygen consumption observed with thyroxine alone.

Thyroxine gives green and blue colour reactions with methylene-blue and methyl-violet, respectively.

A. COHEN.

Action of thyroxine. E. ABDERHALDEN and E. WERTHEIMER (Z. ges. exp. Med., 1930, 72, 472—489; Chem. Zentr., 1930, ii, 1567).—Protracted administration of thyroxine to rabbits, guinea-pigs, or rats leads to a diminution almost to zero of the heart muscle-glycogen, large quantities remaining in the liver and skeletal muscle. Differences have been observed between rats and guinea-pigs in the effect on the storage of glycogen of simultaneous administration of dextrose.

A. A. ELDRIDGE.

Effect of substitution in the thyroxine molecule on its action. E. ABDERHALDEN and E. WERTHEIMER (Z. ges. exp. Med., 1928, 63, 557—577; Chem. Zentr., 1930, ii, 1716).—Deiodothyroxine does not affect the metamorphosis of tadpoles or axolotls. Other substances related to thyroxine were active, but the necessary dose was higher than for thyroxine. Iodophenols have no action. Thyreoglobulin, iodoalbumin, and serum-iodoalbumin were active for axolotls, doubtless owing to their content of 3:5-di-iodotyrosine.

A. A. ELDRIDGE.

Hormone of heart motion. XVII. Gastro-intestinal musculature of cold- and warm-blooded animals. L. HABERLANDT (Pflüger's Archiv, 1930, 225, 384—388; Chem. Zentr., 1930, ii, 2147—2148).—The heart hormone (1 in 50—1000) promotes movement of the frog's stomach or of the intestine of warm-blooded animals, and hence differs from adrenaline; the effect is also observed after treatment with atropine.

A. A. ELDRIDGE.

Vitamins of milk and their behaviour towards chemical, physical, and thermal attack. W. WEITZEL (Z. Fleisch. Milchhyg., 1930, 40, 389—393; Chem. Zentr., 1930, ii, 1791).—The vitamin-A, -B, and -C content of milk is increased when green fodder is substituted for dry fodder. Vitamin-C is most sensitive to chemical, physical, and thermal conditions. Lack of vitamin-D can be remedied by ultra-violet irradiation; the vitamin-E content is insufficient.

A. A. ELDRIDGE.

Carotene and vitamin-A. L. K. WOLFF, J. OVERHOFF, and M. VAN ECKELEN (Deut. med. Woch., 1930, 56, 1428—1429; Chem. Zentr., 1930, ii, 2149).—The minimal rat-dose of carotene is 2—3 γ per day. Vitamin-A is not considered to be identical with carotene; both occur in animal products, but the former seldom in plants. Carotene may be converted by the organism into vitamin-A. The determination of vitamin-A in presence of carotene is described.

A. A. ELDRIDGE.

Vitamin-A in serum and liver. B. VON EULER (Svensk Kem. Tidskr., 1930, 42, 302—304).—Vitamin-A has been identified and determined by the antimony trichloride method in ethereal extracts of the serum and liver of rabbits and of the serum of sheep (wethers). The presence of more than traces of carotene to account for the reaction is ruled out. No differences with sex were found in rabbits. The subcutaneous fat gave no reaction.

R. K. CALLOW.

Unsaponifiable material. III. Relation to avitaminosis-A. E. IGARASHI (Sci-i-kwai Med. J., 1930, 49, No. 3, 15—31).—The substance was prepared from various organs by the method previously described (A., 1929, 952, 1328); it is an oil, f. p. 20°, having an acid reaction. In experiments on rats the substance was successfully used as a substitute for vitamin-A.

CHEMICAL ABSTRACTS.

Vitamin-C in sauerkraut. B. A. LAVROV and N. JARUSOVA (Biochem. Z., 1930, 229, 115—127).—As regards its prophylactic antiscorbutic activity, the juice obtained from sauerkraut has about 5—10% of the potency of orange juice and is approximately as potent as unboiled cow's milk.

W. MCCARTNEY.

Effect of vitamin-D supplements on laying hens. J. H. MARTIN, S. E. ERIKSON, and W. M. INSKO, jun. (Kentucky Agric. Exp. Sta. Bull., 1930, No. 304).—Egg production from yearling hens was increased by irradiation, exposure to sunlight, and the addition of 2% of cod-liver oil to the ration. Cod-liver oil used alone had no beneficial effect on pullets. Vitamin-D supplements improved the hardness and thickness of eggshells and improved hatchability. Analyses of bone ash contents and the inorganic phosphorus contents of the blood of chicken are recorded.

A. G. POLLARD.

Assay of irradiated ergosterol. H. NASER (Arch. exp. Path. Pharm., 1930, 158, 201—210).—The method of assay proposed depends on the determination of the increase in inorganic serum-calcium and phosphorus caused by oral administration of irradiated ergosterol to rabbits (cf. Demole and Fromherz, A., 1930, 257). The effect of a dose of about 2 mg. per kg. body wt. can be detected. The calcium content is generally increased by 20—30%, but phosphorus increases more markedly, reaching a value three times as great as the normal on a super-toxic dose (above 10 mg. per kg. body-wt. daily). It is claimed that these effects are observed in 12 hrs., which is much earlier than the appearance of morphological changes.

No calcification is observed when cavities of teeth are filled with irradiated ergosterol.

A. COHEN.

Irradiated ergosterol. A. WINDAUS.—See this vol., 320.

Conversion and action of ergosterol. W. HIRSCH.—See this vol., 320.

Hypervitaminosis in hens. E. J. KING and G. E. HALL (Biochem. Z., 1930, 229, 315—322).—Administration of large harmful overdoses of irradiated ergosterol to hens has only a slight effect on the calcium and phosphorus contents of the blood-serum and causes no deposition of calcium in the organs.

The phosphatase content of the bones and of the kidneys (but not of the intestines) is reduced, as a result of the treatment, to less than half of the normal value.

W. MCCARTNEY.

Feeding power of plants. W. THOMAS (Plant Physiol., 1930, 5, 443—489).—The literature concerning the effects of root exudations, of the reaction of cell-sap, of the permeability of the root-cell membranes, and other factors on the rate and extent of the intake of minerals by plants is critically discussed. An extensive bibliography is appended.

A. G. POLLARD.

Conception of balance with respect to the absorption of nitrogen, phosphorus, and potassium by plants and the influence of the level of nutrition. W. THOMAS (Science, 1930, 72, 425—427).—A discussion.

L. S. THEOBALD.

Salt permeability of protoplasts. H. WEINL-HOFMANN (Protoplasma, 1930, 11, 210—277).—The course of the plasmolysis of the red epidermal cells of *Lamium purpureum* by hypertonic solutions of potassium chloride (0.2—0.5M) is examined, together with the effect of more concentrated solutions of potassium chloride alone and mixed with calcium chloride on the permeability of the cells and the nature of the plasmolytic effects.

A. G. POLLARD.

The plasmolysis of algal cells. B. VON CHOLNOKY (Protoplasma, 1930, 11, 278—297).—Addition of cocaine to plasmolytic solutions increased the permeability of the cells. Characteristic differences occur in the effect of cocaine on mother and daughter cells.

A. G. POLLARD.

Relationship between the concentration of the soil solution and the physico-chemical properties of the leaf tissue fluids of cotton. J. A. HARRIS and T. A. PASCOE (J. Agric. Res., 1930, 41, 767—788; cf. B., 1926, 842).—A positive correlation is established between the f.p. depression, specific conductivity, the chloride and sulphate contents of the leaves of cotton, and the conductivity and chloride and sulphate contents of the soil in which they are grown.

A. G. POLLARD.

Hydrogen-ion concentration and buffer action of the expressed sap of maize. J. D. SAYRE (Ohio Agric. Exp. Sta. Bull., 1930, No. 446, 38—39).—The sap of the sheath tissues of maize was more acid than that from any other part of the plant. The buffer effect of leaf-blade and sheath sap averaged 5—6 times that of stems. The phosphate, nitrate, total nitrogen, amino-acid, and colloidal contents and the conductivity of leaf-blade sap were higher than those of stems, but the sugar content was lower. There is no relationship between the p_H or total acidity of the sap and infestation by the European maize borer.

A. G. POLLARD.

Cambium and its derivative tissues. VI. Effect of hydrogen-ion concentration in vital staining. I. W. BAILEY and C. ZIRKLE (J. Gen. Physiol., 1931, 14, 363—383).—Two types of vacuole (A, B) occur, each with distinct staining properties. Auramine and many thiazine dyes stain both types, although type B rarely stains on the acid

side of p_H 5.4—5.8. Many azo-dyes and dyes of the acridine and triphenylmethane series accumulate only in type A vacuoles, whilst the effect of the external p_H is variable. A third group of dyes has no staining effect on either type A or B at any external p_H unless injury has previously taken place. The p_H of the contents of the vacuoles is an important factor in vital staining. P. G. MARSHALL.

Necessity and function of manganese in the growth of *Chlorella* sp. E. F. HOPKINS (Science, 1930, 72, 609—610).—Manganese, as well as iron, is essential for growth of *Chlorella* sp.; at p_H 7.0, the increase in growth due to manganese is about 17-fold, and at p_H 8.0 about 170-fold. The optimum concentration of manganese is approximately 1 in 5×10^6 and at higher concentrations (1 in 5×10^4) a toxic effect becomes pronounced. The manganese appears to function by controlling the ratio of ferrous to ferric iron. L. S. THEOBALD.

Changes in the phosphorus content of growing mung beans. J. E. WEBSTER and C. DALBOM (J. Agric. Res., 1930, 41, 819—824).—The inorganic phosphorus content of any particular organ of the mung bean remains practically constant after the early stages of growth. Phosphorus is stored in the tissues in an organic form. The amount of lipid phosphorus in green tissue is very small and varies but little during growth. Variations of 2—3 weeks in the time of harvesting do not involve appreciable alterations in the total phosphorus content of the crop. There is no indication of the translocation of phosphorus from leaves to stems. Localisation of phosphorus probably follows the normal ash intake and is not the outcome of metabolic changes.

A. G. POLLARD.

Natural chemical equilibrium regulative of growth by increase in cell number. F. S. HAMMETT (Protoplasma, 1930, 11, 382—411).—The growth of plant and animal tissue involving increased cell numbers is considered as a manifestation of chemical reactions and governed by the laws of chemical equilibrium. The thiol group in chemical compounds is a specific stimulant of cell division and its partly oxidised reaction products specifically retard cell increase. The oxidation process is induced by living protoplasm, of which both types of sulphur compounds are natural constituents.

A. G. POLLARD.

Diastatic and peroxidative activity of plants as influenced by external factors. H. KERN (Z. Bot., 1928, 21, 193—252; Chem. Zentr., 1930, ii, 412—414).—The maximum diastatic activity of maize seedlings is observed 5—12 days after germination; maintenance at 60° considerably decreased the activity. Removal of water in a desiccator increased the saccharifiability in the whole seedling as well as in the root tips. Differences in the diastatic properties of the whole seedling and the root tips under different conditions of treatment are recorded. Ether narcosis diminishes the starch-forming power of the leaves and promotes the degradation of starch. The peroxidase activity was maximal after 8—9 days' germination. Moist heating at 50° diminished the peroxidase activity of the whole seedling and that

of the root tips; dehydration in a desiccator also diminished the peroxidase activity.

A. A. ELDRIDGE.

Distribution of dry matter and carbohydrates in the maturing maize stem. V. H. MORRIS and E. A. WELTON (Ohio Agric. Exp. Sta. Bull., 1930, No. 446, 39—40).—Examination of sections of growing maize stems from the lowest joint upwards shows an increasing dry matter and sucrose content and a decreasing proportion of reducing sugars. Periodical analyses of the whole stem from the period of tasselling to maturity show a progressive increase in dry matter and sucrose contents and a decline in the amount of reducing sugars with age. More than half of the total amounts of these constituents of the stem are situated in the lower four joints. This may be associated with the tendency of the maize borers to work in the lower portions of the stems.

A. G. POLLARD.

Effects of defloration on fruit-spur composition and fruit-bud formation in the Oldenburg apple. G. F. POTTER, H. R. KRAYBILL, S. W. WENTWORTH, J. T. SULLIVAN, and P. T. BLOOD (New Hamps. Agric. Exp. Sta. Tech. Bull., 1930, No. 41, 25 pp.).—Comparison is made of the chemical composition of fruiting and non-fruiting spurs and of deflorated spurs of apples. The nitrogen content is highest and the starch content lowest in fruiting spurs, the proportions in deflorated spurs being affected by the presence of adjacent fruiting spurs. Among the three types of spurs, no consistent differences were observed in the contents of reducing substances, sucrose, or phloridzin. Variations in the phosphorus contents were similar to those of nitrogen. Ash constituents were lower in fruiting spurs than in others. During ripening of the fruit there is a steady increase in the proportions of sucrose and reducing sugars (which predominate) which considerably exceeds the corresponding change in the spur. The starch content of the spur always exceeds that of the fruit. Phloridzin is persistent in spurs but gradually disappears from maturing fruit. The percentage of nitrogen in the fruit, initially greater than in the spur, steadily declined with maturation to a very small figure.

A. G. POLLARD.

Composition of, and fruit-bud formation in, non-bearing spurs of the Baldwin apple. G. F. POTTER and T. G. PHILLIPS (New Hamps. Agric. Exp. Sta. Tech. Bull., 1930, No. 42, 43 pp.).—Relationships between fruit-bud formation and the chemical constituents of the spurs were examined. Conditions leading to the accumulation of insoluble nitrogen compounds in the spur were also those favouring fruit-bud formation. Accumulation of soluble carbohydrates in the spur is associated with decreased fruit-bud formation (cf. Kraybill *et al.*, *ibid.*, Bull. 29, 1925).

A. G. POLLARD.

Distribution of saponin in plants during different stages of maturity. L. KROEBER (Heil-Gewürz-Pflanzen, 1930, 12, 131—137; Chem. Zentr., 1930, ii, 76).—In *Saponaria*, the saponin content increases in the order leaves, roots, and flowers, and it also increases with the development of the plant. In August, the root contains twice as much saponin

as in November. Quick drying at 55° yields a stronger drug than is obtained by drying at the ordinary temperature. *Solidago serotina* is a saponin plant of unusually high hæmolytic titre and the highest saponin content appears in the leaves.

L. S. THEOBALD

Stimulatory effects of ultra-violet radiation on higher plants. H. J. FULLER (Science, 1930, 72, 535—536).—When irradiated for 5 weeks by a quartz mercury vapour arc at a distance of 100 in. tomatoes and cucumbers show increased growth. The former show an increase of 33% over controls and the latter about 34%. The dry weight percentages of wet and ash weight percentages of dry weight are also greater by 19 and 13%, respectively, in the case of tomatoes. Filters transmitting wave-lengths of 313 m μ and 289 m μ were employed. L. S. THEOBALD.

Active constituents of Korean *Ledum palustre*. H. SUZUKI (Folia Pharmacol. Japon., 1930, 9, 297—309).—The oil (yield 0.43%) has *d* 0.9987, b. p. 130—195°/80 mm. Its physiological effects are described.

CHEMICAL ABSTRACTS.

Jegosaponin, an active constituent of *Styrax Japonica*. Saponin-cholesterol combination. T. KONDO (Folia Pharmacol. Japon., 1930, 9, No. 4, 256—261).—The preparation of a jegosaponin-cholesterol, comparable with Windaus' digitonin-cholesterol, is described. The compound has m. p. 297° and appears to be a chemical individual; it has no hæmolytic effect on red blood-cells.

CHEMICAL ABSTRACTS.

Constituent of the rhizome of *Cimicifuga fatida*, L., var. *intermedia* regel. K. OGIC (Folia Pharmacol. Japon., 1930, 10, 11—12).—*Cimitin*, C₂₀H₃₄O₇, precipitated on dilution of the methyl-alcoholic extract (after preliminary extraction with ether and benzene), and recrystallised from hot 70% acetone, has m. p. 169°, decomp. 175°.

CHEMICAL ABSTRACTS.

Japanese persimmon grown in Florida. I. Analysis. J. TILT and R. B. HUBBELL. II. Vitamin-B complex. J. TILT, R. B. HUBBELL, and L. INMAN (J. Home Econ., 1930, 22, 757—762, 762—765).—Analysis gave: water 76.27—81.71, reducing sugar 11.53—17.39, protein 0.43—0.87, ash 0.30—0.58, fibre 0.11—0.49%; the ash contained calcium, phosphorus, magnesium, sulphur, iron, copper, and manganese. The Tane Nashe variety is a poor source of vitamin-B.

CHEMICAL ABSTRACTS.

Constituents of the root of *Lindera strychnifolia*, Vill. II. H. SUZUKI (J. Pharm. Soc. Japan, 1930, 50, 714—720).—The unsaponifiable oil (Kondo and Sanada, *ibid.*, 1925, No. 526, 1047), C₁₅H₁₈O₂, b. p. 158°/5 mm., [α]_D²⁰ —83° 1' (in acetone), contains a double linking; it does not contain a hydroxyl group or form an oxime or semicarbazone. On catalytic reduction it forms a compound, b. p. 129—132°/5 mm., [α]_D²⁰ —16° 36'. Catalytic reduction of linderan affords a compound, m. p. 211°.

CHEMICAL ABSTRACTS.

Esculetin dimethyl ether, a constituent of the fruit of *Artemisia capillaris*. I. S. SERA and C. SHIBUYE (J. Agric. Chem. Soc. Japan, 1930, 6, 600—609).

CHEMICAL ABSTRACTS.

Constituents of *Patrisia acuminata*. K. W. MERZ (Arch. Pharm., 1930, 268, 592—593).—The root contained nothing volatile in steam, even in presence of alkali. Aqueous tartaric acid extracts a syrup containing an acidic substance, m. p. 268—270° (decomp.), physiologically inactive, but no alkaloid. A 10% alcohol extract yields, after purification with lead acetate, a hygroscopic material which is four times as toxic as the original drug.

H. E. F. NOTTON.

Vegetable proteins. I. Proteins of *Dolichos lab lab*. D. NARAYANAMURTI and C. V. RAMASWAMI (Biochem. J., 1930, 24, 1650—1654).—The nitrogen of the globulin dolichosin forms about 80% of the nitrogen of the meal of *D. lab lab*. The best yield is obtained when the meal is extracted with four parts of water. The nitrogen distribution and the nutritionally essential amino-acids have been determined. The nutritional value of dolichosin as deduced from its composition is higher than that of other globulins. A method in which the extract is subjected to electrodialysis in order to avoid tyrosinase action is described.

S. S. ZILVA.

Hydrogen cyanide. XXVI. New occurrences [in plants]. L. ROSENTHALER (Pharm. Acta Helv., 1929, 4, 196—199; Chem. Zentr., 1930, ii, 932).—Additional occurrences of hydrogen cyanide in plants (12) are recorded.

A. A. ELDRIDGE.

Hydrogen cyanide. Detection of substances which combine with hydrogen cyanide in distillates containing hydrocyanic acid. L. ROSENTHALER (Pharm. Acta Helv., 1929, 4, 62—63; Chem. Zentr., 1930, i, 3086).—A method for determining whether distillates contain combined as well as free hydrogen cyanide is described. No combined hydrogen cyanide is present in the distillate obtained from *Schleichera trijuga*.

L. S. THEOBALD.

Soya-bean lecithins. I. Separation of α - and β -series. B. SUZUKI and Y. YOKOYAMA (Proc. Imp. Acad. Tokyo, 1930, 6, 341—344).—Experimental details are given for the isolation of lecithins from an alcoholic extract of soya beans as cadmium chloride double salts, from which fatty acids (saturated 44%, unsaturated 56%), α - and β -glycerophosphoric acids, and choline are obtained. The saturated acid is palmitic acid, and the unsaturated fraction contains oleic acid (47% of total acids), and smaller quantities of two acids which, on bromination, yield hexa- and tetra-bromostearic acids, m. p. 177—178° and 112—113°, respectively. Separation of the cadmium chloride salts of the α - and β -lecithins is effected by acetone, in which the α -complex is far less soluble. From the α -lecithins palmitic, di-, tetra-, and hexa-bromostearic acids have been obtained in the proportions 24.3, 32.4, 44.2, and 1.1%, whilst in the β -series the proportions are 20.1, 53.8, 24.8, and 1.4%.

A. COHEN.

Anthocyanins. L. W. KUILMAN (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 876—888).—The relations between anthocyanins and the assimilation process in plants are discussed. It is not possible to establish a lower assimilation value for cells containing anthocyanins, except when those cells have also a lower content of chlorophyll.

E. S. HEDGES.

Colouring matters of red grapes and wines. L. CASALE (Annali Chim. Appl., 1930, 20, 559—566).—Variations in the colour of the colouring matter of the red grape as a result of salification are related to the amphoteric character of the colouring matter. The isoelectric point of oenin chloride (cf. Willstätter and Zollinger, A., 1915, i, 286) lies between p_H 5.4 and 5.8, and the two dissociation constants corresponding with the acid and basic forms are about $10^{-7.66}$ and $10^{-10.88}$, respectively. T. H. POPE.

Blossom xanthophylls. Pigment of the sunflower. L. ZECHMEISTER and P. TUZSON (Ber., 1930, 63, [B], 3203—3207).—The isolation is described from the blossoms of *Helianthus annuus* of a colourless, crystalline, sterol-like compound and of a pigment, $C_{40}H_{56}O_2$, m. p. 195° , $[\alpha]_D^{25} +75^\circ$ in chloroform, identical with the lutein from egg-yolk. It is established that in the normal green leaf more than one type of xanthophyll, in addition to carotene and chlorophyll, exists, whereas the blossom pigments are either a mixture of xanthophylls comparable with that in the leaf or an individual xanthophyll. The use of the polarimeter for distinguishing between the different varieties of xanthophyll is advocated. H. WREN.

Degradation of nicotine in tobacco. A. FODOR and A. REIFENBERG (Biochem. Z., 1930, 228, 327—328).—The results of Faitelowitz (A., 1930, 1484) cannot be confirmed and his explanations are rejected. The process is not bacterial. W. MCCARTNEY.

Alterations occurring in the nitrogenous constituents of tobacco during air-drying. A. J. SMIRNOV and V. P. IZVOSCHIKOV (Biochem. Z., 1930, 228, 329—353).—During air-drying the amounts of proteins, polypeptides, nicotine, ammonia, and other bases and of other nitrogenous compounds in tobacco leaves undergo considerable variations. The mechanism of these changes and their connexion with the physiological processes which occur during drying are discussed. W. MCCARTNEY.

Influence of mosaic disease on nicotine content of the tobacco plant. K. SILBERSCHMIDT (Ber. deut. bot. Ges., 1930, 48, 122—129).—The nicotine content of tobacco leaf is increased by 40—100% in mosaic disease. A rise is also observed in leaves growing after inoculation of the plant with virus sap, and in cut leaves in the absence of sunlight. This is discussed in relation to a possible plant synthesis of nicotine from nitrous acid and formaldehyde. A. COHEN.

Fluorescence analysis of plants. G. KLEIN and H. LINSE (Oesterr. Bot. Z., 1930, 79, 125—163; Chem. Zentr., 1930, ii, 1257).—The fluorescence in ultra-violet light of various plant organs has been observed and compared with that of organic substances. The distribution of aesculin and fraxin in *Aesculus hippocastanum* can thereby be determined. A. A. ELDRIDGE.

Analysis of metachromatic colorations of plant tissues by organic dyes. A. T. CZAJA (Ber. deut. bot. Ges., 1930, 48, 100—104).—A substantive dye in colloidal solution is fractionally

filtered by the cell-walls of plant-tissue. Different types of tissue, under the action of a single dye, may pass and retain fractions of different degrees of dispersion, resulting in different colourings. Basic dyes behave as indicators, and the colour of the tissue depends on the p_H of the cell-wall. A. COHEN.

Hydroxyquinoline sulphate as a preservative for plant tissues. C. F. SWINGLE (Bot. Gaz., 1930, 90, 333—334).—Botanical specimens are covered with water and hydroxyquinoline sulphate is added to make a solution of 0.1—1%. The preservative inhibits bacterial action, does not penetrate the tissues, and its action is not affected by exposure to the atmosphere. Precipitates are formed with iron salts. A. G. POLLARD.

Use of uricase-free seed of *Soya hispida*. Determination of allantoin. R. FOSSE, A. BRUNEL, P. DE GRAEVE, P. E. THOMAS, and J. SARAZIN (Compt. rend., 1930, 191, 1388—1390).—For recognition of allantoin in a dilution of 1:100,000 the solution is warmed with soya extract, containing no uricase, at 40° for 30 min. in the presence of chloroform. 1.0N-Hydrochloric acid is added to the filtrate to bring the normality to 0.1N and the liquid heated for 1 min. at 100° . To the warm solution 1% phenylhydrazine hydrochloride (4 drops per c.c.), 5% potassium ferricyanide (2 drops per c.c.), and concentrated hydrochloric acid (2.5 c.c. per c.c.) are added, when a red colour develops. For characterisation of allantoin in blood the proteins are removed by means of trichloroacetic acid and the above procedure is applied to the filtrate. A larger amount of potassium cyanide is required to inhibit the production of allantoinic acid from uric acid by uricase when allantoin is present than in its absence. P. G. MARSHALL.

Micro-determination of iodine in organic substances. L. SCHEFFER (Biochem. Z., 1930, 228, 426—436).—Organic matter in the dried finely-powdered material is destroyed by heating at 250 — 300° in a nickel crucible on a sand-bath for several hours with potassium hydroxide, potassium nitrate being added if desired. The iodine in the residue is extracted with alcohol after all potassium hydroxide has been converted into carbonate by treatment with saturated ammonium carbonate solution and subsequent evaporation of all ammonia, and the alcoholic solution is evaporated to dryness without being allowed to boil. The residue is again heated for 10—30 min. in a porcelain crucible with potassium hydroxide solution, the product is extracted with water, and the extract acidified with nitric acid. Nitrite solution is then added and the mixture extracted with carbon tetrachloride. When the solution in this solvent is shaken with dilute phosphoric acid and saturated bleaching-powder solution the iodine is converted into iodate, which is determined, after concentration of the solution, by addition of potassium iodide and titration with sodium thiosulphate solution. Complete destruction of organic matter is not essential provided that the residue is moistened with warm water before being extracted with alcohol. W. MCCARTNEY.