

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1931.

General, Physical, and Inorganic Chemistry.

Under-water spark spectra in the infra-red. B. SETNA (Indian J. Physics, 1931, 6, 29—34).—The spectra of condensed discharge under H_2O between Cu, Zn, Cd, Fe, W, and Mo electrodes have been studied in the visible and infra-red up to 0.85μ .

A. J. MEE.

"Ultimate" radiations of condensed spark spectra. T. NEGRESCO (Bull. Mat. Phys. Ecole Poly. Bucarest, 1931, 11, 93—94).—High-potential radiations, not recorded among existing data for ultimate radiations, emitted by atoms in various states of ionisation have been found for many elements.

N. M. BLIGH.

Appearance of spectral lines in a condensed spark. H. V. KNORR (Physical Rev., 1931, [ii], 37, 1611—1621).—The variation of intensity of lines with time after the beginning of the spark, measured photometrically, gave results not in agreement with those obtained visually by the Kerr cell method. The order of appearance was, by the former method: air lines excited in the spark gap; spark lines; arc lines of Cd; arc lines of Zn.

N. M. BLIGH.

Edge discharge and edge breakdown. L. INGE and B. WUL (Naturwiss., 1931, 19, 424—425).—The dependence of breakdown on edge discharge is experimentally investigated for glass plates 1.4 mm. thick in liquid media of differing dielectric const.

W. GOOD.

Quantitative spectral analysis by means of the negative glow of an arc. R. MANNKOPFF and C. PETERS (Z. Physik, 1931, 70, 444—453).—The spectrum of most substances is enhanced near the cathode of an arc, and this allows the measurement of smaller quantities than the ordinary method.

A. B. D. CASSIE.

Intensity and natural width of spectral lines. E. F. M. VAN DER HELD (Z. Physik, 1931, 70, 508—515).—Theoretical.

A. B. D. CASSIE.

Field distribution and sources of error in the Stark effect using the Lo Surdo method. W. STEUBING (Ann. Physik, 1931, [v], 10, 296—310).—The relative advantage and disadvantages of the Lo Surdo method are discussed. Good spectrograms can be obtained only by keeping pressures, discharge voltage, current strength, and other conditions const. during the whole exposure.

A. J. MEE.

Application of the slitless spectrograph to the measurement of the Doppler shift. N. DEISCH (J. Opt. Soc. Amer., 1931, 21, 248—249).—A supplementary note (cf. this vol., 135).

W. GOOD.

Zeeman effect with high-frequency [discharge]. L. BLOCH, E. BLOCH, E. ESCLANGON, and P. LACROUTE (Compt. rend., 1931, 192, 1717—1720).—The electrodeless discharge was used. Good results were obtained with Hg and Ne in a field of 26,250 gauss.

C. A. SILBERRAD.

Temperature of the electric arc and the Saha theory. L. S. ORNSTEIN and H. BRINKMAN (Naturwiss., 1931, 19, 462—463).—Spectra from arcs of different composition are those to be expected from the Saha theory.

W. R. ANGUS.

Widths of the lines in the B band, due to atmospheric oxygen in the solar spectrum. R. VAN DER R. WOOLLEY (Astrophys. J., 1931, 73, 185—193).—Measurements of lines in the B band in the solar spectrum show that the width is not in agreement with Unsöld's formula.

L. S. THEOBALD.

Molecular spectra in sun-spots. R. S. RICHARDSON (Astrophys. J., 1931, 73, 216—246).—Many lines in certain bands of TiO, MgH, and CaH have been identified with lines in the solar spectrum. Evidence for the presence of SiF, AlO, AlH, ZrO, and H_2 in sun-spots and the reversing layer is also given. MgH probably exists in the reversing layer, whilst TiO is probably confined entirely to sun-spots. Both the Swan bands of C and the TiO bands are present in the spot spectrum.

L. S. THEOBALD.

Interpretation of spectrophotometric observations of weak Fraunhofer lines. R. VAN DER R. WOOLLEY (Astrophys. J., 1931, 73, 194—204).—The legitimacy of inferring a number of atoms from observations of line width or equiv. breadth of a weak Fraunhofer line is discussed.

L. S. THEOBALD.

Emission spectrum of compressed hydrogen and some pressure phenomena in metal vapour spectra. W. FINKELNBURG (Z. Physik, 1931, 70, 375—394).—Spark discharges were observed in H_2 at pressures between 1 and 30 atm. Broadening of Balmer lines can be accounted for by the interat. Stark effect of fields between 2×10^5 and 2×10^6 volts per cm. Spectra due to Fe, Al, and Cu, vaporised from the electrodes, showed broadening proportional to the partial pressure of the metal vapour, and this is dependent on the total pressure.

A. B. D. CASSIE.

Continuous spectrum of the hydrogen molecule. D. CHALONGE (Compt. rend., 1931, 192, 1551—1553; cf. A., 1930, 1073).—A further elabor-



ation with illustrative curves of deductions previously arrived at.

C. A. SILBERRAD.

Relationships between the continuous and the many-lined spectra of hydrogen. II. Y. HUKUMOTO (Sci. Rep. Tôhoku, 1931, 20, 178—196).—Apparatus, procedure, results, and discussion of spectroscopic examination of the light emitted from the various types of strata in the striated discharge in H_2 .

W. GOOD.

Stark effect in the Balmer series of hydrogen. K. SJÖGREN (Naturwiss., 1931, 29, 640).—A determination of the abs. value of the Stark effect in the Balmer series of hydrogen.

A. B. D. CASSIE.

Asymmetry observed in the Stark components of H_α . D. R. McRAE (Proc. Roy. Soc., 1931, A, 132, 257—265).—With the exception of certain unexplained discrepancies, the asymmetry observed in the displacements of the Stark components of H_α is in qual. agreement with the calculations of Schlapp (A., 1928, 806).

L. L. BIRCUMSHAW.

Excitation of the secondary and Balmer spectrum of hydrogen by electronic impact in molecular hydrogen and by protons of high velocity. L. S. ORNSTEIN, A. A. KRUTHOF, and W. A. M. DEKKERS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 610—614).—Excitation curves for singlet and triplet lines in the secondary spectrum of H_2 and for Balmer lines excited in mol. H_2 are given and discussed.

W. R. ANGUS.

Structure of the helium arc line 3888. R. C. GIBBS and P. G. KRUGER (Physical Rev., 1931, [ii], 37, 1559—1561).—Three components, predicted by theory, were found.

N. M. BLIGH.

Excitation potentials of metallic lithium. H. W. B. SKINNER (Nature, 1931, 128, 114).—Photoelectric measurements give a val. of approx. 5.3-5 volts for the min. excitation potential for the K -radiation of Li metal.

L. S. THEOBALD.

Intensity measurements in the band spectrum of lithium. W. R. VAN WIJK and A. J. VAN KEVERINGE (Proc. Roy. Soc., 1931, A, 132, 98—107).—The measured intensity ratio of the strong to the weak rotational lines in the bands 4900, 4838, and 6554 Å. is 1.63, in agreement with the value given by Harvey and Jenkins (A., 1930, 649). For band 4900 Å. the ratio of the Q to the P lines is 2.0. From the optical determination of the relative abundance of the isotopes the ratio of Li^7 to Li^6 atoms is 7.2 : 1; the ratio calc. from the at. wts. is 13 : 1.

L. L. BIRCUMSHAW.

Some "brush" bands of the negative nitrogen group. D. COSTER and H. H. BRONS (Z. Physik, 1931, 70, 492—497).—Two N_2^+ bands degraded towards the red were photographed under high dispersion and are shown to belong to the same electronic transition as bands degraded towards the violet (cf. A., 1928, 808).

A. B. D. CASSIE.

Absorption spectrum of oxygen at high temperatures. D. MALAN (Compt. rend., 1931, 192, 1720—1721).—The absorption spectrum of O_2 at 1400° indicates no formation of O_3 , but extension of the absorption bands as far as 2500 Å. The heads of

24 overlapping bands were observed between 2160 and 2360 Å.

C. A. SILBERRAD.

Difference in the self-reversal of neon lines excited by direct and alternating currents. II. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1931, 7, 192—194).

N. M. BLIGH.

Zeeman effect in the noble gas spectra in connexion with "anomalous" coupling of quantum vectors. C. J. BAKKER (Arch. Neerland., 1931, [III A], 13, 121—195).—Experimental details for investigating the Zeeman effect in the spectra of ionised inert gases are described. Results for the Zeeman effect in the spectra of Ne II, A II, Kr II, and Xe II are given and discussed.

W. R. ANGUS.

Intensity anomalies in rare gas spectra. E. RASMUSSEN and H. SWENSON (Nature, 1931, 128, 188).—Intensity irregularities parallel with deviations in term values have been observed in the spectra of A and Kr.

L. S. THEOBALD.

Spectrum of Na II. S. FRISCH (Z. Physik, 1931, 70, 498—507).—The spark spectrum due to Na II was excited in a discharge tube and investigated under high dispersion.

A. B. D. CASSIE.

Resonance spectrum of sulphur vapour. J. FRIDRICHSON (Z. Physik, 1931, 70, 463—467).—Investigation of the variation with pressure of the relative intensity of the 3132 and 3126 Å. doublet series suggests that the accepted allocation of this doublet is incorrect.

A. B. D. CASSIE.

Accommodation coefficients of positive ions of argon, neon, and helium. C. C. VAN VOORHIS and K. T. COMPTON (Physical Rev., 1931, [ij], 37, 1596—1610; cf. A., 1927, 1001).—The heat produced by positive ions striking a collector and being neutralised at its surface is much less than the equiv. of the kinetic energy which they should acquire from the attracting field. Correcting for energy scattering at collisions and the effect of secondary electron emission, the accommodation coeffs. are: A 0.75 ± 0.05, Ne 0.65 ± 0.05, He 0.35—0.55 ± 0.05.

N. M. BLIGH.

Band spectra of zinc hydride. M. FUKUDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 227—245).—The results of investigations on the band spectrum of ZnH are given and discussed.

W. GOOD.

Multiplets in the spark spectrum of bromine (Br II). L. BLOCH, E. BLOCH, and P. LACROUTE (Compt. rend., 1931, 193, 232—233).—By the method previously described (cf. this vol., 991) two triplets belonging to the system of quintuplets of Br II have been measured. Deb's results are not confirmed (cf. A., 1930, 651).

C. A. SILBERRAD.

Third spark spectrum of krypton. D. P. ACHARYA (Indian J. Physics, 1931, 6, 35—39).—Some of the lines previously published in the list of the second spark spectrum of Kr are classified, and are due to the different transitions of Kr^{++} . Only quadruplets have been discovered.

A. J. MEE.

Absorption spectrum of rubidium vapour. S. DATTA and H. S. MAITRA (Z. Physik, 1931, 70, 548—551).—The absorption spectrum of Rb vapour was

measured between 3000 and 8000 Å., and is arranged in term series.

A. B. D. CASSIE.

Interferometric wave determinations of the Bergmann series and secondary series of rubidium. R. RAMB (Ann. Physik, 1931, [v], 10, 311—324).—The Rb spark spectrum was investigated within the range 5169—10075 Å. From the course of the $\Delta\nu$ of the Bergmann series it may be concluded that the F -term is also inverted.

A. J. MEE.

Structure of the F -term of rubidium. K. W. MEISSNER and O. MASAKI (Ann. Physik, 1931, [v], 10, 325—328).—The conclusion of Ramb (cf. preceding abstract) on the inversion of the F -term is further investigated.

A. J. MEE.

Hyperfine structure of spectrum lines of silver arc in the visible and ultra-violet regions. W. MOHAMMAD and P. N. SHARMA (Indian J. Physics, 1931, 6, 75—80).—The lines are classified and a term scheme is drawn up.

A. J. MEE.

Vibrational analysis of antimony oxide bands. B. C. MUKHERJI (Z. Physik, 1931, 70, 552—558).—The band spectrum of Sb_2O_3 was photographed between 3300 and 8000 Å. and analysed; the heat of dissociation of the ground state is 3.5 volts.

A. B. D. CASSIE.

Nuclear moment of caesium and lead. H. KOPFERMANN (Naturwiss., 1931, 19, 675—676).—The spectrum of Cs^+ has been investigated in the visible; it has a complicated hyperfine structure. The lines of wave-lengths 5371, 4953, 4527, and 5274 Å., however, have especially simple hyperfine structure. The rotation impulse of the Cs nucleus, i , must either be equal to or greater than 2. From the interval rule it is either $7/2$ or $9/2$, but it is not possible to say with certainty which of the two is correct. The spectrum of Th-Pb is also mentioned. The extraordinarily great displacement of the hyperfine structure of Pb^{208} is definitely proved.

A. J. MEE.

Arc spectrum of rhenium. W. F. MEGGERS (Bur. Stand. J. Res., 1931, 6, 1027—1050).—The arc and spark spectra from 2100 to 8800 Å. have been photographed, and more than 3000 new lines have been recorded. Hyperfine structure is observed. About 500 lines have been classified as combinations of 115 levels belonging to quadruplet, sextet, and octet systems. The ultimate line is that at 3460.47 Å. The lowest term corresponds with an ionisation potential of 7.85 volts.

H. F. GILLBE.

Luminous vapours from the mercury arc. M. RAM and K. C. NANDA (Indian J. Physics, 1931, 6, 15—27).—The luminosity of the Hg vapour distilled from the Hg arc is due to the presence of positively-charged Hg atoms. The life of the afterglow is 0.03 sec., so that the particles present in the afterglow are probably metastable Hg atoms.

A. J. MEE.

Bands near the resonance line of mercury. H. HULUBEI (Compt. rend., 1931, 193, 154—156).—Re-examination of spectrograms of the emission of a Hg lamp burning in H_2O has shown numerous bands near the resonance line (cf. this vol., 276).

C. A. SILBERRAD.

Nuclear moment and explanation of hyperfine structure of mercury. H. SCHULER and J. E. KEYSTON (Naturwiss., 1931, 19, 676).—The nuclear moment of Hg^{199} is 0.5; that of Hg^{201} is 1.5. The theoretical hyperfine structure is worked out, and the results agree with experiment.

A. J. MEE.

Intensity of absorption of the 2537 Å. line by dissolved mercury. H. REICHARDT (Z. Physik, 1931, 70, 516—518).—Hg absorbs the 2537 Å. line with equal intensity whether free or dissolved in hexane.

A. B. D. CASSIE.

Hyperfine structure of Tl II. J. C. MCLENNAN and M. F. CRAWFORD (Proc. Roy. Soc., 1931, A, 132, 10—21).—From a consideration of the observed intensities and separations of the components of the hyperfine multiplets, an interpretation of the hyperfine structure of Tl II has been deduced. The analysis confirms the term classification previously given (A., 1929, 1354). No evidence is found for the existence of isotopes.

L. L. BIRCUMSHAW.

Applications of the differential filter method of obtaining monochromatic X-rays. H. KÜSTNER (Z. Physik, 1931, 70, 468—491; see below).—The method was applied to determination of the absorption coeff. of Sn and to determination of electron emission by Ta and W at different wave-lengths, and to an investigation of the relative intensities of the Cu series.

A. B. D. CASSIE.

Relation between the K -absorption edge and the $K\beta_2$ line of nickel, copper, and zinc. S. KAWATA (Mem. Coll. Sci. Kyoto, 1931, A, 14, 55—57).—Experimental.

W. GOOD.

Influence of temperature on K -absorption of iron. J. D. HANAWALT (Z. Physik, 1931, 70, 293—305).—Fine structure at 10—20 volts on the short-wave side of the Fe K -absorption edge moves away from the edge as temp. is raised, and disappears completely at 800°. Monat. gases show no such effect.

A. B. D. CASSIE.

Absorption coefficient for X-rays near the K -absorption edge of Cu and Zn. D. COSTER and J. VELDKAMP (Z. Physik, 1931, 70, 306—316).— K -Absorption edges of Cu and Zn show max. and min. which diminish in intensity and become further apart as the distance from the edge increases.

A. B. D. CASSIE.

Fine structure in X-ray absorption spectra. R. DE L. KRONIG (Z. Physik, 1931, 70, 317—323).—Fine structure described in the two preceding abstracts does not arise in double electronic transitions, but in the discrete zones that an electron may occupy when moving in the periodic potential field of a crystal.

A. B. D. CASSIE.

Intense monochromatic X-ray beams obtained without a spectrometer. H. KÜSTNER (Z. Physik, 1931, 70, 324—347).—A difference method of distinguishing characteristic from scattered radiation by means of filters is described.

A. B. D. CASSIE.

X-Ray wave-length change by partial absorption. J. M. CORK (Physical Rev., 1931, [ii], 37, 1555—1558; cf. this vol., 277).—The change of wave-length reported by Ray (cf. A., 1930, 1334) on

passing an X-ray beam through an absorber was not observed in *L*-radiation through B, Be, C, N₂, and O₂.
N. M. BLIGH.

Effect of chemical combination on the X-ray spectra of copper. E. A. OWEN and T. E. WILLIAMS (Proc. Roy. Soc., 1931, A., 132, 282—295).—No change is found in the wave-length of the Cu-*K* α_1 line or in the width of the Cu-*K* $\alpha_1\alpha_2$ doublet when the Cu atom is present in the element, the oxides, or in Cu₃As, Cu₃Sn, Cu₂Sb, CuSn, Cu₃P, CuZn ($\alpha + \beta$) or ϵ . In the case of the oxides, any change that might occur would be masked by the decomp. that takes place when the oxide is placed on the target. The positions of the *K* absorption edges of Cu in the above substances and in CuCl, CuSO₄, Cu(NO₃)₂, CuCO₃, and CuCl₂ have been determined. In Cu, the Cu^I salts, and the alloys, the edge corresponds with the wave-length 1377.4X, whereas in all the inorg. Cu^{II} salts the edge moves about 1X towards the shorter wave-lengths. The results indicate that if a chemical linking exists between the elements in the intermetallic compounds considered, not more than one electron is supplied by the Cu atom in each case. The Cu atom is in the Cu^I state, agreeing with the views of Hume-Rothery (A., 1926, 356).
L. L. BIRCUMSHAW.

Ionisation of air by X-rays of different hardnesses and degrees of homogeneity in cylindrical chambers of 2—70 cm. diameter. H. KÜSTNER (Ann. Physik, 1931, [v], 10, 616—648).—The accuracy of the method is discussed. For accurate results, neither the photo-electrons nor the reflected electrons must reach the chamber walls. The harder and more homogeneous the radiation, the greater must be the diameter of the chamber. The smaller the chamber the greater is the error.
A. J. MEE.

Atomic photo-effect with hard exciting rays. F. SAUTER (Ann. Physik, 1931, [v], 9, 217—248).—Theoretical.
W. GOOD.

Photo-electric properties of cadmium, especially the effect of gases on them. H. BOMKE (Ann. Physik, 1931, [v], 10, 579—615).—The prep. of thin Cd layers and their photo-electric properties are described. By vaporisation at a pressure of about 10⁻⁴ mm. in a non-heated cell, Cd layers are obtained with a long-wave limit of 320—330 m μ . The photo-electric sensitivity of the cell is greatly affected by the adsorption of gases. Dry gases (O₂, H₂, N₂, A, CO₂) invariably reduced the sensitivity, whilst moist gases (air and A were tried) may increase or diminish the sensitivity, according to circumstances. The increased sensitivity for moist gases is ascribed to the H₂O vapour present.
A. J. MEE.

Course of activation of thoriated tungsten and molybdenum. A. GEHRTS (Z. tech. Physik, 1931, 12, 66—71; Chem. Zentr., 1931, i, 2172).

Directional distribution of electrons liberated from potassium vapour by polarised light. A. KRAUS (Naturwiss., 1931, 19, 617—618).—The directional distribution of electrons set free from K vapour by polarised light was investigated, K being chosen because it has a comparatively long-wave limit for

ionisation, and the K atom is similar to that of H. The theoretical distribution curve was followed.

A. J. MEE.

Loss of energy by slow electrons in hydrogen. H. RAMIEN (Z. Physik, 1931, 70, 353—374).—Electrons of less than 9 volts lose energy proportional to the number of collisions with H₂ mols., due to excitation of vibrational levels. No dissociation energy loss of 4.2 volts was observed.
A. B. D. CASSIE.

Electron interference produced by thin sheets of celluloid and collodion. F. KIRCHNER (Naturwiss., 1931, 19, 463—464).—Three different types of electron interference diagram are found; their origin is discussed.
W. R. ANGUS.

Analogy of crack and electron. T. TERADA (Proc. Imp. Acad. Tokyo, 1931, 7, 215—217).

A. J. MEE.

Temperature function in the gas equation and the properties of the electron. R. D. KLEEMAN (Z. Elektrochem., 1931, 37, 371—373).—It is shown theoretically that the equation of state of a perfect gas is $pv^{1+\alpha} = RMT^{1+\beta}$, where *p*, *v*, *R*, *M*, and *T* have their usual significance and α and β are positive quantities, the latter being independent of the nature of the gas (cf. this vol., 406). It is deduced that when the internal energy of a charged or an uncharged gas particle decreases with decrease in *v* the excess energy must be lost by a process of radiation of a type as yet unknown.
R. CUTHILL.

Influence of magnetic fields on "polarised" electron beams. E. RUPP and L. SZILARD (Naturwiss., 1931, 19, 422—423).—An electron beam (220 kv.) after reflexion on Au was passed through a magnetic field in the direction of the lines of force. The Debye-Scherrer diagram was photographed and a rotation was observed in it the magnitude of which is approx. proportional to the magnetic field strength and the length of the field traversed by the electrons.
W. GOOD.

Polarisation of a beam of electrons by scattering. E. G. DYMOND (Nature, 1931, 128, 149—150).—Predicted polarisation (A., 1929, 861) has been detected with Au foil.
L. S. THEOBALD.

Emission of electrons under the influence of chemical action. A. K. DENISOFF and O. W. RICHARDSON (Proc. Roy. Soc., 1931, A, 132, 22—50).—The electron emission from NaK₂ under the action of COCl₂ has been investigated over the pressure range 2 × 10⁻⁷ to ~10⁻³ mm. Full details are given of the methods of obtaining const. pressure of COCl₂ in the reaction chamber, of measuring *p*, and of obtaining a uniform flow of drops of the liquid alloy into the chamber. The total emission varies as *p* at the lowest pressures, but the rate of increase falls at 10⁻⁵ mm. A sharp max. of electron current occurs near 3 × 10⁻⁵ mm.; with increase in *p* a steadily diminishing decrease of *i*₀ takes place, until at about 10⁻³ mm. *i*₀ is approx. const. The effective temp. of the emitted electrons is 2370° abs. over the range 2 × 10⁻⁷ to 10⁻² mm.
L. L. BIRCUMSHAW.

Constitution of lithium. F. W. ASTON (Nature, 1931, 128, 149).—A provisional value now found for

the ratio of the relative abundance of Li^6 and Li^7 is 10.2 ± 0.5 ; this gives an at. wt. $\approx 6.923 \pm 0.006$.

L. S. THEOBALD.

Periodic regularity in atomic nuclei. G. I. POKROVSKI (Naturwiss., 1931, 19, 573).—When the number of isotopes existing in an interval $N \pm 5$ is plotted against the at. wt. N , a curve is obtained analogous to the at. vol. curve.

J. W. SMITH.

Method of recording coincidences between Geiger counters. J. C. JACOBSEN (Nature, 1931, 128, 185).

L. S. THEOBALD.

Thyratrons for high-speed automatic counting of physical phenomena. C. E. WYNN-WILLIAMS (Proc. Roy. Soc., 1931, A, 132, 295—310).—A number of circuits are described whereby thyratron valves can be used for recording voltage impulses separated by as little as 0.002 sec.

L. L. BIRCUMSHAW.

Magnetic spectrum of α -rays of active deposit of actinon. (MME.) P. CURIE and S. ROSENBLUM (Compt. rend., 1931, 193, 33—35).—Using a specially intense source (cf. A., 1930, 517), the complexity of the 5.5-cm. particles from actinium (cf. A., 1930, 1338) is confirmed by the magnetic spectrum in a field of 24,000 gauss. The velocities of the rays α , α_1 , α_2 of Ac-C, Ac-C', and Ac-C'' are respectively as 1 : 0.973 : 1.062.

C. A. SILBERRAD.

Number of pairs of ions produced in air by an α -particle of polonium. GRÉGOIRE (Compt. rend., 1931, 193, 42—44).—The ratio I/i (I the ionisation current produced by a bundle of α -particles for the solid angle 2π , i the current due to the charge carried by them) for α -particles of Po is 0.765×10^5 . Assuming the α -particles to be practically all doubly charged, the number of pairs of ions = $2I/i = (1.53 \pm 0.02) \times 10^5$. From this and other results (cf. A., 1930, 8) the number of α -particles emitted by Ra per g. per sec. is 3.56×10^{10} (cf. A., 1929, 6).

C. A. SILBERRAD.

Homogeneous groups of long-range α -particles from radium-C. K. PHILIPP (Naturwiss., 1931, 19, 618—619).—The Wilson cloud method provides a further method of analysis of the long-range α -particles from Ra-C.

A. J. MEE.

α -Particles of the actinium series. P. MISCIATTELLI (Atti III Cong. Naz. Chim., 1929, 388—394; Chem. Zentr., 1931, i, 2164).—Measurements have been made of the range of α -particles from Ra, Ac, and Ac-X.

A. A. ELDRIDGE.

Absorption and scattering of γ -rays. J. C. JACOBSEN (Z. Physik, 1931, 70, 145—158).—Measurements of the relative absorption of γ -radiation from Ra and mesothorium indicate that absorption per electron increases continuously with the at. no. of the absorbing atom, and that the increase is greater for radiation from Th-C'' than from Ra.

A. B. D. CASSIE.

Determination of niton in the atmosphere. W. MESSERSCHMIDT (Physikal. Z., 1931, 32, 548—549).—Apparatus for measuring the amount of niton in the atm. is described. Results during different weather conditions are illustrated.

W. R. ANGUS.

Method of atomic disintegration. H. POSE (Physikal. Z., 1931, 32, 584).—The dependence of

the vagueness of the observed groups of protons emitted on disintegration (cf. this vol., 783) on the experimental conditions or on vagueness of nuclear levels is discussed. In the case of Al it is certain that the first is the case.

A. J. MEE.

Artificial disintegration of aluminium. M. DE BROGLIE and L. LEPRINCE-RINGUET (Compt. rend., 1931, 193, 132—133).—By the method previously referred to (cf. this vol., 889) the "velocity" spectrum (measured by the range) of the H -particles (protons) emitted by Al on bombardment with monokinetic groups of α -particles of Po have been determined. There is no continuous spectrum, only a series of groups of range varying with the energy of the incident particles.

C. A. SILBERRAD.

Radioactive disintegration. F. STÖBER (Chem. Erde, 1931, 6, 368—375).—Disintegration of radioactive elements may be due to the action of cosmic rays.

L. J. SPENCER.

Microcalorimetric determination of the life period of polonium. A. DORABIALSKA (Rocz. Chem., 1931, 11, 469—476).—The value of the half-life period of Po, calc. from determinations of the variation in heat production of a sample with time, is of the same order as that determined by different methods. The rate of decay is, contrary to Bogoiavlenski (A., 1929, 737), unaffected by the altitude at which the sample is kept.

R. TRUSZKOWSKI.

Evidence for the spin of the photon from light scattering. (SIR) C. V. RAMAN and S. BHAGAVANTAM (Nature, 1931, 128, 114—115).—Under certain conditions of encounter between a mol. and a photon, a change in sign of the circular polarisation of the photon will occur.

L. S. THEOBALD.

Neutron. R. M. LANGER and N. ROSEN (Physical Rev., 1931, [ii], 37, 1579—1582).—The explanation of at. and cosmic phenomena is simplified by assuming the existence of a neutron, of small size and low energy, formed by the combination of a proton and an electron.

N. M. BIGH.

Nomenclature and standards for biologically effective radiation. M. LUCKIESH and L. L. HOLLADAY (J. Opt. Soc. Amer., 1931, 21, 420—427).

Ideal gases at the highest temperatures; a discussion of the problem: matter and radiation. K. BENNEWITZ (Z. Physik, 1931, 70, 429—443).—Theoretical.

A. B. D. CASSIE.

New light source for investigations in the blue and ultra-violet. W. M. COHN (Physikal. Z., 1931, 32, 559—561).—When Th, under certain conditions, is bombarded by cathode rays a blue light is emitted which can be used as a source of light for absorption measurements and radiation in the blue and ultra-violet. This blue light gives a continuous spectrum between 2200 and 6000 Å. with max. intensity at 4500 Å.

W. R. ANGUS.

Ultra-violet radiation. J. H. CLARK (J. Opt. Soc. Amer., 1931, 21, 240—247).—A ZnS method of measuring ultra-violet radiation is described and the results of 3 years' observations on Baltimore sunshine are given.

W. GOOD.

Band spectrum of boron hydride. W. LOCHTE-HOLTGREVEN and E. S. VAN DER VLEUGEL (*Z. Physik*, 1931, **70**, 188—203).—Two bands at λ 4332.7 and 4367.1 Å., due to BH, were photographed under high dispersion and analysed. Faint satellites were ascribed to the isotopic mol. B¹⁰H. A. B. D. CASSIE.

Spectrum of flame of carbon disulphide. A. FOWLER and W. M. VAIDYA (*Proc. Roy. Soc.*, 1931, **A**, **132**, 310—330).—The most characteristic bands of the CS₂ flame, extending from the blue to the near ultra-violet, are due to S₂ mols. Many of the ultra-violet bands are also due to S₂, whilst fainter bands in this region are attributed to SO. When the flame is enclosed in a chimney, strong absorption bands of SO₂ appear. Similar results are obtained in experiments on S and H₂S flames, the latter also showing bands of HO. The spectrum of the "phosphorescent flame" of CS₂, as photographed by Emeléus (*A.*, 1926, 777), has been re-examined and found to include bands of S₂, SO, and CS, the SO bands being relatively much stronger than in the normal flame. Preliminary investigations have been made of a group of bands in the ultra-violet which have been provisionally attributed to COS. These have not been found in any of the flame experiments. L. L. BIRCUMSHAW.

Absorption spectra in relation to the colour of solutions of iodine monochloride. A. E. GILLIAM and R. A. MORTON (*Proc. Roy. Soc.*, 1931, **A**, **132**, 152—167; cf. *A.*, 1929, 977).—ICl solutions show two colours, yellow (in AcOH and AcOEt) and brown (in CCl₄), corresponding with brown and violet I solutions. Yellow solutions of ICl in CCl₄, CHCl₃, AcOH, HCl, Et₂O, and AcOEt are characterised by an absorption max. about 360 m μ , the brown about 460 m μ , mol. extinction coeff. being 150—160 in each case. The most important factor influencing the colour and absorption spectrum of ICl solutions is dichroism, conditioned by the occurrence or non-occurrence of solvation. Aq. NaCl and HCl solutions of ICl have a higher extinction coeff. than the others, and there is a slight displacement of the max. towards the shorter wave-lengths. This is considered to indicate the formation of the compounds ICl.HCl and ICl.NaCl. The analogy with I solutions extends to the variation of the colours in certain solvents with temp., and to the fact that traces of EtOH in CHCl₃ cause the 460 m μ max. to be replaced by that at 360 m μ . L. L. BIRCUMSHAW.

Comparative absorption spectra of complex chromic and cobaltic salts. (MME.) M. CHATELET-LAVOLLAY (*Compt. rend.*, 1931, **193**, 30).—The difference in the frequencies ($\Delta\nu$) of the max. of the absorption band in the ultra-violet of corresponding luteo-, rosco-, and purpureo-chromic and -cobaltic salts is const. (120 mm.⁻¹). For the xantho-chromic and -cobaltic salts $\Delta\nu$ is 340, but for the isoxantho-cobaltic it is 120 mm.⁻¹ The xanthochromic salt therefore to the isoxantho-series and is [Cr(NH₃)₅ONO]Cl₂. C. A. SILBERRAD.

Radiation accompanying hydration of quinine sulphate. M. CURIE and M. PROST (*Compt. rend.*, 1931, **192**, 1729—1730).—By working in a vac. (save for H₂O vapour from ice at -15°), it is shown that the range of radiation emitted on hydration of quinine

sulphate exceeds 1 mm. at a pressure of H₂O vapour of 1 mm. (cf. *A.*, 1911, ii, 356; 1926, 910).

C. A. SILBERRAD.

Absorption in liquid and solid solutions of rhodamine-B in a mixture of alcohol and colloidion. A. A. DIXON (*J. Opt. Soc. Amer.*, 1931, **21**, 259—261).—Experimental curves showing absorption in relation to wave-length are given. W. GOOD.

Zeeman effect of the absorption lines of potassium chromium selenate. K. SCHNETZLER (*Ann. Physik*, 1931, [v], **10**, 373—392).—KCr(SeO₄)₂.12H₂O crystallises in the alum type, and has at -190° a sharp doublet at 6710 Å. The transverse Zeeman effect for this doublet was investigated. A. J. MEE.

Ultra-violet absorption of benzene derivatives and the theory of induced alternate polarity. K. L. WOLF and W. HEROLD (*Z. physikal. Chem.*, 1931, **B**, **13**, 201—231).—The ultra-violet absorption spectra of dil. solutions of a number of mono- and di-substituted C₆H₆ derivatives are described. The displacement of the first absorption band caused by introduction of polar substituents may be calc. additively for the *p*-disubstituted compounds without regard to the charge, relative to the C₆H₆ ring, of the central atoms of the groups. The oscillation bands are most marked in *m*-substituted compounds if the charges in the substituents are similar, and in *p*-compounds if the charges are of opposite sign; it appears, therefore, that the strengthening or weakening of the induced alternate polarity caused by the introduction of one polar substituent, according to the nature and position of the second substituent, is in accordance with Vorländer's theory.

H. F. GILLBE.

Spectral region 20—40 μ . J. STRONG (*Physical Rev.*, 1931, [ii], **37**, 1565—1572).—% transmission and reflexion are tabulated for several substances. SO₂ shows zero reflectivity at 20.75 and 8.7 μ , where it has strong absorption bands. β -MgO has a max. reflectivity at 23 μ . KI is transparent above 33 μ .

N. M. BLIGH.

Infra-red region of spectrum. III. Absorption spectrum of carbon disulphide. IV. Monochromator method in the infra-red. C. R. BAILEY and A. B. D. CASSIE (*Proc. Roy. Soc.*, 1931, **A**, **132**, 236—251, 252—257; cf. this vol., 144).—III. Four bands, ν 878, 1523, 2179, 2330 cm.⁻¹, have been located in the region 1—22 μ ; of these, the first three have been resolved into *P* and *R* branches with a frequency difference of 12—13 cm.⁻¹ The infra-red has been co-ordinated with the Raman spectrum, and the fundamental frequencies of the mol. are deduced. The mol. is rectilinear with one moment of inertia, I_0 264 \times 10⁻⁴⁰ g.-cm.² The doublet structure of the Raman spectra of CS₂ and CO₂ is attributed to the excitation of two types of vibration associated with slightly different amounts of energy and corresponding with two types of linking. The force consts. characteristic of the linkings in CS₂ and similar mols. have been calc. CS₂ differs from CO₂ in having single linkings, the C atom being apparently bivalent.

IV. The monochromator method eliminates from the absorption tube all radiation emitted by the

Nernst filament except the small range of wave-lengths passing through the telescope slit.

L. L. BIRCUMSHAW.

Raman effect in some gases. P. DAURE and A. KASTLER (Compt. rend., 1931, 192, 1721—1723).—The Raman spectra of H_2 , C_2H_2 , C_2N_2 (at atm. pressure), and H_2O (saturated vapour at 130°) have been determined with 4358.3, 4046.7, and 3650.1 of the Hg arc. The two last give respectively $\Delta\nu=2330\pm 5$ and 3655 ± 5 cm^{-1} ; former results are confirmed.

C. A. SILBERRAD.

Anomalous polarisation of Raman radiation. R. BÄR (Naturwiss., 1931, 19, 463).—Conditions under which anomalous polarisation of Raman lines is manifested are discussed and the polarisation factors for $CHCl_3$, CCl_4 , and C_6H_6 are given.

W. R. ANGUS.

Polarisation of Raman scattering by hydrogen gas. S. BHAGAVANTAM (Nature, 1931, 128, 70).—Raman lines representing the rotational transitions $0\rightarrow 2$ and $1\rightarrow 3$ in H_2 are polarised only to an extent of approx. 25%; polarisation of the vibration lines appears to be complete.

L. S. THEOBALD.

Circular polarisation in the Raman effect. W. HANLE (Physikal. Z., 1931, 32, 556—558).—Apparatus for investigating circular polarisation of Raman lines is described. The character and amount of circular polarisation are the same for all Raman lines arising from similar mol. vibrations. Linear polarisation effects are compared with those obtained. Comparisons of the effects with CCl_4 and $CHCl_3$, and with C_6H_6 and PhMe and $C_6H_4Me_2$, are made. Corresponding lines of different substances show the same circular polarisation.

W. R. ANGUS.

Intensity problems connected with the Raman effect. J. REKVELD (Arch. Neerland., 1931, [III A], 13, 73—120).—The ratio of the intensities of Stokes and anti-Stokes Raman lines is expressed by an equation derived on the assumption of thermodynamic equilibrium between radiation and matter; experimental values agree well with this theory. A new optical method of determining h/k is based on these intensity measurements. The dependence of the scattered energy on frequency is discussed and experimental data on CCl_4 , MeOH, and COMe₂ are given. A method of heterochromatic photometry in the ultra-violet is described.

W. R. ANGUS.

Raman effect. A. CARRELLI (Rend. Accad. Sci. fis. mat. Napoli, 1930, 36, 61—68; Chem. Zentr., 1931, i, 2169).—Raman rotation frequencies are emitted with much smaller (0.001) intensity than the Tyndall frequency. For substances which absorb in the ultra-violet the intensity of the Raman frequency increases with diminishing wave-length more rapidly than accords with the λ^{-4} law.

A. A. ELDRIDGE.

Intensity of rotation lines in the Raman effect of diatomic molecules. E. SEGRÈ (Nuovo Cim., 1930, 7, 380—387; Chem. Zentr., 1931, i, 2169).—A quantum-theoretical study.

A. A. ELDRIDGE.

Continuous Raman spectrum and its behaviour at the critical point. G. PLACZEK and W. R. VON WJJK (Z. Physik, 1931, 70, 287—292).—Deter-

mination of depolarisation of Rayleigh and Raman radiation in liquids shows that the increase of continuous radiation near a Raman line at the crit. point is due to an increase of continuous Raman radiation and not to an increase in Rayleigh scattering.

A. B. D. CASSIE.

Effect of pressure on Raman spectra. S. BHAGAVANTAM (Nature, 1931, 128, 188).—Estimated pressures at which distinctness of quantisation of the different rotations would disappear in the commoner gases are in agreement with observed pressures above which lines in the rotational Raman spectrum are replaced by a continuous spectrum.

L. S. THEOBALD.

Raman effect for liquid hydrazine. S. IMANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 16, 1—7).—The spectra are nearly the same under low dispersion, showing the NH_3 N-H triplet frequency (3210, 3289, 3339 Å.), and two lower frequencies due to the N-N linking. The appearance of this triplet in the N_2H_4 spectrum supports the polymerisation theory of liquid NH_3 . A value of 1000 cm^{-1} is obtained for the N-N linking in liquid N_2H_4 . This may be halved in the vapour state. Gaseous N_2H_4 dissociates into two NH_2 groups on absorption of light of a certain wave-length.

A. J. MEE.

Raman effect in amorphous solids. S. BHAGAVANTAM (Indian J. Physics, 1931, 6, 1—6).—Flint glass shows the effect much more strongly than crown. All the glasses show bands at about 500, 800, 1080, and 1330 cm^{-1} . The most prominent are at 500 and 1080.

A. J. MEE.

Raman spectra of inorganic crystals. III. P. KRISHNAMURTI (Indian J. Physics, 1931, 6, 7—13).—The Raman spectrum of S crystals at the temp. of liquid air, excited by 4358 Å., was investigated. The crystals absorb this radiation completely at room temp., but at the temp. of liquid air they become much lighter in colour, and the Raman lines appear sharply. $HgCl_2$ crystals give a very strong line at 313 cm^{-1} and a weaker one at 3.1 cm^{-1} , whilst $HgBr_2$ gives only one intense line at 187 cm^{-1} . The MeOH solution of $HgCl_2$ gives a slightly broadened out line. $(NH_4)_2HgCl_4$ powder gave a line at 273 cm^{-1} . A conc. aq. solution gave a broad line in a similar position.

A. J. MEE.

Raman spectra of sulphuric acid. R. M. BELL and W. R. FREDRICKSON (Physical Rev., 1931, [ii], 37, 1562—1564; cf. A., 1930, 978).—As concentration decreases the lines decrease in number and intensity and disappear; at this point a broad line 4817 Å. appears, and persists in dil. solution. An exception is 4566 Å., present at all concentrations and of increasing intensity with decreasing concentration. HNO_3 gives a line of the same wave-length and intensity variation.

N. M. BLYGH.

Raman effect in solutions of inorganic complex salts. G. JOOS and I. DAMASCHUN (Physikal. Z., 1931, 32, 553—554).—Complex salts containing co-ordinated H_2O or NH_3 groups were examined. None of the aquo-co-ordinated complex salts exhibited Raman displacements. Sulphates of hexammines gave displacements corresponding with 9.1, 10.2,

16.6, and 23.3 μ , agreeing with infra-red data on solid sulphates. A displacement is assumed to arise from the ammine complex, and its value is determined by the metallic radical, viz., $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ —24.8 μ ; $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ —24.5 μ ; $\text{Zn}(\text{NH}_3)_6\text{SO}_4$ and $\text{Zn}(\text{NH}_3)_6\text{Cl}_2$ —23.4 μ ; $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ —29.5 μ . Ni and Ag amines gave no shifts and Co amines are unsuitable for investigation because of their colour. Solutions of NH_3 exhibit three displacements corresponding with (in order of sharpness) 3.0, 2.9, 3.1 μ ; $\text{Zn}(\text{NH}_3)_6\text{SO}_4$ showed only two displacements, 3.1 (sharper) and 3.0 μ (weaker). The shift corresponding with 36.5 μ shown by $\text{Zn}(\text{NH}_3)_6\text{Cl}_2$ is explained as due to the formation of $(\text{NH}_4)_4(\text{ZnCl}_6)$ and the subsequent dissolution of ZnCl_6^{--} in ZnCl_2 gives rise to the displacement.

W. R. ANGUS.

Depolarisation of the lines of the CO_3^{--} ion in the spectrum of light diffused by calcite. J. CABANNES and (MLLE.) D. OSBORNE (Compt. rend., 1931, 193, 156—158).—Revised figures for the Raman lines of calcite are +28.13, +15.45, -15.74, -28.38, -71.21, -108.73, -143.66, and -175.20 mm^{-1} . 71.21, 108.73, and 143.66 are three of the four fundamental frequencies of the CO_3^{--} ion (assumed plane). The polarisation of 108.73 differs from that of the other two, confirming the authors' view (cf. A., 1930, 15) in opposition to Schaefer's (cf. *ibid.*, 1499).

C. A. SILBERRAD.

Raman spectra of some organic sulphides. S. VENKATESWARAN (Indian J. Physics, 1931, 6, 51—74).—The Raman spectra of Me, Et, Pr, Bu⁺, Bu⁺, and allyl sulphides, and of Me_2S_2 and Et_2S_2 have been examined. The Me_2S model is triangular. There are two frequencies associated with the C-S linking, one sharp and intense at $\Delta\nu$ 691, and one diffuse at $\Delta\nu$ 746. These frequencies are not appreciably affected by changes in the group attached to the C atom, or by the difference in the chemical linking between the S and C atoms. The disulphides show a prominent line at $\Delta\nu$ 512 due to the S-S linking. There is a difference between the linking of S atoms in S_2 and in the disulphides, for this frequency is a good deal lower than that obtained from fluorescence and absorption bands for S vapour. The C-S and S-S oscillations have a tendency to split into components in Et and higher members of the series. There is a slight shift in the C-S oscillation of Me_2S in Me_2S_2 . Allyl sulphide shows a prominent line at $\Delta\nu$ 1634, characteristic of the ethylenic linking. There are also differences in the nature of the C-H band in the normal and corresponding *iso*-compounds.

A. J. MEE.

Raman effect. XI. Raman spectra of cyanogen compounds. A. DADIEU (Monatsh., 1931, 57, 437—468).—Method and results are given. Constitutional relations in carbimides, thiocarbimides, carbylamines, and HCN are discussed. W. GOOD.

Raman effect. XII. Raman spectra of chlorinated hydrocarbons. M. PESTEMER (Monatsh., 1931, 57, 469—487).—The results of an experimental study of the Raman effect in 15 chlorohydrocarbons are given and discussed. W. GOOD.

Raman effect. XIII. Raman spectra of halogen derivatives. A. DADIEU and K. W. F. KOHLRAUSCH

(Monatsh., 1931, 57, 488—511).—6 org. halogen compounds are examined for the first time. The results, as well as those for 5 other compounds, are given and discussed.

W. GOOD.

Thermoluminescence excited by exposure to radium. F. G. WICK (J. Opt. Soc. Amer., 1931, 21, 223—231).—This has been experimentally studied in CaSO_4 containing a small amount of Mn and in fluorite. The effect of subjecting these materials to high pressure before and after exposure to Ra was also studied.

W. GOOD.

Radiation from phosphors in strong varying electric fields. H. HINDERER (Ann. Physik, 1931, [v], 10, 265—295).—The behaviour of different phosphors in const. and changing electric fields is investigated. For a ZnS-Mn phosphor the intensity of the light is dependent on the metal content for both types of field. A new method of determining the duration of the luminescence of phosphors in an electric field is described. The duration of the luminescence for ZnS-Mn phosphors is independent of the centre size and field strength and lies between 9 and 10 sec.

A. J. MEE.

Fluorescence of bonellin. C. DHÉRE and M. FONTAINE (Compt. rend. Soc. Biol., 1931, 105, 843—846; Chem. Zentr., 1931, i, 2218).—Solutions of bonellin (from *Bonellia viridis*) in EtOH, Et₂O, and pyridine exhibit 3 fluorescence bands. The living animal fluoresces (red) only in intense violet and ultra-violet light.

A. A. ELDRIDGE.

Additive colouring of alkali halide crystals. I. Macroscopic diffusion. E. REXER (Z. Physik, 1931, 70, 159—187).—Diffusion of Na into rock-salt was studied at different temps. and for different samples of crystal.

A. B. D. CASSIE.

Molecular association and optimum of fluorescence: influence of salts. E. PERRIN (Compt. rend., 1931, 192, 1727—1729).—The more rapid decrease of fluorescence with increasing concentration and the smaller optimum concentration of a solution of fluorescein in one of KCl (3.9*N*) as compared with one in H₂O support the view that the decrease in fluorescence on increasing concentration beyond the optimum is due to association of mols. (cf. A., 1889, 554). The mechanism of the deactivation is discussed (cf. A., 1930, 133).

C. A. SILBERRAD.

Phosphorescence of zinc sulphide. I. Explosion method. R. COUSTAL (J. Chim. phys., 1931, 28, 277—298).—A mixture of Zn powder and flowers of S, with S slightly in excess of mol. proportions, on explosion yields ZnS. The phosphorescence of the pure substance is similar to that of ZnS prepared by older methods and activated by Cu. The presence of Pb has no effect on the phosphorescence, but Mn, Fe, Co, Ni, and Cu are extremely active. Other metals change the phosphorescence slightly, non-metals very little, whilst compounds frequently displace the phosphorescence towards a longer wavelength.

J. W. SMITH.

Phosphorescence of zinc sulphide. II. Physical study. R. COUSTAL (J. Chim. phys., 1931, 28, 345—361; cf., preceding abstract).—Two phosphorimeters are described; one aims at rapidity of measure-

ment and the other at accuracy. The decrease of intensity I of pure, phosphorescent ZnS with the time t is given by $I = C/t^n$, where C is a const. depending on the size of the crystals of ZnS and n is a function of the temp.
E. S. HEDGES.

Relation of the intensity of fluorescence to the concentration in solid solutions. A. A. DIXON (J. Opt. Soc. Amer., 1931, 21, 250—258).—Experimental investigation of fluorescence in both liquid and solid solutions (rhodamine-B in EtOH-collodion) shows that the intensity of fluorescence increases exponentially with a decrease in concentration over a wide range.
W. GOOD.

Accuracy obtainable with gas-filled photo-electric cells. W. R. G. ATKINS (Sci. Proc. Roy. Dublin Soc., 1931, 20, 67—73).—A gas-filled CsH cell, after a momentary glow discharge, showed 33% variation in emission at 143 volts anode potential. The sensitivity decreases about 2% per min. and subsequently rises. A KH gas-filled cell similarly tested varied 2% at 5 microamp. and 59 volts and more at 166 volts. Measurements should be made immediately after a discharge, which should be momentary, as the sensitivity falls 2% at 166 volts and more than 3% at 59 volts.
C. W. GIBBY.

Influence of water in photo-electric cells. R. AUDUBERT (Compt. rend., 1931, 193, 165—166).—The explanation of the photo-electric effect as due to the photolysis of H_2O (cf. A., 1930, 173) is supported by the fact that electrodes of CuI, Cu_2O , CuO, Ag_2S , or Hg_2I_2 in various non-aq. solvents, e.g., $COMe_2$, Et_2O , MeOH, MeOAc, etc., rendered conducting by NaI, give relative to a Hg_2Cl_2 electrode, a const. potential, but no photopotential. The presence of very little H_2O causes such to appear, its influence being chiefly exerted as an adsorbed layer on the electrode.
C. A. SILBERRAD.

Photo-electric effect in Cu_2O -Cu rectifier. E. PERUCCA and R. DEAGLIO (Ann. Physik, 1931, [v], 10, 257—261).—The general photo-electric phenomena occurring in a Cu_2O -Cu cell are described, complicating factors being pointed out.
A. J. MEE.

Photo-electric effect in the Cu_2O -Cu rectifier. O. VON AUWERS and H. KERSCHBAUM (Ann. Physik, 1931, [v], 10, 262; cf. preceding abstract).—The work of the two sets of investigators is compared, and differences are indicated.
A. J. MEE.

Photo-electromotive force in cuprous oxide crystals. H. DEMBER (Physikal. Z., 1931, 32, 554—556).—An e.m.f. within a crystal can be originated by a light source only if the light is able to liberate electrons so that these may diffuse in the interior of the crystal. Observations preclude the contributory effect of a unidirectional layer.
W. R. ANGUS.

Electric spectrum of water. M. ALIMOWA (Ann. Physik, 1931, [v], 9, 176—178).—Using the method of damped oscillations a value 9.004 ± 0.001 was found for n^{17} of H_2O in the range of wave-lengths 2200—2900 mm.
W. GOOD.

Dielectric strength of degassed liquids. L. INGE and A. WALKER (Z. tech. Physik, 1930, 11, 369—372; Chem. Zentr., 1931, i, 2022).—At temp.

and pressures sufficiently removed from the vaporisation temp. and pressure the dielectric strength of well-degassed xylene is independent of pressure. For a.c. the val. decreases with rise of temp., but remains const. for d.c. or discharge.
A. A. ELDRIDGE.

Dipole moment and spatial configuration of some inorganic halides. E. BERGMANN and L. ENGEL (Z. physikal. Chem., 1931, B, 13, 232—246).—The dipole moments of a number of halides and of $Fe(CO)_5$, dissolved in C_6H_6 or CCl_4 , have been determined. $SbCl_5$ possesses a definite moment, and one Cl atom therefore occupies a position in the mol. different from that of the other 4; a similar condition obtains for $Fe(CO)_5$. The moments of $SiCl_4$ and $TiCl_4$ are zero and the compounds are therefore of tetrahedral structure, but $SnCl_4$ is anomalous in possessing a moment of 0.8×10^{-18} ; the possible structure of the mol. is discussed. Measurements with trihalides indicate a pyramidal structure.
H. F. GILLBE.

Reactions of atoms. M. PÓLÁNYI (Z. angew. Chem., 1931, 44, 597—602).—The general problem of the reaction of atoms with mols. is discussed and the "rarefied flame" (A., 1928, 1339) and the diffusion methods for the study of the action of Na atoms on the halogens, halogen acids, and Hg halides are outlined. The investigation has been extended to the Me halides.
H. INGLESON.

Internal structure of solid inorganic compounds at high temperatures. III. Electrical conductivity, diffusivity, and reactivity of some spinels in the solid state. W. JANDER and W. STAMM (Z. anorg. Chem., 1931, 199, 165—182; cf. A., 1930, 1351).—The conductivity of ZnO at 400—1030° and of MgO at about 1000° shows these compounds to be electronic conductors, and Al_2O_3 is probably of the same type. In $ZnAl_2O_4$ and $MgAl_2O_4$ the conductivity at 900—1100° is mainly ionic, whereas in $MgCr_2O_4$ and $ZnCr_2O_4$ it is electronic. Measurements of the rate of diffusion of these compounds into each other and the rate of reaction with MgO, Cr_2O_3 , and Al_2O_3 at 1230° show that Al and Cr exchange places more rapidly than Mg and Zn. From these results it is concluded that $MgAl_2O_4$ and $ZnAl_2O_4$ have ionic lattices at 900—1250°.
R. CUTHILL.

Electric conductivity and optical absorption in metals. E. H. HALL (Proc. Nat. Acad. Sci., 1931, 17, 392—401).—A theoretical discussion.
J. W. SMITH.

Electric conductivity and optical absorption in metals (supplementary). E. H. HALL (Proc. Nat. Acad. Sci., 1931, 17, 427—430).—Transit conductivity in optical experiments is dependent on the ratio wave-period/transit period in the same general way in which, according to both the Thomson formula and the Wilson-Jeans formula, free-electron conductivity is dependent on the ratio wave-period/free-path period.
E. S. HEDGES.

Dispersion of aluminium in the range 1.1—2.3 A. H. STEPS (Naturwiss., 1931, 19, 617).—The dispersion curve for Al is normal within this range.
A. J. MEE.

Indices of refraction of liquids. M. MASIUS and W. E. LAWTON (J. Opt. Soc. Amer., 1931, 21, 232—

239).—A theoretical treatment of the determination of the index of refraction of a liquid enclosed in a hollow prism. W. GOOD.

Invariant of magnetic rotation of some fused organic substances. C. SALCEANU (Compt. rend., 1931, 193, 161—162).—If Λ is Verdet's constant, n refractive index, and d density, the expression $\Lambda nd / (n^2 - 1)^2$ should be independent of the physical state (cf. A., 1927, 8; this vol., 148). From m. p. to 180° for 2-MeC₁₀H₇, CHPh₃, and phenanthrene it increases slowly with rise of temp. This is probably connected with the effect on the strong magnetic dispersion of these substances of change in position of the absorption bands with temp.

C. A. SILBERRAD.

Magneto-electric rotatory power. J. BECQUEREL and L. MATOUT (Compt. rend., 1931, 193, 158—161; cf. this vol., 787).—An alternative explanation of the phenomenon. With xenotime two kinds of absorption bands, quite distinct from each other, were observed.

C. A. SILBERRAD.

Rational system of symbols for organic and inorganic compounds. W. MADELUNG (Z. Elektrochem., 1931, 37, 377—378).—Supplementary to a previous paper (this vol., 548).

R. CUTHILL.

Exact partitioning [of space] and co-ordination number. F. LAVES (Z. Krist., 1931, 78, 208—241).—The connexion between 11 possible methods of partitioning of space and the relations between the co-ordination numbers of the constituents of a compound $A_m B_n$ are discussed.

C. A. SILBERRAD.

Single electron linking. J. H. SIMONS (J. Physical Chem., 1931, 35, 2118—2124).—A discussion. The hypothesis of a single electron linking as a valency force is regarded as invalid and in direct opposition to electronic theories of valency. The parachor cannot be employed to establish the existence of such a linking.

H. F. GILLBE.

Quantum mechanics applied to benzene problems. I. Electron configurations of benzene and its derivatives. E. HÜCKEL (Z. Physik, 1931, 70, 204—286).—Six detached electrons determine the aromatic character of ring systems. Wave mechanics is applied first to a system with one electron associated with each CH group, and, secondly, to an electron moving in the potential field due to the ring and remaining detached electrons. The second method indicates that the ring may be regarded as a quasi-at. core, and that the detached electrons form completed groups of 2, 6, 10, etc. electrons: 2 electrons form an ordinary covalent linking, and 6 the C₆H₆ ring. These groups are complete even when the number of detached electrons does not equal the number of members of the ring, e.g., Ph⁻K⁺. Term values due to different electron configurations are determined, and details of the different hydrobenzenes are discussed.

A. B. D. CASSIE.

Energy relationships of inorganic halides. Determination of atomic radii. E. BERGMANN and L. ENGEL (Z. physikal. Chem., 1931, 13, B, 247—267).—By assuming that the direction of operation of a valency force is governed by the polarisation of the atoms concerned, and that the homopolar linking

approximates to an extremely deformed ionic linking, it is shown that the configuration of trihalides must be pyramidal, and not planar, and that SnCl₄ also, unlike CCl₄ and SiCl₄, is of pyramidal structure (cf. this vol., 999). A method for calculating from the electronic polarisation the distance between the central and outer atoms in such compounds is described; the vals. of the at. radii, calc. from the results so obtained, are in close agreement with those in the lit. The formula used is applicable both to dil. solutions and to gases.

H. F. GILLBE.

Theoretical magneton numbers in Weiss units. C. J. GORTER (Nature, 1931, 128, 68—69).—Theoretical values given by various authors for the rare earths and the Fe group are compared.

L. S. THEOBALD.

Magnetic susceptibility, absorption spectra, and constitution of iron nitrososulphides. L. CAMBI and L. SZEGÖ (Atti R. Accad. Lincei, 1931, [vi], 13, 168—172).—The magnetic susceptibility of the tetra- and hepta-nitroso-salts indicates that they are ferrous-ferric compounds containing halogenoid NO groups, and this structure is supported by the absorption spectra of the two series of salts in the visible and ultra-violet regions.

O. J. WALKER.

Oxide hydrates and active oxides. XLIII. Magnetic susceptibilities of preparations of hydrated ferric oxide. G. F. HÜTTIG and H. KITTEL (Z. anorg. Chem., 1931, 199, 129—148; cf. this vol., 804).—Goethite and anhyd. Fe₂O₃ are paramagnetic. Variations in the susceptibility, κ , of anhyd. Fe₂O₃ are due to the presence of varying amounts of the unstable γ form, to incomplete crystallisation, and to deviations of the ratio Fe : O from the value 2 : 3, an excess of either Fe atoms or dissolved O causing a marked increase in κ . The hydrohaematites are ferromagnetic, κ decreasing with increase in the field strength. The products formed by reaction of ferric salts with aq. NH₃ are initially paramagnetic, but tend to become ferromagnetic on ageing.

R. CUTHILL.

Number of magnetons in ferromagnetic substances. A. WOLF (Z. Physik, 1930, 70, 519—538).—Theoretical. The number of magnetons per ferromagnetic element is calc. assuming the constituent atoms in possible states of different multiplicity.

A. B. D. CASSIE.

Diamagnetism and the colloidal state. S. R. RAO (Nature, 1931, 128, 153).—With colloidal C, diamagnetic susceptibility, χ , decreases in proportion to an increase in surface area of a given mass. With Sb and Bi, the decrease of χ can be explained by a fall due to reduced particle size and to oxidation (cf. A., 1930, 673).

L. S. THEOBALD.

Diamagnetism of liquid mixtures. V. C. G. TREW and J. F. SPENCER (Nature, 1931, 128, 152).—A reply to criticism (this vol., 900).

L. S. THEOBALD.

Valency and diamagnetism of titanium in the tetrachloride. V. I. VAIDYANATHAN (Nature, 1931, 128, 189).—The diamagnetism of TiCl₄ (-0.287×10^{-6} at 35°) suggests that the paramagnetism of Ti is due to the two pairs of valency electrons being in different orbits. In Ti compounds, paramagnetism

is due to the unsymmetrical nature of the valency linkings.

L. S. THEOBALD.

New relation between electrical resistance and energy of magnetisation. W. GERLACH and E. ENGLERT (*Nature*, 1931, 128, 151—152).—Above the Curie point the decrease of resistance of ferromagnetic wires is proportional to the square of the true magnetisation, and at temp. just above this point the external field produces true magnetisation and a form of ferromagnetic magnetisation. True magnetisation diminishes electrical resistance proportionately to the true magnetic energy.

L. S. THEOBALD.

Sugden's parachors. V. Mercaptans. B. SINGH and R. SINGH (*J. Indian Chem. Soc.*, 1931, 8, 209—213; cf. *A.*, 1930, 1349).—The parachors of various mercaptans indicate absence of association.

R. CUTHILL.

Heat of evaporation of water and specific volume of saturated steam up to 310° (100·7 atm.). M. JAKOB and W. FRITZ (*Tech. Mech. Thermodyn.*, 1930, 1, 173—183, 236—240; *Chem. Zentr.*, 1931, i, 2028).—Values correct to 0·25% are given.

A. A. ELDRIDGE.

Exchange of energy between organic molecules in a molecular beam and metallic surfaces. F. O. RICE and H. T. BYKE (*Proc. Roy. Soc.*, 1931, A, 132, 50—66).—No decomp. of COMe_2 or HgMe_2 was observed when a mol. beam of these substances collides with a Pt target at temp. up to 1600°, from which it is concluded that no adsorption of any appreciable fraction of the mols. or the trapping of mols. in surface crevices occurs. When COMe_2 vapour or HgMe_2 comes into temp. equilibrium with a target at 1600°, the fraction of mols. having the energy of activation 65,500 g.-cal. is too small to be detected. It is concluded that the transfer of energy from a heated target to the internal degrees of freedom of an org. mol. is not 100% efficient. When COMe_2 or HgMe_2 in a mol. beam collides with a heated W target no decomp. takes place up to 1085°, after which a surface reaction occurs with formation of WC and liberation of CO and H_2 . With a Ta target a similar reaction begins at 1400°.

L. L. BIRCUMSHAW.

A tetrahedrally symmetrical field of influence as a general structure unit of all crystal lattices. R. REINECKE (*Z. Krist.*, 1931, 78, 334—362).

Lattice distance of bismuth and its reflective power for X-rays. E. ADINOLFI (*Rend. Accad. Sci. fis. mat. Napoli*, 1930, 36, 69—75; *Chem. Zentr.*, 1931, i, 2163—2164).—The value $3\cdot970 \pm 0\cdot005$ Å. is recorded.

A. A. ELDRIDGE.

Crystal structure of silicon. A. G. NASINI and A. CAVALLINI (*Atti III Cong. Naz. Chim.*, 1929, 463—470; *Chem. Zentr.*, 1931, i, 2163).—Specimens of Si prepared in various ways always possessed a structure of the diamond type; a 5·21 Å. Differences in the interference lines in accord with Laue's formula were observed.

A. A. ELDRIDGE.

Lattice constants of rhenium. K. MOELLER (*Naturwiss.*, 1931, 19, 575).—Using a precision method, the following values have been obtained: a 2·755, c 4·450 Å., c/a 1·615 (cf. *A.*, 1929, 382; this vol., 448).

J. W. SMITH.

Cold-working of platinum wires and fibrous texture thereby produced. G. GREENWOOD (*Z. Krist.*, 1931, 78, 242—250).—Cold-working of Pt wire produces a fibrous structure, the crystallites arranging themselves so that [111] is approx. parallel to the direction of drawing (cf. *A.*, 1929, 743). The effect is more marked towards the centre of the wire. The unit cell has a 3·912 Å. (cf. *A.*, 1925, ii, 447).

C. A. SILBERRAD.

Crystal structure of anhydrous halides of bivalent metals. A. FERRARI (*Atti III Cong. Naz. Chim.*, 1929, 452—460; *Chem. Zentr.*, 1931, i, 2162).—A tabulation and discussion.

A. A. ELDRIDGE.

Apparent hemihedrism of crystals of lead chloride and some other salts. F. D. MILES (*Proc. Roy. Soc.*, 1931, A, 132, 266—281).—The fact that etch figures on the faces of a crystal may indicate a symmetry lower than that usually ascribed to the crystal is discussed. The phenomenon is probably due to the asymmetry of the etching agent. In certain conditions PbCl_2 (normally showing holohedral orthorhombic symmetry) can be obtained from hot solutions containing dextrin in microscopic crystals consisting of a single form (bisphenoid) which can have only axial symmetry. The same phenomenon is shown to a smaller extent by PbBr_2 and HgBr_2 . In each case the identity of the anhyd. normal crystal and of the modification was confirmed by chemical analysis and by X-ray powder diagrams. The four Pb atoms in the PbCl_2 structure lie in the planes of simple symmetry (100) and (200), in an approx. hexagonal close packing.

L. L. BIRCUMSHAW.

Spinel structure: example of variate atom equipoints. T. F. W. BARTH and E. POSNJAK (*J. Wash. Acad. Sci.*, 1931, 21, 255—258).—Comparisons of the observed and calc. intensities on MgFe_2O_4 and MgGa_2O_4 show that, instead of having Mg in 8f and (Fe, Ga) in 16c, 8 (Fe, Ga) ions occupy positions in 8f and 8 (Fe, Ga) ions and 8 Mg ions are in 16c. The possibility that different atoms replace one another in structurally equiv. positions of a crystal in this way is probably not confined to spinels. It is proposed to call unit cells of such crystals "cuts with variate atom equipoints."

N. H. HARTSHORNE.

Structure of Tutton's salts. II. W. HOFMANN (*Z. Krist.*, 1931, 78, 279—333; cf. this vol., 415).—The following values are now given for a , b , c , for the series $\text{M}^{\text{II}}\text{M}^{\text{II}}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$: $\text{M}^{\text{II}}\text{M}^{\text{II}} = (\text{NH}_4)_2\text{Zn}$, 9·205, 12·475, 6·225; $(\text{NH}_4)_2\text{Cd}$, 9·35, 12·705, 6·27; $(\text{NH}_4)_2\text{Fe}$, 9·28, 12·57, 6·22; K_2Mg 9·04, 12·24, 6·095; Ti_2Mg 9·22, 12·42, 6·185; $(\text{NH}_4)_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, 9·42, 12·72, 6·30. The unit cell contains 2 mols.; space-group C_{2h}^2 . A complete structure is deduced indicating physical properties in good agreement with the facts. The small effect of change in M^{II} is explained by the ion being surrounded by an octahedron of $6\text{H}_2\text{O}$. The structure can be represented as pseudocubic, closely resembling that of the alums.

C. A. SILBERRAD.

Crystal structure of lithium iodate. W. H. ZACHARIASEN and F. A. BARTA (*Physical Rev.*, 1931, [ii], 37, 1626—1630).—The crystals are hexagonal with 2 mols. per unit cell; space-group D_6^2 ;

a 5.469±0.003, c 5.155±0.005 Å. Atom positions and grouping are detailed. N. M. BLIGH.

Crystal structure of tysonite. I. OFTEDAL (Z. physikal. Chem., 1931, B, 13, 190—200).—Tysonite has a 7.124±0.007, c 7.280±0.007 Å.; space-group D_{6h}^3 , or possibly D_6^3 ; the unit cell contains 6 mols. The structure appears to be simpler than that previously described (A. 1929, 1223). H. F. GILLBE.

Lattice dimensions and space-group of braunite. G. AMINOFF (K. Svensk. Vetén. Handl. Stockholm, 1931, [iii], 9, No. 5, 14—22).—The space-group is probably D_{3h}^{20} . The unit cell, a 13.28, c 18.58, contains 8 mols. of $3\text{MnMnO}_3 \cdot \text{MnSiO}_3$.

L. J. SPENCER.

X-Ray diffraction by incandescent carbon. M. HIRATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 219—226).—The positive and negative incandescent electrodes of a C arc were examined by X-rays. The thermal expansion of graphite takes place in the direction perpendicular to the (002) plane. Reflexions due to the oblique planes and to second order (002) in the incandescent state are much diminished in intensity. W. GOOD.

Nature of the specific properties of molecular surface fields. Structure of active charcoal and the inversion effect for heats of adsorption and wetting. II. B. ILJIN and J. SIMANOV (Z. Physik, 1931, 70, 559—561; cf. this vol., 421).—Debye photographs which showed no difference in structure between hydrophobic and quasihydrophilic C detected 2% of graphite deposited on the hydrophilic form.

A. B. D. CASSIE.

X-Ray investigations of the crystals of copper formate dihydrate. M. PRASAD and H. M. MAPARA (Indian J. Physics, 1931, 6, 41—49).—The rotating-crystal method gives a 8.952, b 6.726, c 8.235 Å.; the unit cell contains 4 mols.; they are asymmetric.

A. J. MEE.

Crystal form of paraffin hydrocarbons. G. H. GRAVES (Ind. Eng. Chem., 1931, 23, 762).—Photomicrographs of synthetic hydrocarbons containing 22, 23, 30, and 40 C atoms are given. The crystal plates are similar in form to the waxes $\text{C}_{18}\text{H}_{38}$ to $\text{C}_{43}\text{H}_{88}$ obtained from paraffin wax. T. A. SMITH.

Crystal structure of methane. H. H. MOOY (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 660—662).—The separation of the C and H atoms in solid CH_4 at 20.5° abs. is 0.09 Å., whereas the value deduced from infra-red data is 1.13 Å. The space-group structure is T_d^2 . W. R. ANGUS.

Crystal structure of natural amino-acids and related compounds. J. D. BERNAL (Z. Krist., 1931, 78, 363—369).—The following data are given: dimensions of unit cell, a , b , c , (where not 90°) β , no. of mols. therein, and space-group: α -glycine 5.04, 12.1, 5.41, 111° 38', 4, $C_{2h}^2 2_1 n$; β -glycine 5.18, 6.18, 5.29, 114° 20', 2, C_2^n ; l -cystine 5.40, 5.78, 5.40, 120°, 6, $D_6 6_1 2$; dl -alanine 6.0, 12.0, 5.8, 4, $C_2^2 bn$ (pseudo bnm); d -alanine 6.0, 12.1, 5.75, 4, $V^4 2_1 2_1 2_1$ (pseudo bnm); d -phenylalanine 30.8, 11.0, 4.8, 8, $V^4 2_1 2_1 2_1$; l -aspartic acid 5.1, 6.9, 15.1, 96°, 4, $C_2^2 2_1$; asparagine 5.6, 11.8, 9.86, 4, $V^4 2_1 2_1 2_1$; l -glutamic acid 7.06,

10.3, 8.75, 4, $V^4 2_1 2_1 2_1$; diketopiperazine 5.19, 11.5, 3.96, 83°, 2, $C_{2h}^2 2_1 a$; α -glycylglycine, 7.7, 9.56, 9.5, 125° 20', 4, $C_{2h}^2 2_1 a$; β -glycylglycine, 17.3, 4.65, 8.4, 125° 20', 4, $C_{2h}^2 2_1 a$; γ -glycylglycine, 8.1, 9.36, 7.7, 4, $C_2^2 bc$; diglycylglycine dihydrate 22.0, 9.8, 4.7, 4, $C_{2h}^2 ca$; BaCl_2 -glycine 7.96, 14.7, 9.21, 4, $V_1^4 6mn$. β -Glycine is obtained by adding EtOH to a glycine solution. Diglycylglycine was obtained in only one form, whether crystallised from H_2O or aq. EtOH. The positions of the atoms are sketched.

C. A. SILBERRAD.

Physico-chemical researches on amino-acids. VII. T. YAGINUMA and K. HAYAKAWA. VIII. T. YAGINUMA (J. Soc. Chem. Ind. Japan, 1931, 34, 215—216B, 216—218B).—I. The identity of a substance isolated in a biochemical research by S. Shiraishi, and believed to be histamine picrate, has been confirmed by comparing its crystallographic properties with those of chemically prepared histamine picrate. The latter is monoclinic, sphenoidal, β 100° 39', $a:b:c=1.2216:1:1.2266$. Values of n_a , n_β , n_γ , and ν for three wave-lengths are given.

II. d - and l -Leucine have the following crystallographic properties: orthorhombic, $a:b:c=1.5139:1:1.0025$, n_a 1.5331, n_β 1.5361, n_γ 1.5514. d - and l -Norleucine are orthorhombic, $a:b:c=1.3924:1:2.8662$; n_a 1.5100, n_β 1.5104, n_γ 1.5385.

N. H. HARTSHORNE.

Theory of X-ray interference in p -azoxyanisole. E. BUCHWALD (Ann. Physik, 1931, [v], 10, 558—578).—Simple models are proposed for the explanation of the interference of X-rays in p -azoxyanisole observed by Hermann and others. In a magnetic field all the aggregates are arranged in the same direction, and the max. are perpendicular to the N-S direction; without the field the aggregates are irregularly disposed, and the max. are given, not by Bragg's formula, but by that of Keesom. A. J. MEE.

X-Ray diffraction of organic substances in the solid and liquid state. S. TANAKA, G. OKUNO, and A. TSUJI (Mem. Coll. Sci. Kyoto, 1931, A, 14, 67—71).—From a study of the relation of the crystal lines to the liquid bands it is concluded that the crystal planes which produce intense reflexion seem to maintain their properties when the crystal becomes liquid. W. GOOD.

Relation between m. p. and crystal structure. A. FERRARI (Atti III Cong. Naz. Chim., 1929, 449—451; Chem. Zentr., 1931, i, 2162—2163).—The m. p. is considered to depend on the number, mass, and distance of the atoms surrounding a given atom. Increasing distance should depress the m. p. The m. p. of halides of univalent metals falls with increasing radius of the negative ion. A regular depression of m. p. is not observed when the crystal structures of the halides differ, as in halides of bivalent metals. For elements of similar structure and nearly equal at. radii (V, Mo, W, Ta) the m. p. is given approx. by the formula $2700\sqrt{\text{at. wt.}/a^2}$, where a is the length of side of the unit cell. In body-centred lattices the m. p. is approx. proportional to at. wt.^{1/2}. For Al, Ag, and Au the formula $400 \times \text{at. wt.}^{1/2}$ holds.

A. A. ELDRIDGE.

Micelle structure of the wool fibre. J. B. SPEAKMAN (Proc. Roy. Soc., 1931, A, 132, 167—191; cf. A., 1930, 1370).—On immersion in H_2O , dry Cots-wold wool fibres increase in length and diameter by 1.19 and 17.5%, respectively. The inter-micellar distance in the dry fibre is of the order of 6 Å., but in fibres swollen in H_2O it is 41 Å. The internal surface of the fibre is estimated as 0.77×10^6 sq. cm./g. approx. The total inter-micellar H_2O adsorbed by wool from saturated air is 20.5% of the dry wt. The value deduced from a study of the change in rigidity of wool with H_2O adsorption is 21.6%. The energy required to stretch wool fibres is less in HCO_2H and $AcOH$ than in H_2O , and observations on swelling in the two acids suggest that their action on wool is due to a reversible destructive action on the micelle structure, the long-chain protein mols. being partly freed from one another. Aq. solutions of a number of other acids have the same action on wool.

L. L. BIRCUMSHAW.

Relation of ferromagnetism to conductivity. H. SACHSE (Z. Physik, 1931, 70, 539—547).—The difference in electrical conductivity of Fe_2O_3 and Fe_3O_4 observed by Ghosh (this vol., 673) is too great, and probably bears no relation to their different magnetic properties.

A. B. D. CASSIE.

Anisotropy of magnetisation in ferromagnetic single crystals. F. BLOCH and G. GENTILE (Z. Physik, 1931, 70, 395—408).—Theoretical. An investigation of interaction of elementary magnets in ferromagnetic single crystals.

A. B. D. CASSIE.

Cohesion of natural fluorite crystals. E. REXER (Z. Krist., 1931, 78, 251—256).—Using Blank's method (cf. A., 1930, 845) the mean tensile strength perpendicular to an octahedral face of fluorite varied from 1323 to 4930 g. per sq. mm. for crystals of various origins, the purest giving the lowest figures. Variations are due to impurities (cf. A., 1930, 675).

C. A. SILBERRAD.

Deformation of crystals at high pressures and temperatures. F. HEIDE (Z. Krist., 1931, 78, 257—278).—Using Rose and Mügge's apparatus (cf. A., 1923, ii, 852) pressures up to 17,000 atm. and temps. to 400° applied to crystals of barytes, celestite, and anglesite caused translations along (001), (011), (102), (010), and probably (110), and slipping with $K_1=(110)$, $K_2=(110)$. Heat greatly facilitates the action of pressure. The production of Grahmann's modifications of barytes and celestite by heat (cf. A., 1913, ii, 586) is confirmed.

C. A. SILBERRAD.

Mutual orientation and the forces at crystal faces. C. A. SLOAT and A. W. C. MENZIES (J. Physical Chem., 1931, 35, 2005—2021).— KCN , KBr , $RbCl$, and $RbBr$, when deposited on PbS , are oriented if contamination of the surface of the substrate by oil is prevented. Royer's results with the substrate $NaCl$ have been confirmed, except for $RbCl$. In salts which exhibit orientation the ratio of the radius of the anion to that of the cation is relatively large; the tendency to orientation therefore increases with decrease of symmetry of the field of the ion pair. Mutual orientation is readily obtained by using an org. solvent, and is favoured by solvents of low dielectric const. The apparent hydrophobia of galena

is due merely to the affinity of the mineral for grease. The orientation of salts on Ag demands a smaller difference of parameter than does that on a salt substrate; the results described are attributed to the presence of a positive charge on the Ag crystal. The change of habit observed when crystals grow in presence of a foreign substance is not due to preferential adsorption. The forms of NH_4Cl and NH_4Br which are stable at high temp. are oriented when deposited from the vapour phase on $NaCl$ or KCl . Mutual orientation does not apparently occur between electrovalent and covalent compounds.

H. F. GILLBE.

Dimorphism of certain higher aliphatic compounds. J. W. C. PHILLIPS and S. A. MUMFORD (J.C.S., 1931, 1732—1737).—Cetyl and octadecyl acetates, cetyl chloride, and Et cetylmalonate show monotropic dimorphism. The large and transparent crystals first obtained when the liquid is cooled are transformed into a finer, more opaque, and higher-melting form when seeded with crystals which have been cooled below 0°. Cetyl bromide, cetyl iodide, margaritrile, Et margarate, and Et cetyl ether can only be said with certainty to exist in one form, although it is possible that another is produced momentarily. In the first three cases the modification obtained corresponds with the β -variety of the first substances mentioned, and in the case of the latter two compounds to the α -form. The margaric ester on further cooling changed into a more opaque form, the transition temp. being $14.5 \pm 3^\circ$. This behaviour is not shown by the palmitic and stearic esters. The cooling curves of the other compounds and also of *n*-hexadecane show no discontinuity down to -10° , although that of cetyl alcohol showed a well-defined discontinuity at about 40° .

A. J. MEE.

Physics of real crystals. A. SMEKAL (Physikal. Z., 1931, 32, 581—583).—A summary of recent work.

A. J. MEE.

Calculation of the latent heat of fusion of camphor from vapour pressure-temperature data. R. J. W. LE FÈVRE and C. G. TIDEMAN (Nature, 1931, 127, 972—973).—Attention is directed to errors in Jouniaux's calculation (A., 1912, ii, 625).

L. S. THEOBALD.

Glass. VI. Specific heat of boron trioxide. S. B. THOMAS and G. S. PARKS. **VII. Conductivities and dielectric constants of dextrose and boron trioxide glasses.** S. B. THOMAS (J. Physical Chem., 1931, 35, 2091—2102, 2103—2111).—VI. The sp. heat ($\pm 4\%$) of B_2O_3 glass and liquid has been determined at temp. from 35° to 350° by a specially designed calorimeter. The temp.-sp. heat curves are analogous to those obtained with org. glasses, but exhibit variations according to the rate of cooling during the prep. of the glass.

VII. The conductivities and dielectric consts. of dextrose and of $Na_4B_2O_7-B_2O_3$ mixtures throughout the interval of transition from a viscous liquid to a glass are functions of the viscosity, and vary continuously.

H. F. GILLBE.

Specific heats of five pure organic liquids and of ethyl alcohol-water mixtures. F. E. BLACET, P. A. LEIGHTON, and E. P. BARTLETT (J. Physical Chem., 1931, 35, 1935—1943).—The sp. heats of $PhEt$,

CH_2Ph_2 , NH_2Ph , and C_{10}H_8 over a range of temp. have been determined. NH_2Ph and PhEt yield anomalous temp.-sp. heat curves, but those of the other substances are linear. The max. deviation from the ideal law of the sp. heat of $\text{EtOH-H}_2\text{O}$ mixtures at 30° occurs at 30% EtOH , and with rise of temp. the max. moves regularly, until at 70° it occurs at 55% EtOH .
H. F. GILLBE.

Melting curve of hydrogen to 450 kg. per sq. cm.²
W. H. KEESOM and J. H. C. LISMAN (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 598—601).—Previous work is repeated and extended (A., 1929, 387). Good agreement between experimental and theoretical values of p is obtained.
W. R. ANGUS.

F. p. of platinum. W. F. ROESER, F. R. CALDWELL, and H. T. WENSEL (Bur. Stand. J. Res., 1931, 6, 1119—1129).—The f. p. of Pt, determined with the optical pyrometer, is $1773.5^\circ \pm 1^\circ$.
H. F. GILLBE.

Gas thermometric determination of the fixed points below 0° in combination with vapour pressure and resistance thermometers. W. HEUSE and J. OTTO (Ann. Physik, 1931, [v], 9, 486—504).—Using a He thermometer the following points on the thermodynamic temp. scale have been fixed: m. p. H_2 , -38.832° , sublimation pt. CO_2 , -78.483° , b. p. O_2 , -182.962° , b. p. H_2 , -252.780° . The first two temps., measured by two Pt resistance thermometers, showed values less than 0.05° lower than the above.
J. W. SMITH.

Molecular association and internal pressure. G. G. LONGINESCU and I. N. LONGINESCU (Bul. Chim. Soc. Române, 1930, 33, 1—7).—The phenomena attributed to mol. association may be considered as due to high internal pressure.
C. W. GIBBY.

Mathias' coefficient and the formula of G. G. Longinescu. I. N. LONGINESCU (Bul. Chim. Soc. Române, 1930, 33, 1—3).—Theoretical. Mathias' reduced coeff., in his equation dealing with the relative densities of substances in the liquid and gaseous states, is four times that of Longinescu.
C. W. GIBBY.

Thermal properties of toluene. K. NESSELMANN and F. DARDIN (Wiss. Veröff. Siemens-Konz., 1931, 10, [2], 129—154).—Curves have been constructed for the vapour tension, sp. heat of the vapour and liquid, sp. gr. and vol. of the liquid, and latent heat of vaporisation of PhMe at temps. up to 250° and pressures up to 10 atm.
A. R. POWELL.

Behaviour of the two modifications of liquid helium under pressure. W. H. KEESOM and K. CLUSIUS (Naturwiss., 1931, 19, 462).—The pressure-temp. curve for the two modifications of He is reproduced and discussed.
W. R. ANGUS.

Transition under pressure of liquid helium I to liquid helium II. W. H. KEESOM and K. CLUSIUS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 605—609).—The temp. of transition is lowered as the pressure is increased. By a linear extrapolation the transition curve intersects the pressure-temp. curve at 30 atm. and 1.75° abs.
W. R. ANGUS.

Vapour-pressure measurements. I. Vapour pressure of nitrobenzene. H. BRÜCKNER (Z. anorg. Chem., 1931, 199, 91—92).—The v. p. has been measured between 0° and 50° .
R. CUTHILL.

Gaseous state. C. ZENGHELIS (Chim. et Ind., 1931, 26, 3—8).—A discussion. The conditions under which a substance is gaseous at the ordinary temp. and pressure are (1) great stability of the peripheral electrons of the atoms or of the mols. if the substance is diatomic; (2) electronegative properties; (3) diat. constitution, unless the substance is non-reactive; and (4) a low chemical equiv.
H. F. GILLBE.

Temperature coefficient of gaseous friction. M. TRAUTZ (Ann. Physik, 1931, [v], 10, 263—264).—Mathematical.
A. J. MEE.

Molecular composition of binary liquid mixtures. G. TAMMANN (Z. anorg. Chem., 1931, 199, 117—119; cf. A., 1928, 698).—If the formation of a compound in a binary liquid mixture involves a decrease in the mol. wt. a min. or point of inflexion may appear on the viscosity-composition curve.
R. CUTHILL.

Variations in the azeotropic concentration of ethyl alcohol-benzene mixtures in relation to pressure. W. SWIENTOSEAWSKI and R. KOPCZYŃSKI (Rocz. Chem., 1931, 11, 440—448).—The composition of azeotropic mixtures of EtOH and C_6H_6 is determined for pressures of 760—1743 mm., using a differential ebullioscope.
R. TRUSZKOWSKI.

Application of resistance thermometers to ebullioscopy and tonometry. II. Azeotropy of ethyl alcohol-benzene mixtures. A. ZMACZYŃSKI (Rocz. Chem., 1931, 11, 449—468).—A modification of Swientoslawski's differential ebullioscope for work at high pressures is described. For azeotropic mixtures at different pressures the composition and b. p. are: 760 mm., 32.38% EtOH , b. p. 68.02° ; 3460 mm., 51.30% EtOH , b. p. 116.75° ; 5920 mm., 58.97% EtOH , b. p. 137.75° . Azeotropy persists at pressures up to 7500 mm., but is probably absent at higher pressures.
R. TRUSZKOWSKI.

Refractive index, atomic size, and packing in glasses. J. T. RANDALL and N. GEE (J. Soc. Glass Tech., 1931, 15, 41—53r).—Using Wasastjema's values for ionic refractivities with slight modifications, the calc. values of n_D for a series of glasses are shown to agree satisfactorily with recorded data. From the ionic diameters given by Bragg, it is shown that the mol. vol. of a glass bears an almost const. ratio to the sum of the at. vols. The degree of packing of the glasses examined is more nearly const. than that of the crystals.
M. PARKIN.

Thermal expansion of alloys of iron, nickel, and cobalt. H. MASUMOTO (Sci. Rep. Tôhoku, 1931, 20, 101—123).—The mean coeff. of thermal expansion (α) between 30° and 100° in binary and ternary alloys of Fe, Ni, and Co has been measured and the relation between α and the equilibrium diagrams of these systems studied. Alloys of small expansibility were investigated between the temp. of liquid air and the crit. point and the range of temp. available for this small expansibility was determined.

The smallest value of α found was 10^{-7} . A theory is advanced to explain the small expansibility of invar.

W. GOOD.

Thermal measurement of latent energy in cold-worked metal and alloys. S. SATO (Sci. Rep. Tôhoku, 1931, 20, 140—177).—The thermal changes which occur during the heating of cold-worked metals and alloys have been investigated and the energy retained as internal energy has been determined. The apparatus and procedure used are described.

W. GOOD.

Dependence of magnetic properties of cobalt-chromium mixed crystals on temperature. F. WEVER and H. LANGE (Mitt. Kaiser-Wilh. Inst. Eisenforsch., 1930, 12, 353—363; Chem. Zentr., 1931, i, 2178).—Solid solutions containing up to 20% Cr were studied. The polymorphic transformation shows a large temp. hysteresis. Both modifications possess a characteristic temp.-concentration curve for the loss of magnetisability.

A. A. ELDRIDGE.

System aluminium-silver. E. CREPAZ (Atti III Cong. Naz. Chim., 1929, 371—379; Chem. Zentr., 1931, i, 2158).—The phase diagram of Al-Ag alloys has been studied thermally, and the solubility of Ag in solid Al has been investigated microscopically. The compounds Ag_3Al , Ag_2Al , and Ag_3Al_2 are formed. The eutectic temp. for a saturated solution of Ag in Al and the compound Ag_3Al_2 is 567° (39.5% Al); the solubility of Ag in Al is 45% Ag at the eutectic, and <0.5% at room temp.

A. A. ELDRIDGE.

Equilibrium diagram of the chromium-carbon system. K. HATSUTA (J. Study Met., 1931, 8, 81—88).—Four carbide phases, ϵ , η , ξ , and κ , correspond respectively with Cr_4C (cubic), Cr_7C_3 (trigonal), Cr_3C_2 (orthorhombic), and (?) CrC . A eutectic ($\alpha+\epsilon$) lies at 1485° , 3.7% C. The ϵ and η phases are peritectically formed thus: $\eta+\text{melt} \rightarrow \epsilon$ (1530°); $\xi+\text{melt} \rightarrow \eta$ (above 1600°). The ξ phase probably has the max. m. p. on the liquidus curve, and forms a eutectic with the κ phase; a transformation takes place at 1505° in this phase.

CHEMICAL ABSTRACTS.

Improvement of eutectic structures. F. DE CARLI (Atti III Cong. Naz. Chim., 1929, 432; Chem. Zentr., 1931, i, 2157—2158).—Addition of small quantities of metals or alkali fluorides leads to homogeneous distribution of the crystal particles; alkali metals retard the growth of crystals on solidification.

A. A. ELDRIDGE.

Atomic size and isomorphism. G. NATTA and L. PASSERINI (Atti III Cong. Naz. Chim., 1929, 365—370; Chem. Zentr., 1931, i, 2159—2160).—Systems of oxides and hydroxides of bivalent metals with ionic radius 0.70—1.06 Å. were studied by the X-ray powder method. The systems NiO-CoO, CoO-MgO, CoO-MnO, CoO-CdO, $Co(OH)_2$ - $Mn(OH)_2$, $Mn(OH)_2$ - $Cd(OH)_2$, $Ca(OH)_2$ - $Cd(OH)_2$, $Ni(OH)_2$ - $Co(OH)_2$, $Mg(OH)_2$ - $Co(OH)_2$, and $Ni(OH)_2$ - $Mg(OH)_2$ form solid solutions in all ratios; with CdO-MnO, NiO-MnO, MgO-MnO, CoO-MnO, ZnO-MgO, NiO-ZnO, CoO-ZnO, $Zn(OH)_2$ - $Mg(OH)_2$, $Zn(OH)_2$ - $Ni(OH)_2$, and $Zn(OH)_2$ - $Co(OH)_2$ there is partial, and with NiO-CdO, NiO-CaO, MgO-CaO, CoO-CaO, MgO-CdO, CrO-CdO, $Mg(OH)_2$ - $Ca(OH)_2$, and $Ni(OH)_2$ - $Ca(OH)_2$ no,

formation of solid solutions. Two cubic oxides of bivalent metals give solid solutions in all ratios only when the difference between the cationic radii is not much greater than 13% of the radius of the smaller cation. Partial solid solutions are obtained when the difference of the cationic radii is less than 25% of the smaller radius; solid solutions were not observed when the difference was >30%. The hydroxides show an increase in solubility limits with increasing dimensions of the unit cell. Carbonates are also considered.

A. A. ELDRIDGE.

Liquid ammonia and lithium nitrate. N. KAMEYAMA (J. Soc. Chem. Ind. Japan, 1931, 34, 236B).—The vapour pressures of saturated $LiNO_3$ solutions between 10° and 50° are higher than those previously recorded.

C. IRWIN.

Solubility of sodium fluosilicate in aqueous sodium sulphate solutions and the activity coefficients of sodium fluosilicate and the fluosilicate ion. (MISS) A. G. REES and L. J. HUDLESTON (J.C.S., 1931, 1648—1652).—Solubility data are given for 17° and 20.8° . The activity coeffs. of Na_2SiF_6 and SiF_6^{2-} have been determined; comparison of the results with those of Lewis and Randall for K_2SO_4 indicates that the latter should be multiplied by 1.033.

H. F. GILLBE.

Solubilities of metallic cyanides. K. MASAKI (Bull. Chem. Soc. Japan, 1931, 6, 143—147).—The ionic conductance of CN' has been measured and from it the solubilities of the cyanides of Cd, Ni, Zn, and Co have been calc.

F. J. WILKINS.

Crystallisation of anhydrous sodium acetate from aqueous solution at room temperature. W. W. CONNER (J. Amer. Chem. Soc., 1931, 53, 2806—2807).—Complete dissolution of NaOAc occurs when $NaOAc \cdot 3H_2O$ is heated at 80° in a sealed tube. Anhyd. NaOAc crystallises when the tube is cooled to 0° , and is not converted into $NaOAc \cdot 3H_2O$ until cooled in liquid NH_3 .

J. G. A. GRIFFITHS.

Molasses formation. I. Equilibrium of the system sucrose-water-alkali chloride at 30° and the viscosity of the liquid phase. K. NISHIZAWA and M. AMAGASA (J. Soc. Chem. Ind. Japan, 1931, 34, 236—238B).—Equilibria between NaCl and KCl, sucrose, and H_2O at 30° have been examined. Chloride and sucrose mutually increase the solubility, but the effect of the former on the latter is very slight until the chloride concentration reaches 25 g. per 100 c.c. KCl has a greater influence than NaCl. No compound of sucrose and chloride exists in the solid state. There is a very marked increase in the viscosity of the solutions saturated with sucrose consequent on the presence of NaCl. This does not occur with KCl, and the formation of some metastable compound in the liquid phase is suggested.

C. IRWIN.

Discontinuities in adsorption isotherms. A. F. BENTON and T. A. WHITE (J. Amer. Chem. Soc., 1931, 53, 2807—2808; cf. A., 1930, 990).—Many of the adsorption isotherms for H_2 , N_2 , and CO at pressures between 0 and 1 atm. on Ni, Cu, and Fe, in the range -200° to 200° , exhibit stepwise increases of adsorption with pressure which are characteristic of physical or

"secondary" adsorption and occur under conditions precluding liquid or multimol. films. It is suggested that the steps represent the formation of concentric rows of adsorbed mols., first at the edges of each crystal face with successive building up towards the centre.

J. G. A. GRIFFITHS.

Adsorption of hydrogen. II. Maintenance of a unimolecular layer and liberation of recombined atoms with emission of energy. M. C. JOHNSON (Proc. Roy. Soc., 1931, A, 132, 67—82; cf. A., 1929, 639).—Numerical values are obtained for the several processes contributing to the maintenance of a loosely-packed layer of adsorbed H by the analysis of curves of the fall of pressure in an electrodeless discharge. The chance that a collision between an atom in the adsorbed layer and an atom from the gaseous phase should result in recombination and desorption decreases exponentially as the concentration of neighbouring at. H in the layer is increased. This is interpreted as indicating that the valency of a H atom in the adsorbed state is not completely unsaturated (unless it be the only atom present on the surface), and that therefore the adsorbed layer possesses the character of a lattice. It is shown theoretically, and verified experimentally by measurement of the heating of a W wire, that for a given partial pressure of at. H in the gaseous phase, the total emission of energy by recombination of atoms leaving the layer increases with rise in the initial temp. of the surface, and passes through a max.

L. L. BIRCUMSHAW.

Electrical condition of hot surfaces during the adsorption of gases. IV. Carbon and copper surfaces at temperatures up to 850°. G. I. FINCH and J. C. STIMSON (Proc. Roy. Soc., 1931, A, 132, 192—200).—A C rod does not become "normalised" (i.e., show const. and reproducible surface potential values) until the initial evolution of occluded gases has ceased. Such gas is regarded as chemically bound by the surface, which suffers structural alteration on its removal. A Cu sheet is not fully "normalised" until some time after the initial gas evolution has ceased. In this case sintering is probably occurring. O₂ forms a stable oxide completely blanketing the surface, which does not exhibit a surface potential either in vac. or in contact with O₂. Previous results obtained for Au, Ag, Ni, and Pt (A., 1927, 1135; 1928, 1087; 1929, 875) are discussed. The surface potentials acquired by any of the surfaces under similar experimental conditions tend to approach zero as the "normalisation" temp. is raised. At 850° the surface potentials fall into 3 groups: (1) O₂; (2) in vac., N₂, A, and CO; and (3) H₂. At this temp. the sp. effect of the surface is much reduced.

L. L. BIRCUMSHAW.

Critical increment of the adsorption of hydrogen on amorphous carbon at 400—520°. F. E. T. KINGMAN (Nature, 1931, 128, 272).—The rates of adsorption of H₂ by amorphous C for pressures from 1 cm. to 10⁻³ cm. Hg are given by $-dp/dt = k(Ap + p^2)$, where k is the velocity coeff. and A is a const. containing the area. A is practically doubled by a rise in temp. from 400° to 520°. Log k plotted against T^{-1} gives a straight line and a calc. crit. increment of 3×10^4 g.-cal. The results are discussed.

L. S. THEOBALD.

Porosity of charcoal and the time required for the attainment of adsorption equilibrium. M. DUBININ (Z. physikal. Chem., 1931, 155, 116—122).—The time required for the attainment of the equilibrium state in the adsorption from aq. solution of propionic, valeric, and heptonic acids, HCl, H₂SO₄, and H₃PO₄ on charcoal of varying porosity has been investigated. The reversal of the order of the adsorption series in the fatty acids, observed with fine-pore charcoals, becomes less pronounced when time is allowed for equilibrium to be established.

J. W. SMITH.

Adsorption of aliphatic acids by "gas-free" charcoal. L. LEPIN (Z. physikal. Chem., 1931, 155, 109—115).—The adsorption of the lower fatty acids on charcoal decreases with outgassing. The difference between the quantities adsorbed in air and in a vac. decreases with increasing length of the C chain, and becomes practically zero at C₅. According to the views of Schilov and Tschmutov (A., 1929, 1140; 1930, 991), this decrease in the adsorption with outgassing is explained by the removal from the C of surface basic oxides, which would cause chemical combination with the surface as well as mol. adsorption. This additional adsorption can occur only when the acid chain is oriented with its CO₂H group towards the charcoal. Hence with the higher acids for which the total surface energy becomes const. and which are oriented only with the Me group towards the charcoal, outgassing does not affect the adsorption.

J. W. SMITH.

Adsorption by silica and carbon from binary organic liquid mixtures over the entire concentration range. F. E. BARTELL and G. H. SCHEFFLER (J. Amer. Chem. Soc., 1931, 53, 2507—2511; cf. A., 1929, 757, 999).—MeOH, EtOH, PrOH, BuOH, and isoamyl alcohol are preferentially adsorbed by SiO₂ from C₆H₆ over the greater portion of the concentration range and in an order decreasing with increase of mol. wt. The positive preferential adsorption by blood charcoal is much less and is limited to a much smaller range of concentrations. S-shaped adsorption curves are obtained in all cases except in the systems MeOH—C₆H₆—SiO₂ and isoamyl alcohol—C₆H₆—C which exhibited no preferential adsorption of C₆H₆ and alcohol, respectively (cf. A., 1930, 1110). The modified Freundlich equation applies to all cases. The greater is the solubility, in a given solvent, of a member of a series of compounds with similar adhesion tensions against an adsorbent, the smaller is the tendency for the solute to be adsorbed.

J. G. A. GRIFFITHS.

Adsorption by silica from non-aqueous binary systems over the entire concentration range. F. E. BARTELL, G. H. SCHEFFLER, and C. K. SLOAN (J. Amer. Chem. Soc., 1931, 53, 2501—2507; cf. A., 1929, 999).—The binary systems of Et₂CO₃ with C₆H₆, MeOBz, and NPhMe₂, and of EtOH with C₆H₆ have been investigated interferometrically and the results represented by the equation previously developed. The component with the higher adhesion tension against SiO₂ is preferentially adsorbed over the greater portion of the concentration range and for each system an S-shaped adsorption curve is obtained which is very nearly the inverted and reverse form of that obtained with the same binary system and C as ad-

sorbent. This result is related to the general rule that the order of increasing adhesion tensions of a series of liquids against C is the reverse of the order of increasing values against SiO_2 .

J. G. A. GRIFFITHS.

Hysteresis effects in the absorption of water by human hair. N. H. CHAMBERLAIN and J. B. SPEAKMAN (*Z. Elektrochem.*, 1931, 37, 374—375, 376—377).—It is claimed that, contrary to the observations of Fricke and Lüke (A., 1930, 542, 1118), the absorption of H_2O by hair exhibits hysteresis.

R. CUTHILL.

[Hysteresis effects in the absorption of water by human hair.] R. FRICKE and J. LÜKE (*Z. Elektrochem.*, 1931, 37, 375—376).—A reply to Chamberlain and Speakman (cf. preceding abstract).

R. CUTHILL.

Theory of static and dynamic displacement. III. D. REICHNSTEIN (*Z. Elektrochem.*, 1931, 37, 365—371; cf. A., 1928, 132).—The application of the theory to adsorption is described and adsorption isotherms are deduced. It is shown that the Freundlich isotherm is in substantial agreement with the theory, and that it is probable that in many cases of adsorption saturation is not reached in a finite time.

R. CUTHILL.

Topochemistry of contact catalysis. VI. Detection of adlineation by radioactive indicators. G. M. SCHWAB, E. PIETSCH, and (FRL.) E. JOSEPHY (*Z. physikal. Chem.*, 1931, B, 13, 13—17; cf. this vol., 919).—Further evidence has been obtained to show that the adsorption of Th-B by crocoisite (A., 1929, 1399) is due to adlineation at the edges of the crystals.

R. CUTHILL.

Adsorption method for determination of area of a powder. W. D. HARKINS and D. M. GANS (*J. Amer. Chem. Soc.*, 1931, 53, 2804—2806).—The area is computed from the decrease in concentration of a solution of oleic acid in very dry C_6H_6 after establishing adsorption equilibrium with the powder (e.g., TiO_2 or SiO_2 dried at high temp. in vac.) and assuming that the area per mol. of adsorbed acid is 20.0 sq. Å. The adsorption becomes almost const. at concentrations greater than 0.01—0.02 g.-mol. of acid per kg. of C_6H_6 .

J. G. A. GRIFFITHS.

Micro-method for the measurement of surface tension. H. MOUQUIN and S. NATELSON (*J. Physical Chem.*, 1931, 35, 1931—1934).—The very simple method described is based on measurement of the pressure necessary to force a drop of the liquid along a conical capillary in the direction of the larger cross-section; a microscope is the only special apparatus required, and the accuracy is comparable with macro-methods.

H. F. GILLBE.

Variability of surface tension of water with increasing thickness of the glass plate. (Experiments with Searle's tensiometer.) B. N. SRIVASTAVA (*Kolloid-Z.*, 1931, 56, 45—49).—In surface-tension determinations using the Searle tensiometer, the values obtained increase linearly with the thickness of the glass plate used.

E. S. HEDGES.

Theory of variability of surface tension with the thickness and section of the glass plate as measured with the Searle tensiometer. S. RAY.

(*Kolloid-Z.*, 1931, 56, 49—51).—A theoretical treatment (cf. preceding abstract).

E. S. HEDGES.

Capillary activity in aqueous solutions. H. MILLS and P. L. ROBINSON (*J.C.S.*, 1931, 1629—1648).—On the basis of surface tension measurements two groups of capillary-active compounds are recognised. For those which show only slight interfacial adsorption the surface tension depression at equimol. concentration is proportional to the fourth power of the parachor; the proportionality const. is 7.9×10^{-8} approx. for a number of acids, alcohols, ketones, and amines. The rule breaks down if the surface concentration is relatively great, but is apparently valid if the bulk concentration alone is considered. A bubbling method for determining the rate of interfacial adsorption in such solutions is described. The rate diminishes with dilution and increases with increase of the ratio of max. adsorption concentration to bulk concentration; initially it is very small.

H. F. GILLBE.

Unimolecular layers of proteins. F. HERÖIK (*Kolloid-Z.*, 1931, 56, 1—7).—The properties of unimol. films of serum, serum- and egg-albumins, and myoprotein, as determined by the surface tension min. method of du Noüy, bear no relation to those recognised by the spreading method of Langmuir and Adam, probably because the latter method gives rise to films of denatured proteins.

E. S. HEDGES.

Capillary systems. XI. Dialytic behaviour of canal-like capillary systems. (Collodion membranes, cellophane, parchment.) E. MANEGOLD and K. VIETS (*Kolloid-Z.*, 1931, 56, 7—40).—A mathematical investigation is made of the dependence of dialysis on the size of cross-section of the capillaries and of the dialysing mols. In the case of membranes of collodion, the H_2O content of the membrane has a considerable influence on the velocity of dialysis of carbamide, urethane, sucrose, HCl, KCl, and LiCl, and in H_2O -rich membranes the mobility of these substances is practically equal to that calc. for free diffusion through the available space in the membrane. Dialysis with cellophane membranes leads to calc. diffusion consts. which are only 20% of the values of the free diffusion consts., suggesting that only a fraction of the capillary space is permeable to the dissolved mols. The results obtained with parchment are similar on the whole, although the possibility of adsorption forces hindering the dialysis, particularly in the early stages, is recognised.

E. S. HEDGES.

Membrane and osmosis. II. F. A. H. SCHREINEMAKERS (*Rec. trav. chim.*, 1931, 50, 883—899; cf. this vol., 422).—In the system H_2O -membrane-solution, the direction in which H_2O diffuses depends on the nature of the membrane, the solute, and (sometimes) the concentration of the solution. Through a membrane of cellophane, H_2O flows into solutions of tartaric or succinic acid. Through a membrane of pig's bladder, H_2O flows into solutions of Na_2CO_3 , out of solutions of oxalic acid, and into conc. but out of dil. solutions of tartaric or succinic acid. Through a membrane of parchment, H_2O flows into solutions of succinic acid. These results are discussed in the light of general theoretical considerations.

R. S. CAHN.

Freezing of dilute, still solutions. V. GIAMBALVO (Z. tech. Physik, 1931, 12, 111—113; Chem. Zentr., 1931, i, 2160).—The f. p. (t_c) and the temp. of max. $d(t_M)$ of an aq. solution are linear functions of the percentage content p . When $t_c = t_M$, $p = a$; the typical cases $p > a$, $t_M < t_c$ and $p < a$, $t_M > t_c$ were studied for NaCl solutions as regards change of concentration and crystallisation phenomena. A. A. ELDRIDGE.

Precision cryoscopy; f.-p. depressions of potassium cobalticyanide and potassium ferricyanide. C. ROBERTSON and V. K. LA MER (J. Physical Chem., 1931, 35, 1953—1984).—The sources of error inherent in cryoscopic measurements are critically reviewed, and an apparatus with an error of $1^\circ \times 10^{-5}$ is described; the f. p. is determined by using a Cu-Ni thermocouple in conjunction with a high-sensitivity galvanometer and a special potentiometer circuit. From a consideration of the magnitude of the individual errors involved a new type of apparatus has been designed. Measurements with 0.0003—0.005M- $K_3Co(CN)_6$ and $K_3Fe(CN)_6$ solutions agree with the form of the osmotic deviation function derived by Gronwall, La Mer, and Sandved by extension of the Debye-Hückel theory. H. F. GILLBE.

Effect of small amounts of impurities on f. p. of organic compounds (apparent and true f.-p. depression). C. WEYGAND and W. GRÜNTZIG (Naturwiss., 1931, 19, 660).—Small amounts of impurities in certain triglycerides which exhibit polymorphism may result in the separation on freezing of a metastable modification, the apparent f.-p. depression being abnormally large in consequence.

R. CUTHILL.

Observation by the ultra-microscope of smoke particles falling on liquid films. P. D. WATSON and A. L. KIBLER (J. Physical Chem., 1931, 35, 2125—2128).—A practical note. Direct evidence has been obtained of the existence of a H_2O film on smoke particles. The reactions between smoke particles and Cl_2 and the influence of Na oleate on the solubility of moist smoke particles in olive oil have been studied.

H. F. GILLBE.

Measurement of particle size for cellulose nitrate dispersion. H. B. DE VORE and W. P. DAVEY (J. Physical Chem., 1931, 35, 2129—2131).—The thickness of a cellulose nitrate film on water bears a linear relationship to the log. of the concentration of the dispersion used. The ultimate particle size is not greater than 1.7×10^{-7} cm., and is therefore not very different from that of the unit cell of cellulose nitrate. H. F. GILLBE.

Phenomenon shown by highly-charged aerosols. W. CAWOOD and H. S. PATTERSON (Nature, 1931, 128, 150).—The formation of a spherical cluster of highly-charged particles in the centre of the discharge vessel in which aerosols are produced is described and explained. L. S. THEOBALD.

Röntgenographic examination of internal structure of soap micelles. R. SPYCHALSKI (Rocz. Chem., 1931, 11, 427—439).—The X-ray diagrams of hydrosols of the Na salts of nonoic, deoic, undeoic, myristic, and oleic acids are identical with those of the corresponding dehydrated gels, indicating that

the structure of the micelle is unaffected by gelation. The micelles are microcryst., consisting of rectangular prisms, the width and depth of which are const. for all soaps examined (5.0 and 3.7—4.0 Å., respectively), whilst the length varies from 22.8 Å. for nonoic acid to 44.8 Å. for oleic acid; the Na atoms are placed at the corners of the prism. During gelation in polar liquids the prisms join at their ends, yielding long threads, whilst in non-polar liquids they join at their edges, forming laminæ. R. TRUSZKOWSKI.

Apparatus for the rapid measurement of the osmotic pressure of colloidal solutions. P. VAN CAMPEN (Rec. trav. chim., 1931, 50, 915—920).—An apparatus with which the osmotic pressure of 10 c.c. of a solution can be determined in <0.5 hr. is described. The wt. of the micelle of commercial (Merck) hæmoglobin is found to be approx. 18,000, 16,900, and 16,130 in H_2O at the concentrations 9.8, 15.3, and 23.9 g. per litre, respectively. R. S. CAHN.

Structure-viscosimetric measurements of cellulose derivatives in organic solvents and the influence of additions on their viscosity. I. Y. NISIZAWA (Kolloid-Z., 1931, 56, 59—67).—Measurements with the overflow viscosimeter show that sols of cellulose nitrate, cellulose acetate, and ethylcellulose in $COMe_2$, CH_2Ph-OH , and mixtures of $EtOH$ and Et_2O exhibit structure viscosity. The strongest effects were observed with cellulose nitrate in $EtOH-Et_2O$ mixtures rich in Et_2O , with cellulose acetate in CH_2Ph-OH , and with ethylcellulose in $EtOH-C_6H_6$ mixtures. As a rule, the structure viscosity increases with the addition of a medium having a pronounced solvent power. E. S. HEDGES.

Action of water on cellulose derivatives. J. DUCLAUX and J. BARBIÈRE (J. Chim. phys., 1931, 28, 313—315).—When small quantities of H_2O (less than 5%) are added to sols of cellulose dinitrate or cellulose acetate in $COMe_2$, the viscosity is diminished, but larger quantities of H_2O increase the viscosity and act as a coagulant. The different behaviour is ascribed to the state of association of the H_2O , which seems to act as single mols. when present in small quantity and as complex mols. when present in larger amount. That the apparent solvent action of small amounts of H_2O is due to interaction of OH radicals with those in the cellulose derivative is confirmed by the fact that when H_2O is added to cellulose trinitrate solutions in $COMe_2$, the viscosity increases from the start. E. S. HEDGES.

Protective effect of salts of organic hydroxy-acids on cupric oxide sol. S. K. BASU and G. NARASHINA-MURTY (Kolloid-Z., 1931, 56, 51—59).—The protective effect of Na salicylate, gallate, and tannate on CuO sols has been studied by experiments on adsorption and cataphoresis and by spectroscopic observations in the visible and ultra-violet regions. These independent lines of investigation indicate the formation of a complex. E. S. HEDGES.

Photophoresis in suspensions and suspensoids. G. FACHINI (Kolloid-Z., 1931, 56, 40—45).—Photophoresis has been observed in isodisperse suspensions of lamp-black in H_2O in the presence of a protective colloid. E. S. HEDGES.

Swelling of gelatin in solutions of calcium salts. W. VON MORACZEWSKI and S. GRZYCKI (Biochem. Z., 1931, 236, 432—443).—In presence of Ca salts, which become less sol. as the temp. rises, gelatin experiences a greater swelling at low temp. than at high, especially with more conc. gelatin solutions. With $\text{Ca}(\text{SCN})_2$ the gel contains a greater proportion of Ca than the residual fluid. An excess of Ca occurs in the residual fluid with higher concentrations of most org. or inorg. Ca salts, whilst with more dil. solutions excess of Ca^{++} is found in the gel. This partition of the Ca depends, not only on the dilution, but also on the reaction of the medium with reference to the isoelectric point of gelatin.

F. O. HOWITT.

Isoelectric point of a standard gelatin preparation. D. I. ИГГЧЕЦОВ (J. Gen. Physiol., 1931, 14, 685—699).—Values obtained for the isoelectric point are (a) p_H 4.86, the limiting val. of the p_H of aq. solutions of gelatin of increasing concentration, (b) p_H 4.85, at which point addition of gelatin does not affect the p_H of acetate buffers, (c) p_H 4.85 by observing max. turbidity of gelatin gels, and (d) p_H 4.80 by determining the p_H corresponding with zero cataphoretic velocity of suspensions of collodion in gelatin solution.

A. COHEN.

Effect of addition of salts on the isoelectric point of proteins. S. J. PRZYŁECKI (Biochem. J., 1931, 25, 713—727).—Serum-albumin solutions coagulate when heated at 100° above p_H 4.7 and below p_H 1. Various mineral salts produce coagulation at a certain crit. concentration (C_K) for each p_H . The C_K is at a max. at p_H about 2 and varies in accordance with the Hardy-Schulze rule. The ratios of C_K for ter-, bi-, and uni-valent anti-ions are as 1 : 30 : 500. The value of C_K of anti-ions depends on the valency of the accompanying iso-ion. The C_K of salts is less in solutions containing acids giving rise to bivalent as compared with univalent ions. The coagulative action of two or more anti-ions at concentrations below the crit. is additive. Salts possessing a univalent anti-ion and a multivalent iso-ion exert in certain concentrations a peptising action. Analogous results are obtained at p_H vals. higher than those of the isoelectric point. Coagulation can be effected by the addition of salts to systems containing 85% EtOH at any p_H . The Hardy-Schulze rule is followed in such systems and the max. vals. of C_K are at p_H 2. The C_K of Na_2SO_4 for caseinogen hydrochloride at p_H 2 has practically the same val. at 20° , 100° , and in 85% EtOH systems; that of SO_4^{--} is considerably higher. Gelatin in 80% EtOH can be flocculated at any p_H by crit. concentrations of anti-ions, the value of C_K varying according to the Hardy-Schulze rule. It varies inversely with the concentration of EtOH. The C_K of Na_2SO_4 increases with the free charge on the gelatin particles up to a certain max., after which it again falls as for albumin. The C_K of anti-ions increases with the valency of the iso-ions. The crit. concentration of EtOH necessary to flocculate gelatin at a given concentration of Na_2SO_4 is higher in the presence of MgCl_2 than in its absence and conversely at a given concentration of EtOH. The C_K of Na_2SO_4 is considerably higher in the presence of multivalent

iso-ions. The peptising action of multivalent iso-ions is not apparent in high concentrations of EtOH in which salts possessing a multivalent iso-ion and univalent anti-ions exert a coagulative action. Isostable proteins can be converted into isolabile proteins by heating at 100° or by addition of EtOH. The C_K of Na_2SO_4 for a given p_H is practically the same for serum-albumin, gelatin, and caseinogen in presence of HCl in 85% EtOH. Salts possessing multivalent anti-ions are able to discharge protein particles at any p_H , C_K being different at each p_H for each salt. The coagulum differs from that obtained at the isoelectric point.

S. S. ZILVA.

Effect of hydrogen-ion concentration on the precipitating and protective actions of proteins on colloidal gold and gum-benzoin. R. H. HORKINS, W. O. KERMAK, and W. T. SPRAGG (Biochem. J., 1931, 25, 829—842).—The effect of gelatin, ovalbumin, serum-albumin, pseudoglobulin, euglobulin, and oxyhæmoglobin has been studied. In very low concentration of protein, precipitation occurs on the acid side of the isoelectric point, but as the concentration increases the zone of precipitation approaches the isoelectric point and when sufficient protein is present the centre of the zone, except in the case of hæmoglobin, is at the isoelectric point. In the presence of 1.25% NaCl min. protection by these proteins except oxyhæmoglobin is at the isoelectric point. With Au the ppts. are usually red in the neighbourhood of the isoelectric point. Oxyhæmoglobin behaves as if its isoelectric point lay below its real value of about p_H 6.8. This is more pronounced with Au than with gum-benzoin. Michaelis and Nakashima's method for the determination of the isoelectric point of protein is therefore not of general application.

S. S. ZILVA.

Electrokinetic properties of proteins. I. Isoelectric point and solubility of wheat proteins in solutions of alcohol. W. M. MARTIN (J. Physical Chem., 1931, 35, 2065—2090).—Proteins are readily adsorbed on the porous diaphragms of filter crucibles, and a streaming potential method based on this fact has been developed for determining the isoelectric point of various proteins. The solubility of the protein extracted by aq. EtOH from wheat gluten is a max. at about 57% EtOH, whilst the relative isoelectric point falls continuously with increase of the EtOH concentration; the rate of change is small at concentrations between 40 and 70%.

H. F. GILLBE.

Generalised thermodynamics including the theory of fluctuations. G. N. LEWIS (J. Amer. Chem. Soc., 1931, 53, 2578—2588).—The laws of thermodynamics and of fluctuations are shown to constitute a generalised thermodynamics developed from a single postulate which is a new statement of the second law of thermodynamics.

J. G. A. GRIFFITHS.

Stability of nitrogen pentoxide at 1000 atm. of oxygen in presence of nitrogen tetroxide. L. LEWON and H. EYRING (J. Amer. Chem. Soc., 1931, 53, 2801—2802).—The reaction $\text{N}_2\text{O}_5 = \text{N}_2\text{O}_4 + \frac{1}{2}\text{O}_2$ in CCl_4 at 25° in presence of O_2 at 1000 atm. proceeds to completion. The equilibrium const. is greater than 1.48×10^4 (atm.), from which the free energy change is

less than -5600 g.-cal., and ΔH is less than 1600 g.-cal.
J. G. A. GRIFFITHS.

Dissociation of strong electrolytes. IV. M. B. JACOBS and C. V. KING (J. Physical Chem., 1931, 35, 1922—1930).—The evidence of crystal structure data, transference no., conductivity, and concentration cell measurements, data employed for testing the Debye-Hückel theory, and the additive properties of ions are discussed in relation to the theory of complete dissociation; indisputable evidence of the presence of undissociated mols. in solutions has not yet been obtained, but is essential if the latter theory is to be accepted.
H. F. GILLBE.

Hydrolysis of cupric sulphate. (MLLE.) QUINTIN (Compt. rend., 1931, 193, 163—164).—Previous results (cf. A., 1927, 729) for CuSO_4 are confirmed and amplified by measurements with the quinhydrone electrode.
C. A. SILBERRAD.

First dissociation [constant] of phosphoric acid in aqueous salt solutions at 18° . J. W. H. LUGG (J. Amer. Chem. Soc., 1931, 53, 2554—2560; cf. this vol., 308).—Negligible liquid junction potential exists between dil. solutions of HCl and H_3PO_4 in a neutral chloride solution, and the e.m.f. is an exact measure of the relative H^+ activities (cf. A. 1929, 140). From determinations of the e.m.f. of the cell quinhydrone electrode $10\cdot0015-0\cdot006M\text{-HCl}$ or $0\cdot002-0\cdot01M\text{-H}_3\text{PO}_4$ in $0\cdot01-1\cdot6M\text{-XCl|KCl(sat.)|calomel}$ electrode, the first dissociation const. of H_3PO_4 is computed to be $pK_1=2\cdot09-\mu^2/(1+x\mu^2)$, where $x=1\cdot6, 2\cdot12, 1\cdot14$, or $0\cdot93$ when $\text{X}=\text{Na}, \text{K}, \text{Mg},$ or Ca , respectively. HCl is completely dissociated even in solutions containing much metal chloride.
J. G. A. GRIFFITHS.

Classical dissociation constant of benzoic acid and the activity coefficient of molecular benzoic acid in potassium chloride solutions [at 25°]. E. F. CHASE and M. KILPATRICK, jun. (J. Amer. Chem. Soc., 1931, 53, 2589—2597; cf. this vol., 566).—From determinations of the solubility of BzOH in KCl solutions and the values of $[\text{H}^+]$ (this vol., 811), the solubility of mol. BzOH has been calc. and the activity coeff. is given by $\log f=0\cdot138c$, where $c=0\cdot1-3M\text{-KCl}$. The classical dissociation const. of BzOH is given by $\log K_c=-4\cdot2-0\cdot14c+c^2/(1+1\cdot7c^2)$. The salting-out const. of the ions of the solvent salts (this vol., 431) decrease with increasing crystal radius of the ions.
J. G. A. GRIFFITHS.

Thermodynamic constants of iodine monobromide. J. McMORRIS and D. M. YOST (J. Amer. Chem. Soc., 1931, 53, 2625—2631).—From an investigation of the equilibrium $\text{CuBr}_2(s)+\frac{1}{2}\text{I}_2(g)=\text{CuBr}(s)+\text{IBr}(g)$ at $115^\circ, 151\cdot2^\circ,$ and 176° , the free energy equation for the reaction $\frac{1}{2}\text{I}_2(g)+\frac{1}{2}\text{Br}_2(g)=\text{IBr}(g)$ is computed to be $\Delta F^\circ=-1270-1\cdot7449T$. The standard free energy of formation of $\text{IBr}(g)$ is $\Delta F^\circ_{298}=903$ g.-cal., and the heat of sublimation of $\text{IBr}(s)$ is $12,545$ g.-cal. The entropy of $\text{IBr}(g)$ ($60\cdot6$) lies between that of $\text{I}_2(g)$ and $\text{Br}_2(g)$. The increase in ΔF° and heat content at 25° attending the formation of $\text{IBr}(g)$ from the atoms lie between those attending the formation of $\text{I}_2(g)$ and $\text{Br}_2(g)$ from atoms. These relationships may be general for gaseous interhalogen compounds.
J. G. A. GRIFFITHS.

Energy of solvation and partition. Extension of Karl Fredenhagen's theory of electrolytic solubility. H. HAMMERSCHMID and E. LANGE (Z. physikal. Chem., 1931, 155, 85—99; cf. this vol., 430).—The thermodynamic significance of the energy of solvation and of partition is discussed from the point of view of Fredenhagen's theory.
J. W. SMITH.

Misleading equilibria encountered in the measurement of dissociation pressures in salt-hydrate systems. A. W. C. MENZIES and C. S. HITCHCOCK (J. Physical Chem., 1931, 35, 1660—1665).—The dissociation pressures of salt hydrates can be quickly measured by allowing equilibrium to be reached with the solid phases in contact with a liquid in which H_2O is, at least, slightly sol. and then determining the aq. partial pressure by means of the authors' apparatus for measuring v. p. lowering of a solvent (cf. this vol., 901). Results for $\text{BaCl}_2\cdot 2\text{H}_2\text{O} \rightleftharpoons \text{BaCl}_2\cdot \text{H}_2\text{O} + \text{H}_2\text{O}$ and $\text{CuSO}_4\cdot \text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + \text{H}_2\text{O}$ are recorded. In salt hydrate systems genuine equilibrium pressures may be reached; these, however, are due to adsorbed H_2O and not to true dissociation pressures.
L. S. THEOBALD.

X-Ray study of the system $\text{Fe}_2\text{O}_3\text{-SiO}_2$. P. SJÖMAN (Tekn. Samf. Handl., 1930, No. 7, 24 pp.; Chem. Zentr., 1931, i, 1737).—When quartz and Fe_2O_3 are heated together, Si atoms in the SiO_2 lattice are partly replaced by Fe atoms within limits of temp. wherein there is a tendency of conversion of quartz into cristobalite. Further, new Fe^{III} silicates are produced. X-Ray examination shows no interaction when Fe_2O_3 is heated with excess of cristobalite or tridymite.
A. A. ELDRIDGE.

System $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$. E. N. BUNTING (Bur. Stand. J. Res., 1931, 6, 946—949).— Cr_2O_3 which has not previously been fused (cf. A., 1930, 847; this vol., 41) has m. p. $2275^\circ \pm 25^\circ$, and its v. p. at this temp. is relatively low. Cr_2O_3 and Al_2O_3 are completely miscible in the liquid state, and form a continuous series of mixed crystals, but no compounds.
H. F. GILLBE.

Compounds of the system calcium oxide-ferric oxide and their rôle in Portland cement. I. J. KONARZEWSKI (Rocz. Chem., 1931, 11, 516—528).— Fe_2O_3 evolves O_2 at 1380° , yielding Fe_3O_4 , with which it forms solid solutions; as a consequence, the partial pressure of O_2 depends not only on the temp., but also on the composition of the solid solution. The m.-p. diagram of the system $\text{CaO-Fe}_2\text{O}_3$ shows the existence of two compounds, $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$, m. p. 1440° , and $\text{CaO}\cdot\text{Fe}_2\text{O}_3$, m. p. 1215° .
R. TRUSZKOWSKI.

Phase diagram of system lead iodide-silver iodide. F. E. E. GERMANN and C. F. METZ (J. Physical Chem., 1931, 35, 1944—1952).— AgI has m. p. $558 \pm 1^\circ$ and PbI_2 $412 \pm 1^\circ$ (lit. 402°). Solid solutions exist within the limits $18\cdot5-57\cdot5$ mol.-% and $85-100$ mol.-% PbI_2 , and in the liquid state the compounds are miscible up to 15 mol.-% AgI . The compound $4\text{AgI}\cdot\text{PbI}_2$ does not exist, but $5\text{AgI}\cdot\text{PbI}_2$ may be formed. The formation of solid solutions and the low crystallisation velocity render the ordinary methods of thermal analysis inapplicable to the determination of the composition of the compound formed.

The phase diagram of the system is the first of its type to be reported.

H. F. GILLBE.

Reactions of amines with sulphur dioxide. I. Aniline and sulphur dioxide. A. E. HILL (J. Amer. Chem. Soc., 1931, 53, 2598—2608).—The absorption of SO_2 by NH_2Ph affords the yellow crystals $\text{NH}_2\text{Ph}\cdot\text{SO}_2$, m. p. 65° (approx.) at 3.5 atm. The heat of vaporisation, 19,630 g.-cal., is computed from v.-p. data between 3.5° and 50° . A phase diagram for the binary compound above the m. p. of its components, showing temp., composition, and pressure as variables, is discussed. NH_2Ph affords the white normal and acid sulphites with H_2O and SO_2 . $\text{NH}_2\text{Ph}\cdot\text{SO}_2$ in moist air loses some SO_2 and absorbs H_2O with the formation of a mixture of the sulphites (cf. A., 1891, 715). J. G. A. GRIFFITHS.

Molecular lowering of f. p. for camphor. R. J. W. LE FÈVRE and (Miss) C. G. TIDEMAN (J.C.S., 1931, 1729—1732).—The f.-p. depression const. of camphor is 396. The fusion diagram of the system salicylic acid-camphor indicates the existence of a compound $2\text{C}_{10}\text{H}_{16}\text{O}\cdot\text{C}_7\text{H}_6\text{O}_3$, m. p. 56° .

H. F. GILLBE.

Ternary system zinc oxide-nitric acid-water. H. G. DENHAM and D. A. DICK (J.C.S., 1931, 1753—1757).—The system has been studied at 25° and 50° ; the diagrams obtained at the two temps. are of similar form. The solid compounds indicated are the basic nitrates, $\text{Zn}(\text{NO}_3)_2\cdot 5\text{ZnO}\cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2\cdot \text{ZnO}\cdot 3\text{H}_2\text{O}$, and the normal hexa- and tetrahydrates.

H. F. GILLBE.

Ternary system lead oxide-nitrogen pentoxide-water. H. G. DENHAM and J. O. KIDSON (J.C.S., 1931, 1757—1762).—The system has been studied at 25° and 50° . The only stable solid phases are $\text{Pb}(\text{NO}_3)_2\cdot \text{PbO}\cdot 2.5\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$.

H. F. GILLBE.

Ternary system K_2O - CaO - SiO_2 : a correction. G. W. MOREY, F. C. KRAČEK, and N. L. BOWEN (J. Soc. Glass Tech., 1931, 15, 57—58r).—The compound (A., 1930, 1374) having the optical consts. $\gamma = 1.59$, $\alpha = 1.575$, is not $\text{K}_2\text{O}\cdot 2\text{CaO}\cdot 6\text{SiO}_2$, but $\text{K}_2\text{O}\cdot 3\text{CaO}\cdot 6\text{SiO}_2$; it crystallises in two enantiomorphic modifications, the β -form having the optical and crystallographic properties previously given for $\text{K}_2\text{O}\cdot 3\text{CaO}\cdot 6\text{SiO}_2$. Transition from α - to β -form is slow, but from β to α is rapid. X-Ray powder photographs confirm the individuality of the compounds.

M. PARKIN.

Transformation of marine salts from a quaternary to a quinary system, in connexion with the treatment of langbeinite. D. LANGAUER (Rocz. Chem., 1931, 11, 477—489).—The system K_2SO_4 - MgSO_4 - H_2O - NaCl has been examined from the point of view of the phase rule. The liquid phase was unsaturated with respect to NaCl , but saturated with respect to the remaining components. The solid phases consisted at 25° of schönite, K_2SO_4 , and astrakhanite, and at 55° and 83° of leonite, K_2SO_4 , and loeveite.

R. TRUSZKOWSKI.

Heat of dissociation of oxygen, determined from its thermal conductivity. E. JENKEL (Z. physikal. Chem., 1931, 155, 100—108).—The energy consumption of a Nernst filament glowing in N_2 and

in O_2 has been measured at different temps. At about 2450° abs. the consumption in O_2 becomes somewhat greater than that in N_2 , owing to dissociation, and from the difference the heat of dissociation is calc. according to the method of Nernst to be 120 kg.-cal. The degree of dissociation of O_2 for temps. between 1800° and 2800° abs. is also calc. J. W. SMITH.

Apparent and partial molal heat capacities in aqueous solutions of 19 uni-univalent strong electrolytes. F. D. ROSSINI (Bur. Stand. J. Res., 1931, 7, 47—55).—The apparent mol. heat capacity of the solute, ϕ_c , is shown to be a linear function of the square root of the mol. concentration for aq. solutions of uni-univalent strong electrolytes from infinite dilution to about 2.5M. Consequently, the partial mol. heat capacity of the solute, C_p , and the partial mol. heat capacity of the H_2O , C_p , are linear functions of the square root of the mol. concentration and the $3/2$ power of the mol. concentration, respectively. Data are tabulated, from which may be computed values of ϕ_c , C_p , and C_p for aq. solutions of the chlorides, bromides, iodides, nitrates, and hydroxides of H, Li, Na, and K for any concentration in the given range at 18° , 21.5° , and 25° .

E. S. HEDGES.

Heats of neutralisation at constant concentration and heat of ionisation of water [at 20°]. R. H. LAMBERT and L. J. GILLESPIE (J. Amer. Chem. Soc., 1931, 53, 2632—2639).—The heat of neutralisation at const. concentration is the heat effect ($-\Delta H$) of the reaction $\text{MOH}\cdot x\text{H}_2\text{O} + \text{HA}\cdot x\text{H}_2\text{O} = \text{MA}\cdot x\text{H}_2\text{O} + (x+1)\text{H}_2\text{O}$. By employing the data of Richards and co-workers in the plot of $1/x^{\frac{1}{2}}$ against $-\Delta H$ for the chlorides and nitrates of K, Na, and Li, a family of curves is obtained which affords the extrapolated value 13,650 g.-cal. (20°) for the heat of neutralisation at infinite dilution and the heat of formation of H_2O from its ions (cf. A., 1929, 511). The temp. coeff. of the latter ($-d\Delta H/dt$) is computed to be -52 g.-cal. per 1° at 20° .

J. G. A. GRIFFITHS.

Heat of combustion of methyl alcohol. F. D. ROSSINI (Proc. Nat. Acad. Sci., 1931, 17, 343—347).—The heat of combustion of liquid MeOH to CO_2 (gas) and H_2O (liquid) at 25° and 1 atm. is 173.63 ± 0.05 kg.-cal. per mol.

J. W. SMITH.

Heat of combustion of methylglyoxal. C. FROMAGEOT and M. E. EMAMI (Bull. Soc. chim., 1931, [iv], 49, 929—936).—The bomb-calorimetric method has given the following data. Heat of formation of methylglyoxalhydrazone -38 kg.-cal.; heat of formation of dinitrophenylhydrazine in 0.33N-HCl $+6$ kg.-cal.; heat of formation of methylglyoxal, aq. $+179$ kg.-cal.; heat of combustion of methylglyoxal $+326$ kg.-cal.

E. S. HEDGES.

Change of transference number of a salt with change of concentration. Modification of the moving-boundary method. E. R. SMITH (Bur. Stand. J. Res., 1931, 6, 917—926).—The moving-boundary method has been modified by observing the vol. through which a junction between two solutions of the same salt at different concentrations moves during the passage of a known quantity of electricity. Satisfactory results are obtained for NaCl

and LiCl solutions; the transference number of KCl is practically const. for the range 0.05—4.7*M*.

H. F. GILLBE.

Dissociation constants of organic acids. IV. Mobilities of the sodium, potassium, and hydrogen ions at 25°, and the determination of cell constants at 25°. G. H. JEFFERY and A. I. VOGEL (J.C.S., 1931, 1715—1729).—Conductivity measurements in 0.0001—0.001*N* solutions yield for Λ_c of KCl (25°), NaCl (25°), and KIO₃ (18°) the expressions 149.83—101.6*c*^{0.547}, 126.18—117.4*c*^{0.551}, and 115.45—58.7*c*^{0.384}, respectively. The *c*- Λ_c curve for HIO₃ passes through a max. at *c* 0.001*N*, but at concentrations above 0.002*N* Λ_c = 351.0—384.1*c*^{0.577}. The curves are compared with those obtained by application of the Debye-Hückel-Onsager equation. The mobilities of H⁺, K⁺, Na⁺, and IO₃⁻ at 25° and of H⁺ at 18° have been calc. SiO₂ vessels must be used for conductivity measurements with acids at concentrations below 0.001*N*.

H. F. GILLBE.

Effect of voltage on the conductivity of strong and weak acids. M. WIEN (Physikal. Z., 1931, 32, 545—547).—With weak acids the effect of voltage on conductivity, although small, is 10 times that with strong acids, arising probably from an increase of ions due to ionic bombardment within the liquid. Data are given for HCl, H₂SO₄, AcOH, propionic and tartaric acid, CH₂Cl·CO₂H, and CHCl₂·CO₂H. The degree of dissociation can be computed and this is shown by reference to KI and LiBr.

W. R. ANGUS.

Influence of sucrose on the conductivity of electrolytes. J. PELLER (Z. Zuckerind. Českoslov., 1931, 55, 643—650).—Measurements of the conductivity of a number of acids and salts in presence of sucrose show that the decrease of conductivity is less the stronger is the acid, and is greater the stronger is the base. The conductivity of solutions of NH₃, (NH₄)₂CO₃, and NH₄OAc is increased by the addition of sucrose up to about 16%, further addition of sucrose causing a decrease. The influence of successive additions of sucrose on the depression of the conductivity decreases with increasing concentration of the sucrose.

E. S. HEDGES.

Constitution of sucrose solutions. E. LANDT and C. BODEA (Naturwiss., 1931, 19, 660).—The product of the viscosity and mol. conductivity at infinite dilution of solutions of NaCl, KCl, BaCl₂, and NEt₄ picrate in aq. solutions of sucrose increases with the sucrose concentration too rapidly to be accounted for entirely by diminishing hydration of the ions. It is suggested that sucrose solutions contain aggregates of sugar mols., or of sugar mols. and H₂O mols. These complexes greatly increase the viscosity and vary in number and size with the temp. and concentration. Their influence on ionic migration is the more pronounced the larger are the ions.

R. CUTHILL.

Electrical conductivity of crystalline and vitreous silicates in the system sodium oxide-silica. R. SCHWARZ and J. HALBERSTADT (Z. anorg. Chem., 1931, 199, 33—47).—Conduction through cryst. Na₂SiO₃ follows Faraday's law. With rise in the temp. the sp. conductivity, κ , increases up to about 800°, and then a period of more rapid rise extends to about 840°, beyond which the rate of increase is nor-

mal. Preheating at 870° causes a marked decrease in κ at 730—790°, probably in consequence of the formation at about 800° of a polyeutectic, with subsequent recrystallisation of the Na₂SiO₃. With Na₂Si₂O₅ glasses the log κ -1/*T* curve is discontinuous near the transformation point, the temp. coeff. beyond this point increasing with increase in the SiO₂ content. The temp. coeff. for a glass is always less than for crystals of the same composition. The high conductivities of glasses containing 30—34% of SiO₂ indicate the absence of any material complex formation, but when the glass contains only 20% of SiO₂ κ is comparatively small and there is probably pronounced complex formation and adsorption of Na⁺. An attempt has been made to utilise conductivity data in constructing the equilibrium diagram.

R. CUTHILL.

Single potential of iron and steel electrodes. H. ENDO and S. KANAZAWA (Sci. Rep. Tōhoku, 1931, 20, 124—139).—The electrode potentials of pure Fe (single crystal), electrolytic Fe in various conditions, Armco Fe, and pearlitic steel (0.1—1.4% C) have been measured. The effect of the grain boundary and slight straining was investigated. The former increases the electrode potential and the latter causes the electrode to become more electropositive.

W. GOOD.

Diffusion of hydrogen through an iron cathode. A. H. W. ATEN and P. C. BLOKKER (Rec. trav. chim., 1931, 50, 943—950; cf. A., 1930, 1125).—Purification of NaOH and H₂SO₄ does not entirely stop the diffusion of H₂ developed at an Fe cathode, but poisoning increases the rate of diffusion and the speed with which it sets in. Results with HgCl₂ in 0.1*N*-H₂SO₄ are similar to those previously obtained with As₂O₃. Addition of too much poison decreases the diffusion, particularly with higher c.d. These phenomena are explained as follows: the concentration of H atoms is greater where Hg has been deposited on the Fe, and consequently, using a little HgCl₂, diffusion through the Fe is more rapid. When sufficient HgCl₂ is used entirely to cover the surface, the Fe is cut off from the liquid and diffusion ceases; with higher current densities the ability of the Hg to form individual drops is diminished, and the effective covering power of a given amount of Hg thus increased. H₂SO₄ solutions show considerable diffusion after several days without poisoning, but alkaline solutions are more const. and, therefore, more suitable for study. Diffusion is greatly increased by addition of a little HgCl₂ to 0.1*N*-NaOH at 0.1—3 amp., and only slightly decreased by further addition of a large excess, whilst there is a rough parallelism between the cathode potential and the rate of diffusion. Results with these substances at 0.01 amp. are abnormal. Figures are given for diffusion through various Ni- and Cr-Fe alloys, using As₂O₃ in H₂SO₄. The connexion between current, potential, and rate of diffusion cannot be arrived at from these results, and the considerations of other authors are inadequate or erroneous.

R. S. CAHN.

Poisoning of hydrogen electrodes. A. H. W. ATEN and P. C. BLOKKER (Rec. trav. chim., 1931, 50, 951—956).—The reaction between O₂ and H₂ at a Pt surface is less influenced by poisoning by As₂O₃ or

HgCl₂ in 0.1*N*-H₂SO₄, or by As₂O₃ in 0.1*N*-NaOH, than is the potential of the electrolytic gas electrode (cf. this vol., 171). It follows that the catalytic action of Pt is only slightly, if at all, due to transformation of H₂ into H atoms. The results may be due either to preferential poisoning of the catalytically most active portions of the surface, or to equal poisoning of the whole surface. When large additions of HgCl₂ in H₂SO₄ have completely stopped the catalytic action, the electrode shows the potential of a Hg electrode.

R. S. CAHN.

Electromotive force of liquid-liquid cells, and the variation on dilution. L. BOUCHET (Compt. rend., 1931, 193, 149—151; cf. A., 1929, 769).—For cells M₁|*N*-M₁SO₄,aq. || *N*-M₂SO₄,aq. | M₂, where M₁-M₂ are Mg-Zn, Mg-Cu, Mg-Ag, Zn-Cu, Zn-Ag, and Cu-Ag, respectively, the e.m.f. are 0.709, 1.810, 2.275, 1.089, 1.502, and 0.444 volts; with M₁-M₂=Zn-Cu, and the solutions of ZnSO₄ 0.1*N*, 0.02*N*, and 0.01*N*, and that of CuSO₄ *N*, the e.m.f. are 1.095, 1.114, and 1.128. All these values are in good agreement with calc. figures. Similar but less regular results are obtained with chlorides, acetates, and nitrates.

C. A. SILBERRAD.

Reaction between sodium nitroprusside and sulphides. III. G. SCAGLIARINI and P. PRATESI (Atti R. Acad. Lincei, 1931, [vi], 13, 199—201; cf. A., 1930, 726).—The oxidation-reduction potential of the reaction [Fe(CN)₅NO]^{'''} + S + 2Θ = [Fe(CN)₅NOS]^{''''} with a Hg electrode is 0.348 volt at 20° for 0.1*N* solutions of the reactants.

O. J. WALKER.

Potentiometric study of adrenaline. E. G. BALL and W. M. CLARK (Proc. Nat. Acad. Sci., 1931, 17, 347—351).—The characteristic potentials of the adrenaline system are close to those of the related pyrocatechol system. The inherent instability of *o*-benzoquinone is enhanced by the presence of a side-chain with oxidisable groups. The reduction potential of the adrenaline system and the chemically undefined "reduction potentials" of the tissues must be such that the cells tend to protect this hormone from an oxidation which would result in its very rapid destruction.

J. W. SMITH.

Oxidation-reduction. XVI. The oxazines: Nile-blue, brilliant-cresyl-blue, methyl-Capri-blue, and ethyl-Capri-blue. B. COHEN (U.S. Publ. Health Serv. Suppl. No. 92, 1—67).—The oxidation-reduction potentials of the above oxazines have been measured at 30° in buffers of various *p*_H values and the results compared with theory. Methyl- and ethyl-Capri-blue are strongly basic, cresyl-blue is rather stronger than NH₃, and Nile-blue about equal to NH₃. Nile-blue sulphate corresponds with C₂₀H₂₀N₃O·SO₄H and aq. solutions of Nile-blue are colloidal. Relatively small but definite concentration and salt effects occur with cresyl-blue, and methyl- and ethyl-Capri-blue. Oxazines react readily with H₂O forming oxazones, and this reaction is accelerated by moderate acidity or alkalinity. They can be used as oxidation-reduction indicators within the range bounded by methylene-blue and indigo-carmin.

J. W. SMITH.

Oxidation-reduction of pyocyanine. II. Redox potentials of pyocyanine. B. ELEMA (Rec. trav.

chim., 1931, 50, 807—826; cf. this vol., 684).—The oxidation-reduction potential of pyocyanine was determined for the range *p*_H 1.3—11.5, using TiCl₂, K₃Fe(CN)₆, or benzoquinone in buffered solutions. Within the range *p*_H 6—9 pyocyanine is intermediate between methylene-blue and indigotrisulphonate. For *p*_H > 7 the titration curves are normal, two electrons are involved in the change, and the colour of the solution changes gradually from blue to colourless. Pyocyanine thus exists in the unimol. form in dil. aq. solution. At *p*_H > 12 the reaction is not reversible, a red pigment being formed on oxidation. Below *p*_H 7 the shape of the titration curves changes gradually until at *p*_H < 3.5 a sharp discontinuity is observable, the system behaving as if it were associated with two consecutive reactions, each involving one electron. Simultaneously, a colour change, red-green-colourless, replaces the normal one. The abnormality is due to the formation, at *p*_H < about 7, of a half-way reductant, which is shown to be a free radical rather than a meriquinone.

R. S. CAHN.

Potential of solutions of sugars. III. R. WURMSER and J. GELOSO (J. Chim. phys., 1931, 28, 260—276; cf. A., 1928, 846; 1929, 1393).—If O₂ is excluded, a solution of dextrose develops slowly an oxidation-reduction equilibrium, and this determines the potential of the solution, which at *p*_H 7.2 and at 20° is given by *E*_H = -0.05 ± 0.02 volt.

J. W. SMITH.

Photodynamic studies. III. Photogalvanic phenomena with irradiated cupric oxide electrodes. M. KARSCHULIN (Biochem. Z., 1931, 236, 312—325).—Using the photogalvanic cell fitted with CuO electrodes (A., 1930, 865) the spectral sensitivity with aq. NaF, NaI, and NaCN as electrolytes was determined. The general light absorption of the electrode and the electrical energy radiated were measured when the element was filled with aq. NaI. The photogalvanic effect does not disappear with positively-charged electrodes, and it follows that the Becquerel effect cannot be explained as a simple photo-electrical phenomenon.

F. O. HOWITT.

Physical chemistry of corrosion. F. GIORDANI (Giorn. Chim. Ind. Appl., 1931, 13, 275—281).—In the corrosion of Sn-plated containers variations in the nature of the contents may change the relative behaviour of the local couples Fe-Sn. Observations show that in acid and alkaline solutions the potential of Sn is lower than that of Fe, whilst for intermediate solutions the behaviour of the couples Fe-Sn is in conformity with the position in the electrochemical series.

O. F. LUBATI.

Energy yield and decomposition voltage in the electrolysis of sodium and potassium chloride solutions. H. RAMSTETTER and O. KAHN (Z. angew. Chem., 1931, 44, 610).—When the energy yield in the electrolysis of NaCl and KCl solutions is taken as 100 × theoretical energy/energy used and the usual method of calculating the val. for the separation of eqivs. of K and Na from the equation (Na/K)Cl + aq. = (Na/K)OH, aq. + Cl + H is used, very different vals. are found for the two metals. This is due to the circumstance that solid, and not dissolved, chlorides are considered. If correctly used, the avail-

able data lead to vals. which agree, whilst the decomp. voltages are also the same, viz., about 2.3 volts. These conclusions have been confirmed by experiments on an industrial scale. H. INGLESON.

The Leclanché cell. A. KELLER (Z. Elektrochem., 1931, 37, 342—348).—Determination of the discharge curves of the positive electrode of the Leclanché cell has shown that for discharge down to 0.7 volt the current yield with an acid electrolyte is 7—10 times that with a neutral or alkaline electrolyte, and that electrodes which have been "run down" may be regenerated by being placed in an acid electrolyte. The rapid fall in voltage during discharge is ascribed to the formation of solid solutions of MnO_2 and Mn_2O_3 , the conversion of the Mn_2O_3 into a manganous salt and MnO_2 by acid being responsible for the regenerative action of the latter. Experimental evidence has been obtained in favour of the theory that the e.m.f. of the electrode depends on the power of the MnO_2 to behave as an element and pass into solution as the MnO_2' ion. According to this view the reaction giving rise to the current is $2MnO_2 + 2H^+ = Mn_2O_3 + H_2O + 2\oplus$ in neutral and alkaline solution and $MnO_2 + 4H^+ = Mn^{++} + 2H_2O + 2\oplus$ in acid solution. R. CUTHILL.

Reaction inertia of excited atoms. G. B. KISTIAKOWSKY and P. E. MILLINGTON (Z. physikal. Chem., 1931, B, 13, 155—156; cf. this vol., 174).—Inertia has been observed in the reaction of excited O atoms with H_2 and with CH_4 . R. CUTHILL.

Kinetics of unimolecular reactions. J. K. SYRKIN (Z. anorg. Chem., 1931, 199, 28—32).—The velocity coeff., k , of many unimol. gas reactions and reactions in solution may be expressed as a function of the temp., T , by the empirical equation $k = e^{A/C - \Delta I/RT}$, where A is the energy of activation and C is a const. for all reactions of a given type. R. CUTHILL.

Experimental methods in the study of the kinetics of gaseous reactions. H. DORSE and W. FRANKENBURGER (Z. angew. Chem., 1931, 44, 605—610).—Some of the practical difficulties met with in the study of gaseous reactions are mentioned, e.g., the prep. of pure materials, the prevention of the entry and formation of small traces of substances which give rise to irregularities. The methods adopted to overcome them are briefly sketched.

H. INGLESON.

Effect of foreign gases on the lower critical oxidation limit of phosphorus vapour. H. W. MELVILLE and E. B. LUDLAM (Proc. Roy. Soc., 1931, A, 132, 108—126).—The effects of N_2 , H_2 , He, A, Ne, CO_2 , N_2O , H_2S , SO_2 , C_6H_6 , C_6H_{14} , C_2H_4 , C_2H_2 , $COMe_2$, $C_6H_3Me_3$, and CH_2Cl_2 on the lower crit. oxidation limit of P vapour have been studied. Although Semenov's equation, $p_F p_0 [1 + p_x / (p_0 + p_F)] d^2 = \text{const.}$ (where p_0 is the lower crit. oxidation pressure, p_F and p_x are the pressures of P vapour and the foreign gas, respectively, d is the diameter of the vessel), represents the results satisfactorily, the slope of the curve connecting $1/p_0$ with the quantity in the bracket depends on the nature of the gas. The equation is modified to $p_0 p_F [1 + D p_x / (p_0 + p_F)] = \text{const.}$, where D is the diffusion coeff. of the chain propagators into

the foreign gas. The slope of the curve is independent of the nature of the surface of the reaction tube. Evidence from the variation of the slope with temp. confirms the view that variation of D is the predominating cause of the differences observed. The results show no correlation with those obtained at the upper pressure limit (cf. A., 1930, 876).

L. L. BIRCUMSHAW.

Explosion waves and shock waves. I. Wave-speed camera and its application to the photography of bullets in flight. W. PAYMAN and D. W. WOODHEAD (Proc. Roy. Soc., 1931, A, 132, 200—213).—An account is given of the continuous (as opposed to the instantaneous or kinematographic) method of Schlieren photography, and its value in investigations in exterior ballistics is indicated.

L. L. BIRCUMSHAW.

Kinetics of the oxidation of hydrogen sulphide. I. H. W. THOMPSON and N. S. KELLAND (J.C.S., 1931, 1809—1827).—The kinetics of the oxidation of H_2S has been studied at temps. in the vicinity of the ignition point, i.e., 220—300°. The reaction proceeds almost entirely according to the equation $2H_2S + 3O_2 = 2H_2O + 2SO_2$, although traces of S were formed. There is an initial induction period which decreases either at a given temp. with increase of pressure or at a given pressure with rise of temp. If the pressure is below the ignition pressure, the subsequent reaction was of a low order which appeared to increase from a value slightly in excess of unity at low temp. to about two at high temp. Excess of O_2 facilitates reaction, whilst H_2S has the opposite effect; N_2 causes a slight retardation. Reaction is much retarded by a decrease in the dimensions of the reaction vessel. It is concluded that the reaction is of the chain type, propagation of the chains being favoured by excess of O_2 . Chains are probably broken by a physical deactivation at the wall and a chemical deactivation by H_2S . The heat of activation is about 18,000 g.-cal. Above the ignition pressure the above measurable reaction becomes an explosion. The ignition pressure increases with fall of temp. and satisfies Semenov's equation. A peculiar phenomenon of successive explosions in the same reaction mixture has been observed. F. J. WILKINS.

Flame propagation through dry carbon monoxide-oxygen mixtures in an electric field. W. A. BONE, R. P. FRASER, and W. H. WHEELER (Proc. Roy. Soc., 1931, A, 132, 1—10; cf. A., 1929, 771).—A comparison is made of the movements of flame, initiated near one of the closed ends of a tube, through intensively (P_2O_5) dried $2CO + O_2$ media (a) with no imposed electrostatic field, and (b) as the flame entered and passed into a strong electrostatic field, the polarity being reversed in successive experiments. The resistance to combustion offered by the dryness of the gases is overcome by the electrostatic field, the conditions near the negative pole being much more, and near the positive pole rather less, favourable to the continuance and propagation of flame than those in the control experiment. A series of similar experiments, but with the flame initiated midway between the boundaries of a field, is described.

L. L. BIRCUMSHAW.

Kinetics of the combustion of methane by means of copper oxide. T. S. WHEELER (Rec. trav. chim., 1931, 50, 874—882).—Equations are derived to explain the results of Campbell and Gray (J.S.C.I., 1930, 49, 432T), and it is tentatively suggested that the reaction takes place at the Cu—CuO interface, and that it is inhibited in the collision area of one or both kinds of resultant mols. on the interface. The heat of activation is 32,000 and 41,000 g.-cal. per g.-mol., as determined by the static and stream experiments, respectively.

R. S. CAHN.

Explosion limit of crude acetylene mixed with oxygen and nitrogen. S. YAGI and K. TAKEOKA (J. Soc. Chem. Ind. Japan, 1931, 34, 205—207B).—The limits of the region of explosibility in mixtures of C_2H_2 , O_2 , and N_2 have been determined with the view of estimating the danger of explosion in storage tanks of CaC_2 . To reproduce the conditions prevailing in practice crude gas (C_2H_2 97.69, H_2O 2.20, H_2S 0.0540, PH_3 0.0571 vol.-%) was used. There is no risk of explosion when the O_2 content is less than 8%, and the C_2H_2 content less than 2.5%. The lower limit of the explosion region runs parallel to the O_2 — N_2 line (the results being plotted on a triangular diagram), attributable to the equality of the mol. heats of O_2 and N_2 . The upper limit runs parallel to the N_2 — C_2H_2 line, although the heat capacity of the mixture increases with the C_2H_2 content.

N. H. HARTSHORNE.

Slow combustion of acetylene. R. SPENCE (Nature, 1931, 128, 153).—Experiments which show that C_2H_2 and O_2 form a reaction chain of considerable length are described (cf. this vol., 572).

L. S. THEOBALD.

Explosibility of acetylene-steam mixtures. RIMARSKI, PLEUS, FRIEDRICH, STREB, NOACK, KEMPER, HOFFMANN, and KONSCHACK (Jahresber. Chem.-tech. Reichsanst., 1930, 8, 43—47; Chem. Zentr., 1931, i, 2418).—Mixtures of C_2H_2 and steam in the ratios 10 : 1 and 1 : 1.5 are not explosive whether the total pressure is 5 or 6 atm. Explosion occurs at a ratio 1.63—1.61 : 1, and becomes more violent with increasing C_2H_2 content.

A. A. ELDRIDGE.

Direct oxidation of hydrocarbons by air. P. MONDAIN-MONVAL and B. QUANQUIN (Ann. Chim., 1931, [x], 15, 309—424).—The inflammation of mixtures of hydrocarbons and air at relatively low temp. is caused by the explosive decomp. of the peroxides which have been described (A., 1930, 167, 1157; B., 1930, 803). This property is not confined to pure hydrocarbons, but is also observed in mixtures, such as paraffin, mineral oils, and motor spirit, and further in ethers, alcohols, and aldehydes. It is probably a property of all compounds possessing a saturated hydrocarbon chain. These views are applied to the processes occurring in the internal-combustion engine.

E. S. HEDGES.

Aminolysis of alanine. S. MOLINARI (Helv. Chim. Acta, 1931, 14, 671—687).—An extension of Wunderly's study of the hydrolysis of alanine to NH_4 lactate in presence of bone charcoal (A., 1924, ii, 841). The reaction ceases before all the alanine is hydrolysed, but the amount of hydrolysis depends on the quantity and sample of charcoal used. The charcoal may be

completely regenerated by filtering and washing. Experiments in closed and in evacuated vessels, and using charcoal ignited in a current of CO_2 , show that atm. O_2 plays no part in the reaction. The velocity of hydrolysis of solutions containing initial concentrations of 1, 2, and 3% of alanine is unimol. in the sense that it is expressed by the equation $0.43K = 1/l \log \xi/(\xi-x)$, where ξ is the amount of alanine which has decomposed at the end of the reaction. With a 0.5% solution of alanine, however, the val. of K decreases as the reaction proceeds. The ratio $[NH_4]^2/[A]$ (where $[NH_4]$ and $[A]$ represent the concentrations of NH_4 and unchanged alanine, respectively, at the end of the reaction), is not const. over a wider range than that studied by Wunderly, nor is the ratio $[NH_4][L']/[A]$, where $[L']$ is the concentration of lactate. $[L']$ is different from $[NH_4]$ because of secondary decomp. of the former, giving $MeCHO$, $H\cdot CO_2'$, $EtOH$, and CO_3'' , all of which have been detected and determined. The ratio $[L']/M$ (where M is the wt. of charcoal) is, however, approx. const., but is little affected by the ratio A/M , where A is the amount of alanine adsorbed on the charcoal. It is suggested that the lactate, as it is formed, is adsorbed on the specially active parts of the charcoal surface, and that when it has occupied all these the reaction stops. The adsorbed lactate sends free lactate into the solution. It is assumed that the charcoal possesses virtually a concentration due to these active parts, the number of which depends on the wt. and specimen of charcoal used. Increase in this number increases the "dissociation tension" of the adsorbed lactate and more free lactate is sent into the solution. The addition of a salt with a common ion to the reaction mixture does not, however, lead to the expected results; NH_4Cl has scarcely any effect, whilst Na and NH_4 lactates, although markedly reducing the hydrolysis, do not do so to the extent required by the above theory.

N. H. HARTSHORNE.

Kinetic study of some reactions of diazoacetic ester in benzene solution. J. N. BRÖNSTED and R. P. BELL (J. Amer. Chem. Soc., 1931, 53, 2478—2498).—The velocity of the reaction of 0.0025—0.011*N*-diazoacetic ester with several substances in C_6H_6 solution has been measured at 15° by means of the N_2 evolved. The velocity coeff., k , of the reaction with a monocarboxylic acid, in large excess, is expressed by $k = \alpha c^2 + \beta c$, where α and β are consts. specific to a particular acid and c is its concentration. The effect of mixtures of these acids has been investigated. The results are consistent with the view that the addition of an acid mol. to the ester is catalysed by the presence of either a similar or a different acid mol., allowing for the progressive dissociation of double acid mols. with increasing dilution. The velocity of addition of picric acid to the ester is directly proportional to the concentration.

The rate of addition of $PhOH$ to the ester is very strongly catalysed by the carboxylic acids, and the catalytic const. l is given, approx., by $l = GK^2$, where K is the electrolytic dissociation const. of the acid in aq. solution and α approaches unity. Picric acid is less catalytically active than is represented by the above relation.

J. G. A. GRIFFITHS.

Chemical inertia. M. LEMARCHANDS and (MME.) M. LEMARCHANDS (Compt. rend., 1931, 193, 49—50).—Two explanations of the difficulty in effecting interaction between some solids and gases, *e.g.*, some metals and Cl_2 or Br_2 , CaO and Cl_2 , Zn , Al , Mg , or Na and CO_2 , SO_3 , N_2O , or P_2O_3 , are suggested: (a) Formation of a protecting film, supported by the fact that only metals, *e.g.*, K , Hg , and Sn , the chlorides of which are volatile under the conditions of the experiment, are attacked by Cl_2 . (b) Adsorption of the gas is a necessary preliminary to chemical action, and like it is exothermic, but rise in temp. checks adsorption and this cannot occur again until the surface has cooled. This explains the failure of a solid to catalyse such a reaction if that solid itself unites with the gas with considerable evolution of heat. C. A. SILBERRAD.

Dissolution velocity of oxygen into water. V. Oxidation velocity of sodium sulphite solution by oxygen in the presence of a molecular film of fatty acid. S. MIYAMOTO, T. KAYA, and A. NAKATA (Bull. Chem. Soc. Japan, 1931, 6, 133—142).—The rate of dissolution of O_2 into aq. Na_2SO_3 increases to a max. val. as the $[\text{SO}_3']$ is increased. Whilst this max. val. is proportional to the area of the liquid-gas interface, covering the surface of the solution with a unimol. film of palmitic or stearic acid has no effect. In these experiments the main portion of the solution is stirred vigorously. Whilst the surface of the solution is not broken, the stirring may cause the fatty acid film to be covered with the solution. F. J. WILKINS.

Rate of combustion of charcoal and graphite as a function of the temperature. G. TAMMANN and G. BANDEL (Z. anorg. Chem., 1931, 199, 109—116).—If the log of the rate of combustion, v , of charcoal in air is plotted as ordinate against the temp., T , as abscissa, the resulting graph consists of two straight lines intersecting at 175° , that corresponding with temps. below 175° having the greater slope. The probable explanation is that up to 175° the gas adsorbed by the C hinders its combustion, but at 175° the amount has become so small that the formation of a unimol. film is no longer possible. The retardation of the combustion is not, however, proportional to the amount of gas adsorbed. For the combustion of graphite between 340° and 480° the log v - T curve consists of a single straight line. Evidence has been obtained to show that the economy in fuel obtained by using a hot blast in the blast-furnace is due, not to an increase in the rate of combustion of the C, but to the increased rate of combustion of the CO at the tuyères. R. CUTHILL.

Transformation of white into grey tin. G. TAMMANN and K. L. DREYER (Z. anorg. Chem., 1931, 199, 97—108).—The linear rate of transformation is a max. at -30° , and decreases with increase in size of the crystallites, but is independent of their orientation. Cold-working increases the rate. The conversion between 0° and -20° can be suppressed by adding 0.5% Bi or Sb. R. CUTHILL.

Significance of hydrogen absorption in the dissolution of iron. E. LIEBREICH (Z. physikal. Chem., 1931, 155, 123—142).—Phenomena quoted

by Evans in support of his theory of corrosion are observed also in an atm. of H_2 . The flake formation can be explained by the depassivating action of the corrosion product. When a film of hydroxide covers the surface of the Fe the diffusion out of the H_2 is impeded and the pressure of H_2 on the surface is raised. Thus Fe covered with fine glass powder is attacked even more readily than usual by dil. H_2SO_4 ; also the cathodic over-potential of a corroded Fe surface is lower than that of a fresh one.

J. W. SMITH.

Corrosion of iron by steam at high temperatures. I. W. KRAUSS (Korrosion u. Metallschutz, 1931, 7, 29—34; Chem. Zentr., 1931, i, 2390).—An apparatus for measuring electrically the interaction between metals and gases is described, and the results of its use with Fe and H_2O at 510° and 630° are recorded. The method was compared with the gravimetric method for interaction at 600° , 700° , and 800° .

A. A. ELDRIDGE.

Spontaneous inflammability of magnesium powder. LENZE, METZ, and RUBENS (Jahresber. Chem.-tech. Reichsanst., 1930, 8, 12—14; Chem. Zentr., 1931, i, 2387).—Finely-divided Mg does not ignite more readily when heated in air than coarser powder or filings; the ignition temp. in air is about 550° . Rise of temp. and liberation of H_2 by the action of H_2O do not lead to inflammation. The transport of Mg is discussed. A. A. ELDRIDGE.

Atmospheric corrosion of metals. I. Copper. W. H. J. VERNON.—See B., 1931, 763.

Reaction between benzyl chloride and water. T. TITANI and K. KURANO (Bull. Chem. Soc. Japan, 1931, 152—162).—A layer of distilled water which was stirred vigorously was placed above one of benzyl chloride, and the progress of the reaction was followed by determining the conductivity of the aq. layer. The rate of reaction is largely affected by the speed of stirring, and it is therefore concluded that the HCl formed inhibits further hydrolysis by its adsorption at the benzyl chloride- H_2O interface.

F. J. WILKINS.

Variation of the velocity of decomposition of cellulose nitrate with temperature. J. DUCLAUX and J. BARBIÈRE (J. Chim. phys., 1931, 28, 257—259).—By observation of the change in the viscosity of solutions of cellulose nitrate in CO_2 , with the previous history of the nitrate it has been shown that for three stable preps. of cellulose nitrate the change occurring in 17 years at 18° is about the same as that which occurs in 18 hr. at about 110° , indicating a temp. coeff. for the reaction of about 2.7 for a 10° interval. For two less stable nitrates the change in 17 years at 18° is comparable with that occurring in 2.5 hr. at 100° , the temp. coeff. being about 3.8.

J. W. SMITH.

Ozonation of aldehydes. Action of ozone on the share of oxygen in the oxidation. E. BRINER, A. DEMOLIS, and H. PAILLARD (Helv. Chim. Acta, 1931, 14, 794—803; cf. A., 1929, 290, 674).—The oxidation of PhCHO dissolved in hexane to BzOH (with some perbenzoic acid) by O_3 containing 0.9—8.0% O_3 has been studied, the gases being passed for 1 hr. at the rate of 10 litres per hr. The optimum

concentration of O_3 is 1.6%, the wt. of BzOH formed being more than 30 times that equiv. to the wt. of O_3 consumed, which, moreover, is min. in this case. The O_3 therefore acts mainly as a catalyst. Substitution of CCl_4 for hexane causes a marked reduction in the rate of oxidation. The mechanism of the reaction is discussed from the point of view of the theory of chain reactions, the O_3 being regarded as a source of energy of activation for the O_2 mols., but no definite chain is proposed.

N. H. HARTSHORNE.

Ozonation of sulphurous acid and of sulphur dioxide. Action of ozone on the share of oxygen in the reaction. E. BRINER, S. NICOLET, and H. PAILLARD (Helv. Chim. Acta, 1931, 14, 804—810).—The action of ozonised O_2 on SO_2 solution is similar to its action on PhCHO (see preceding abstract) and its mechanism is probably of a related type. The optimum concentration of O_3 is about 1%, the wt. of SO_3 formed being about twice that equiv. to the O_3 consumed. The action on dry SO_2 is very slow.

N. H. HARTSHORNE.

Esterification in presence of anhydrous salts. F. M. WHITACRE and H. T. BRISCOE (Proc. Indiana Acad. Sci., 1929, 38, 187—194).—The catalytic effect of anhyd. Cu, Cd, Al, Mn, Fe, Ca, and K Al sulphates on esterification of AcOH with EtOH, and of $CuSO_4$ on that of higher alcohols and acids, was studied. $CuSO_4$ gave the highest yield of EtOAc; $CaSO_4$ retarded esterification, whilst Na_2SO_4 had no effect. The temp. of dehydration is important; the effect is due partly to removal of H_2O and partly to other causes.

CHEMICAL ABSTRACTS.

Iron and cerium compounds and insulin as inductors in oxidation reactions; mechanism of induced reactions. N. R. DHAR (J. Physical Chem., 1931, 35, 2043—2048).—During the induced oxidation of HCO_2Na by air at room temp. in presence of $Fe(OH)_2$ or $Ce(OH)_2$, Fe_2O_3 or Ce_2O_3 is formed as an intermediate compound. The high induction factors sometimes observed are due to the liberation of ions during the primary exothermic oxidation of the inductor. These ions activate further mols. of the reactants, and more ions are then produced; the primary oxidation thus causes the oxidation of a large quantity of the acceptor. When an oxidation is effected by H_2O_2 the intermediate Fe oxide differs from that formed when O_2 is used. When air is passed through a solution of insulin oxidation takes place and CO_2 is formed; dextrose, if added, is also oxidised to CO_2 , and the insulin, which then acts as an inductor, is oxidised more slowly. To this type of reaction is due the physiological action of insulin and the disappearance of the material in the body. The induced oxidation of dextrose is accelerated by Na_2HPO_4 .

H. F. GILLBE.

Positive ion catalysis in the Knoevenagel reaction. K. C. BLANCHARD, D. L. KLEIN, and J. MACDONALD (J. Amer. Chem. Soc., 1931, 53, 2809—2810).—The velocity of condensation of cinnamaldehyde with malonic acid in 50% EtOH in the presence of NH_2 -acids is accelerated by increase of $[H^+]$. Amines exhibit enhanced catalytic activity in acid solution, and very weak bases, e.g., carbamide, which

are inactive in aq. or alcoholic solution, are very active catalysts in AcOH where strong dissociation occurs. This supports the view that the positive ion of the amine is the catalyst.

J. G. A. GRIFFITHS.

Catalysed formation of water from hydrogen and oxygen by platinum as a chain reaction. N. I. KOBOSOV and V. L. ANOCHIN (Z. physikal. Chem., 1931, B, 13, 63—71).—In the catalysed combination of H_2 and O_2 in presence of Pt saturated with O_2 at. H is formed, probably by the reaction $PtO + H_2 = PtOH + H$, and sets up a reaction chain, the direct product of which is principally H_2O_2 , which is decomposed by the Pt, giving H_2O . As a whole, the reaction is not a genuine catalysis, but is rather a case of induced reaction, the Pt-O complex being the inductor, the H the actor, and the O the acceptor.

R. CUTHILL.

Catalysts for the production of hydrogen by the water-gas reaction. I. Activity of an iron oxide catalyst. R. YOSHIMURA (J. Soc. Chem. Ind. Japan, 1931, 34, 193—195b).—The efficiency of two Fe_2O_3 catalysts on the reaction between CO and H_2O ($p_{CO} : p_{H_2O} = 1 : 3.0$) at atm. pressure and with a rate of gas flow of 33.3 c.c. per min. has been studied at 360—410°, 510—710°, and 800°. The same results were obtained with the two catalysts, one of which contained Mn, Al, Si, Ca, P, Ni, Cu, Cr, and S (arranged in order of decreasing quantity) as impurities, and the other only Mn and possibly a trace of P. The optimum temp. range was 510—710°. The deposition of free C on the catalyst surface, which was observed only at the lower temp., increased with falling temp., and also with increasing partial pressure of CO in the resultant gases. In these cases the activity of the catalyst varied irregularly during the course of the reaction, and subsequent treatment of the catalyst with HCl usually revealed the presence of Fe carbide, the formation of which is known to occur in the decomp. of CO ($2CO = CO_2 + C$) at an Fe catalyst. The appearance and magnetic properties of the catalyst after a run showed that reduction to a lower oxide, probably Fe_3O_4 , had occurred. The alteration of the catalyst surface and its dependence on the temp. are discussed.

N. H. HARTSHORNE.

Hydrogenation catalyst. Action of hydrogen on colloidal palladium. M. BOURGUEL, (MLLE.) V. GREDY, and (MLLE.) H. ROUBACH (Bull. Soc. chim., 1931, [iv], 49, 897—925).—The velocity of hydrogenation of various org. compounds in the presence of colloidal Pd is not proportional to the wt. of the catalyst, but depends on the concentration of Pd in the aq. phase. The variation of velocity with concentration is independent of the H-acceptor. At const. concentration of Pd, the velocity of hydrogenation depends on the pressure of H_2 at the moment it first comes into contact with the Pd, and the variation is again independent of the substance undergoing hydrogenation. These results confirm the view that the first stage of catalysis is the formation of a compound Pd_nH_2 , where n depends on the pressure of H_2 and concentration of Pd. This combination is reversible and n is necessarily variable, but its order of magnitude appears to be about 100.

E. S. HEDGES.

Kinetics of decomposition of ammonia in the presence of iron. J. ZAWADZKI and B. MODRZEJEWSKI (Rocz. Chem., 1931, 11, 505—515).—The velocity of the reaction $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$ in the presence of an Fe wire heated at 470—560°, at 1—5 atm., is independent of the pressure. The catalytic action of Fe wire is at first small, but increases with use; at the same time the wire becomes brittle and spongy. R. TRUSZKOWSKI.

Catalytic reduction of carbon monoxide at atmospheric pressure. IX. K. FUJIMURA (J. Soc. Chem. Ind. Japan, 1931, 34, 227—229B).—A Co—Cu—MgO (4 : 1 : 1) catalyst was used at 240° with pumice as carrier; the nitrates were heated with sucrose and the oxide mixtures were reduced with H₂. This process gives a very voluminous catalyst; the complete burning out of the C by long heating is detrimental. Otherwise yields of liquid products per unit catalyst volume were nearly uniform with different methods of prep. Excess of H₂ in the gas mixture results in H₂O formation. Great variation in the CO and CO₂ contents of the exit gases occurred. C. IRWIN.

Oxide hydrates and active oxides. XLIV. **Relations between solubility of zinc oxide and its previous history.** G. F. HÜTTIG and B. STEINER (Z. anorg. Chem., 1931, 199, 149—164; cf. this vol., 1000).—The solubility and rate of dissolution in aq. KOH of ZnO prepared by various methods has been determined with the object of correlating the catalytic activity in the MeOH synthesis, the thermodynamic activity, and the physical uniformity. ZnO obtained by ignition of ZnCO₃ below 300° has a relatively high catalytic activity and is physically practically completely uniform; therefore either all the mols. participate equally in the catalysis, or the active mols. are uniformly distributed. Nevertheless, an increase in catalytic activity may often be expected to accompany a decrease in uniformity. R. CUTHILL.

Characteristics of a calcium—vanadium catalyst and a new catalyst for sulphuric acid manufacture. W. W. SCOTT and E. B. LAYFIELD.—See B., 1931, 716.

Suitability of nickel catalysts for the synthesis of benzene. F. FISCHER and K. MEYER.—See B., 1931, 748.

Compound catalysts for synthesis of methyl alcohol. V. A. PLOTNIKOV, K. N. IVANOV, and D. A. POSPECHOV.—See B., 1931, 751.

[Electrolytic] separation of niobium and tantalum. D. D. PEIRCE (J. Amer. Chem. Soc., 1931, 53, 2810).—Electrolytic reduction of Nb in alkaline solution affords an amalgam at a Hg cathode; Nb alone is deposited, at a current density of 3 amp./sq. dm., on a Cu cathode from a mixture of Nb and Ta oxides in saturated aq. Na₂CO₃ at 103°.

J. G. A. GRIFFITHS.

Electrolyses in liquid ammonia. S. GOLDSCHMIDT and F. NAGEL.—See this vol., 1053.

Preparation of metal powders by electrolysis of fused salts. III. **Tantalum.** F. H. DRIGGS and W. C. LILLIENDAHL.—See B., 1931, 722.

Formation and decomposition of ozone in the electric discharge. L. A. M. HENRY (Bull. Soc. chim. Belg., 1931, 40, 305—314).—The formation of O₃ from O₂ by the action of the discharge in a Geissler tube depends on the production of ions or of excited atoms or mols. The pressure assumes a steady value due to the establishment of an equilibrium caused by partial decomp. of the O₃ by particles with high kinetic energy. With increase of current the velocity of formation increases at a diminishing rate, and the greatest yield is obtained with a narrow tube. He reduces the velocity to a greater degree than does A. At the temp. of liquid air the O₃ decomposes slowly, probably as a result of catalytic action of the deposit of metal, derived from the cathode, on the walls of the tube. H. F. GILLBE.

Formation of nitrogen oxides in the electric discharge. L. A. M. HENRY (Bull. Soc. chim. Belg., 1931, 40, 295—304).—At room temp. O₂ and N₂ do not combine when submitted to the silent electric discharge or to the discharge through a Geissler tube, but at about -180° NO₂ is formed in the latter case, the yield being greatest for the mixture N₂+2O₂. O₂ alone exhibits a contraction during the discharge, and a subsequent slow expansion to the initial pressure. The silent electric discharge does not cause reaction at low temp. Combination can occur only in presence of excited or ionised atoms or mols. of N₂ or O₂. H. F. GILLBE.

Kinetics of the formation of hydrogen chloride and carbonyl chloride as a problem of modern photochemistry. G. B. KISTIAKOWSKY (Z. angew. Chem., 1931, 44, 602—605).—Theoretical. An appreciation principally of the contributions made by Bodenstein to the study of the photochemical formation of HCl and COCl₂. H. INGLESON.

Photo-reaction of hydrogen and iodine monochloride. T. IREDALE and D. P. MELLOR (J. Amer. Chem. Soc., 1931, 53, 2802—2803).—Polemical against Rollefson and Lindquist (A., 1930, 1135; this vol., 578). The reaction occurs in 5461—5791 Å. light with approx. equal pressures of H₂ (about 70 mm.) and ICl (*ibid.*, 180). J. G. A. GRIFFITHS.

Action of light on mixtures of ozone and chlorine. I. **Experimental. Results with low ozone concentrations.** A. J. ALLMAND and J. W. T. SPINKS (J.C.S., 1931, 1652—1666).—The photosensitisation by Cl₂ of the decomp. of O₃ has been investigated in order to study the relation between the quantum efficiency γ and the wave-length. With a Cl₂ concentration >2—3% the rate of decomp. is proportional to the light intensity, but increases less rapidly if the Cl₂ concentration is less than this. For blue light γ is independent of the Cl₂ concentration, but at 365 m μ it rises as the Cl₂ concentration is decreased below 2%. Decrease of wave-length is accompanied by an increase of γ . Change of temp. has no effect on γ . F. J. WILKINS.

"Speed" of photographic emulsions. R. DAVIS and G. K. NEELAND (J. Opt. Soc. Amer., 1931, 21, 416—419).—Errors caused by deviations from the strict H. & D. speed definition are pointed out. Fog densities should always be subtracted from the total densities. J. LEWKOWITSCH.

Application of oxalic acid-uranyl acetate actinometer to measurement of sunlight intensity in connexion with photochemical changes in gasoline. L. C. BEARD, jun., and O. M. REIFF (Ind. Eng. Chem. [Anal.], 1931, 3, 280—281).—The actinometer consists of a solution containing 6.30 g. of $H_2C_2O_4 \cdot 2H_2O$ and 0.2121 g. of $UO_2(OAc)_2 \cdot 2H_2O$ per litre and the amount of decomp. after exposure to sunlight is measured by titrating the $H_2C_2O_4$ with 0.1N- $KMnO_4$. The amount of change in the actinometer is proportional to the discoloration produced in gasoline exposed under similar conditions. Change of temp. has little influence on the discoloration of gasoline by sunlight. E. S. HEDGES.

Photochemical oxidation of organic hydrocarbons. II. Toluene, and the oxidation of benzaldehyde. C. J. KOTHARI and H. E. WATSON (J. Ind. Inst. Sci., 1931, 14A, 11—30; cf. A., 1925, i, 1136).—The solvent has a marked effect on the oxidation of $PhCHO$, C_6H_6 and $PhMe$ retarding the reaction in the dark, but accelerating it in light. The general results appear to be rendered inconsistent through the presence of minute amounts of impurity in $PhCHO$. The similarity of the temp. coeffs. in light and in the dark and the independence of the rate of oxidation and vol. of liquid indicate that reaction is mainly confined to the surface. The oxidation of $PhMe$ takes place slowly or not at all in the absence of a catalyst and appears to be a vol. reaction. $PhCHO$ is not the intermediate product determining the rate of reaction, and the active substance is H_2O_2 or an org. peroxide. E. S. HEDGES.

Photochemical oxidation of alcohols by potassium dichromate. III. E. J. BOWEN, T. A. PEACOCK, and E. R. WELLBURN (J.C.S., 1931, 1866—1870).—The effect of changes in $[H^+]$ and dichromate concentration on the rate of the photochemical oxidation of $MeOH$, $EtOH$, and Pr^sOH has been studied using light of λ 3660 and 4360 Å. The results can be described quantitatively if it is assumed that the photoactive ion is $HCrO_4'$ and that the CrO_4'' ion which is also present acts as an inner filter. E. S. HEDGES.

Photochemical hydrolysis of sucrose. A. K. BHATTACHARYA and N. R. DHAR (Z. anorg. Chem., 1931, 199, 1—6).—The results previously reported (A., 1930, 555) are amplified. R. CUTHILL.

Photo-polymerisation of styrene and vinyl acetate. H. S. TAYLOR and A. A. VERNON (J. Amer. Chem. Soc., 1931, 53, 2527—2536).—The photo-polymerisation of O_2 -free styrene in $PhEt$ and vinyl acetate in $EtOAc$ has been measured by means of the effect of the products on the f. p. of C_6H_6 . The temp. coeff. between 30° and 100° is about 1.3 per 10°. The quantum efficiency, γ , at λ 300—400 $m\mu$ is about 935 for pure vinyl acetate and 4 for styrene; values of γ between 1 and 8 are recorded for λ 2300 and 2536. The results indicate a chain reaction, which is inhibited by quinol. O_2 accelerates the photo-polymerisation of styrene and retards that of vinyl acetate. J. G. A. GRIFFITHS.

Substitution of water of crystallisation by hydrogen peroxide. F. MÜNZBERG (Lotos, 1928, 76, 351—363; Chem. Zentr., 1931, i, 2302).—

$NaNH_4HPO_4$, $MgNH_4PO_4$, $MgNH_4AsO_4$, $NH_4H_2PO_4$, Na_2HASO_4 , K and Na pyroantimonates, NH_4 , K, Ca, Sr, and Ba pyrophosphates can combine additively with H_2O_2 . Equilibria in the systems $Na_2SO_4-H_2O-H_2O_2$, $Na_4P_2O_7-H_2O-H_2O_2$, and $Ba_2P_2O_7-H_2O-H_2O_2$ were studied. Theoretical considerations are discussed. A. A. ELDRIDGE.

Action of sodium hypophosphite on aqueous solutions of nickel salts. C. PAAL and L. FRIEDERICI (Ber., 1931, 64, [B], 1766—1776).—Reduction of aq. $NiSO_4$ by NaH_2PO_2 yields non-homogeneous Ni phosphides containing 13.08—14.17% P. Some of these are scarcely attacked by warm HCl, whereas others are partly sol., leaving a residue containing all the P (approx. Ni_5P_2); the sol. portion is Ni. In presence of NH_3 $NiSO_4$ is reduced more rapidly and with smaller expenditure of NaH_2PO_2 , the product (2.7—3.3% P) consisting of much metallic Ni and little Ni phosphides. The presence of minute amounts of Pd (0.0005—0.00001 g. Pd per g. Ni) greatly accelerates the reaction, yielding products with 2.3—3.7% P. In presence of Na K tartrate, $NiSO_4$ is scarcely reduced by NaH_2PO_2 in absence of Pd; in presence of minute amounts of Pd, a little Ni is first formed followed by a greyish-black to a black ppt. containing Ni, P, and O. Reduction of $NiSO_4$ by NaH_2PO_2 in presence of NaOAc occurs only in presence of Pd, giving a mixture of Ni and Ni phosphides containing an oxygenated compound. In alkaline tartrate solution and in presence of NaOAc the separation of Ni is not quant. H. WREN.

Solid silver hydride. E. PIETSCH [with F. SEUFERLING] (Naturwiss., 1931, 19, 573—574).—Salt-like Ag hydride is obtained by the prolonged action of at. H on Ag foil. It is decomposed by H_2O with evolution of heat. AgH is stable in H_2 up to at least 500° and is also stable in air. It is unacted on by light and is unchanged when heated in a Bunsen flame to dull redness. It shows great analogy to alkali hydrides, especially to LiH. J. W. SMITH.

Compounds of hexamethylenetetramine with certain salts of silver and other metals and the influence of anionic volume on the capacity for association by the central positive atom. P. R. RAY and J. D. GUPTA (Proc. XV Indian Sci. Cong., 1928, 168).—Compounds of various Ag salts (except AgF) with hexamethylenetetramine accord with Ephraim's generalisation that the capacity of a cation to associate with neutral mols. increases with the anionic vol. Compounds with Cu, Cd, and Ag cyanides were also prepared. Ag_2TeO_4 , Ag_3PO_4 , Ag_3BO_3 , $AgIO_3$, Ag_3AsO_3 , and Ag_3AsO_4 did not associate with hexamethylenetetramine. CHEMICAL ABSTRACTS.

Stability of magnesium peroxide. A. WÖHLK. —See B., 1931, 756.

Cyanamides of alkaline-earth and earth metals. (MLLE.) G. BERNHEIM (Compt. rend., 1931, 192, 1647—1649).—The most favourable reaction temp. and corresponding max. yields of cyanamides formed according to the equation $C_2N_2 + MO = CN_2M + CO$ are: M=Ca, 860°, 94.6; Sr 850°, 65.2; Ba 850—900°, 96; Be 550°, 37.5; Mg 900°, 81.1; Zn 1025—1050°, 90; Cd 700°, 93%. C. A. SILBERRAD.

Hydrothermal synthesis of calcium silicates under pressure. I. S. NAGAI (J. Soc. Chem. Ind. Japan, 1931, 34, 222—224B).—CaO, quartz powder, and H₂O in various proportions were heated in an autoclave, and the dried samples analysed. In all cases 3CaO, 2SiO₂ was the first product, being formed at 181°; with longer heating CaO, SiO₂ was produced, most readily with mixtures of low CaO content. A 2 : 1 mixture did not give the second product at the temp. studied. C. IRWIN.

Preparation of mercurous iodide. A. AGRISTINI (Boll. Chim. farm., 1931, 70, 448—450).—SnCl₂ in HCl solution is added to a solution of HgCl₂ (1 mol.) and KI (2 mols.) in EtOH; yield 52—57.5%. An excess of KI decreases the yield but increases the purity of the product. O. F. LUBATTI.

Deflagration and detonation of mercuric fulminate. P. LAFFITTE and M. PATRY (Compt. rend., 1931, 193, 171—174).—Hg fulminate arranged in a line not exceeding 1 cm. wide, in the open air, and ignited by a Bickford fuse, only deflagrates; when placed in a tube it invariably detonates, as does Pb azide in either case. When placed on heated Hg the fulminate inflames after 39 min. at 135°, and after decreasing intervals at higher temp., until it does so instantaneously at 277°. Below 135° it decomposes without inflammation.

C. A. SILBERRAD.

Aluminium chloride- and bromide-acetates. H. FUNK and J. SCHORMÜLLER (Z. anorg. Chem., 1931, 199, 93—96).—The following compounds have been obtained by reaction of AcOH with AlCl₃ or AlBr₃: AlCl₃, 2Al(OAc)₃, Al(OAc)₃, 2AlO(OAc), 2Al(OAc)₃, AlBr(OAc)₂, Et₂O, and Al(OAc)₃, 2AlBr(OAc)₂, 1.5Et₂O. R. CUTHILL.

Hydrates and hydrogels. XIII. Dialuminium hydroxide gel and its transformations. H. KRAUT and H. HUMME (Ber., 1931, 64, [B], 1697—1708).—Addition of aq. Al₂(SO₄)₃ at 48° to 15% aq. NH₃ at the same temp. followed by keeping the mixture at 48—50° for ½ hr. and subsequent rapid washing leads to the isolation of *dialuminium hydroxide*, Al₂O₃, 2H₂O. It is peptised to an almost transparent solution by 0.1—1% HCl, is not appreciably sol. in cold conc. HCl, sol. in warm 5—10% HCl and in 4% NaOH. Under H₂O or dil. HNO₃ it is readily converted into the trihydrate (identified as bayerite by the Röntgen diagram), which, although resembling the dialuminium compound in solubility, is not peptised by very dil. HCl. Separation of the compounds from one another is thus rendered possible. The *B* preps. are mixtures of Al₂O₃, 2H₂O and Al(OH)₃. It is proposed to designate Al₂O₃, 2H₂O as Al hydroxide *B*. Above 60°, ageing of Al₂O₃, 2H₂O is accompanied by loss of H₂O. In 2 days under gently boiling aq. NH₃ or more slowly in boiling aq. suspension, products are formed containing chains of 4—8 Al atoms, thus closely resembling the polyhydroxides *A*. They are highly disperse and cannot be separated from Al₂O₃, 2H₂O by very dil. HCl but differ from the last-named compound, since their H₂O content does not alter during several years. The limit lies at about 27% H₂O, corresponding with a tetra-aluminium hydroxide. All preps. with lower

H₂O content (23—26%) remain unchanged in composition, whereas those with higher content become transformed into bayerite. It is possible that original preps. with 30—35% H₂O contain 3Al(OH)₂—2H₂O as well as 2Al(OH)₃—H₂O and that the trialuminium compound is also converted into bayerite. Al₂O₃, 2H₂O gives the interference lines of böhmite. It is probable that all colloidal Al hydroxides containing Al·O·Al chains in the mol. have a structure analogous to that of böhmite. The ageing of Al₂O₃, 2H₂O is readily followed by the changes in the Röntgen diagram; the intermediate products give the superposed interferences of bayerite and böhmite and are separable by dil. HCl into portions giving the homogeneous lines of the two materials. The transformation of Al₂O₃, 2H₂O into bayerite is a discontinuous process in which the single mols. of Al₂O₃, 2H₂O pass by addition of 1 mol. of H₂O into Al₂O₃, 3H₂O.

H. WREN.

Selenates of neodymium and their solubilities in water and selenic acid solutions. J. A. N. FRIEND (J.C.S., 1931, 1802—1809).—The methods of prep. of the hydrates of Nd₂(SeO₄)₃, including a *dodecahydrate*, are described. The solubility of Nd₂(SeO₄)₃ in H₂O and aq. H₂SeO₄ solutions of various concentrations has been measured over the temp. range 0—100°.

F. J. WILKINS.

Anhydrous acetates and acid acetates of rare-earth metals. A. KOTOVSKI and H. LEHL (Z. anorg. Chem., 1931, 199, 183—192).—The acetates La(OAc)₃, Pr(OAc)₃, Nd(OAc)₃, Sm(OAc)₃, Gd(OAc)₃, and Yt(OAc)₃ have been prepared by the action of Ac₂O on the nitrates. The following intermediate compounds have also been isolated: Pr(OAc)₃, 0.5Ac₂O, Nd(OAc)₃, 0.5Ac₂O, Sm(OAc)₃, 0.5Ac₂O, and Gd(OAc)₃, 0.5Ac₂O. The formation of compounds of the type [Ce₃(OAc)₃](NO₃)₆, 5Ac₂O (cf. A., 1923, i, 291) has been detected. The acid acetates, La(OAc)₃, 3AcOH, Ce(OAc)₃, 3AcOH, Pr(OAc)₃, 3AcOH, Nd(OAc)₃, AcOH, Sm(OAc)₃, AcOH, and Yt(OAc)₃, 3AcOH have been prepared by the action of AcOH on the normal acetates. R. CUTHILL.

Rare earths. I. Preparation of [sulphates and] bromates of cerium group rare earths. J. A. HARRIS (J. Amer. Chem. Soc., 1931, 53, 2475—2477; cf. A., 1926, 810; 1927, 14).—Conc. neutral solutions of the Ce group rare-earth sulphates are easily prepared by adding gradually the calc. vol. of dil. H₂SO₄ to the moistened oxides, evaporating to dryness, and dissolving in the calc. vol. of H₂O.

J. G. A. GRIFFITHS.

Volatile thallium and lead hydrides. E. PIETSCH and F. SEUFERLING (Naturwiss., 1931, 19, 574).—When at. H acts on a film of TlCl the latter is reduced first to Tl and then a film of Tl is gradually deposited on the glass walls of the reaction tube, moving along gradually with the gas stream. The v. p. of TlCl and of Tl are insufficient to account for this vaporisation, which is attributed to the formation of *Tl hydride*, which is vaporised from the surface of the metal but decomposed again on contact with the glass walls of the vessel. Analogous results are obtained with PbCl₂, which must give rise to a volatile *Pb hydride*. J. W. SMITH.

Hydrates and hydrogels. XIV. Simple preparation of monosilicic acid and the course of its condensation. H. KRAUT (Ber., 1931, 64, [B], 1709—1713).—Monosilicic acid is prepared from 1 mol. of $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$ and 1.8 mols. of HCl with addition of AcOH to supply the required p_{H} . Only between p_{H} 3.0 and 3.3 are the solutions sufficiently stable to permit determination of mol. wt. in freezing H_2O . At p_{H} 3.20 the acid can be preserved for several days. The nature of the org. acid appears to influence the reaction. Citric acid has much the same effect as HCl and AcOH, whereas formic acid gives essentially disilicic acid, and oxalic and tartaric acids yield trisilicic acid. The condensation of monosilicic to polysilicic acid is an auto-catalytic process, greatly accelerated by the polysilicic acid produced. Whilst, however, in the strongly acidic region p_{H} 1.5, in the feebly acid region p_{H} 4.3, and at the optimum acidity p_{H} 3.2 this acceleration is invariably observed, at intermediate ranges of p_{H} a delay in the condensation or a complete cessation in the alteration of mol. wt. is frequently observed, probably due to intramol. loss of H_2O leading from the ortho- to the meta-forms of silicic acid. In paraffined vessels increase in mol. wt. takes place more rapidly than in those of ordinary glass.

H. WREN.

Highly-polymerised compounds. LIII. Polymeric silicic esters and acids. R. SIGNER and H. GROSS (Annalen, 1931, 488, 56—73).—The action of SiCl_4 on cyclohexanol affords the compounds $\text{SiCl}_3(\text{O} \cdot \text{C}_6\text{H}_{11})$, b. p. $78^\circ/11$ mm., $\text{SiCl}_2(\text{O} \cdot \text{C}_6\text{H}_{11})_2$, b. p. $156^\circ/11$ mm., d_4^{20} 1.1325, and $\text{SiCl}(\text{O} \cdot \text{C}_6\text{H}_{11})_3$, b. p. $201^\circ/11$ mm., d_4^{20} 1.0653. The ester chlorides are hydrolysed by Ag_2CO_3 in anhyd. Et_2O . The trichloride affords polymeric cyclohexyl disilicate, $[\text{Si}(\text{O} \cdot \text{C}_6\text{H}_{11})_2]_{10}$ as a solid mass which decomposes when heated. The dichloride gives the polymeric metasilicates, $[\text{Si}(\text{O} \cdot \text{C}_6\text{H}_{11})_2\text{O}]_n$, m. p. 216° , sublimable in high vac., and $[\text{Si}(\text{O} \cdot \text{C}_6\text{H}_{11})_2\text{O}]_n$, an oil which decomposes when heated. The monochloride yields the pyrosilicate, $[\text{Si}(\text{O} \cdot \text{C}_6\text{H}_{11})_2\text{O}]_2$, m. p. 217° , sublimable in high vac. Tetracyclohexyl orthosilicate has b. p. $201^\circ/0.1$ mm., m. p. 92° . Hydrolysis of the tetrameric meta-ester and of the pentameric di-ester with HI leads ultimately to silicic acids containing, respectively, 76.93 and 86.96% SiO_2 . The analytical data suggest that the acids correspond in mol. wt. and constitution with the esters from which they are derived, but their insolubility in H_2O is not in harmony with this hypothesis and the question of mol. wt. is therefore undecided. Thermal decomp. of the esters takes place with production of cyclohexene accompanied by a little cyclohexanol and dicyclohexyl ether. The disilicic ester at 140° leaves a silicic acid containing 12.86% H_2O ; an acid of similar composition is derived from the pyro-ester.

H. WREN.

Possibility of partial substitution of lead halide by chromate in lead chloride-phosphate, -vanadate, acid-arsenate (pyromorphite, vanadinite, mimetesite). G. CAROBBI (Atti III Cong. Naz. Chim., 1929, 341—342; Chem. Zentr., 1931, i, 2185—2186).—Fusion of $\text{Pb}_3(\text{PO}_4)_2$, PbCl_2 , PbCrO_4 , and NaCl afforded synthetic pyromorphite,

$3\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbCl}_2 \cdot \text{PbCrO}_4$; synthetic vanadinite and mimetesite were similarly obtained. The max. amount of PbCrO_4 is 6%, 6%, and 4%, respectively.

A. A. ELDRIDGE.

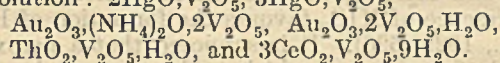
Mechanism of precipitation processes. VI. Reaction between sodium oxalate and lead halides. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1931, 199, 7—16; cf. this vol., 926).—If $\text{Na}_2\text{C}_2\text{O}_4$ is added to excess of a solution of PbCl_2 or PbBr_2 the ppt. of PbC_2O_4 contains Cl or Br, owing to the presence of the compounds $\text{PbC}_2\text{O}_4 \cdot \text{PbCl}_2$ and $\text{PbC}_2\text{O}_4 \cdot \text{PbBr}_2$. If the ppt. is left in contact with the liquid phase the halogen content gradually increases.

R. CUTHILL.

Liquid ammonia and sodium nitrate. N. KAMEYAMA (J. Soc. Chem. Ind. Japan, 1931, 34, 173B).—Solid NaNNO_3 reduces the v. p. of liquid NH_3 to such an extent that the saturated solution obtained can be stored or treated in Fe vessels.

A. R. POWELL.

Vanadates of heavy metals. M. B. RANE and K. KONDIAR (J. Indian Chem. Soc., 1931, 8, 289—292).—The following vanadates have been prepared by reaction of a salt of the metal with NH_4VO_3 or K_3VO_4 in solution: $2\text{HgO} \cdot \text{V}_2\text{O}_5$, $3\text{HgO} \cdot \text{V}_2\text{O}_5$,



R. CUTHILL.

Complexes of antimony halides with sulphonium halides. P. C. RAY, N. ADHIKARI, and A. N. RAY (J. Indian Chem. Soc., 1931, 8, 251—255).—The following compounds have been prepared by reaction of an Sb halide with a sulphonium halide or an alkyl sulphide and an alkyl halide: $\text{SbI}_3 \cdot \text{Et}_3\text{SI}$, m. p. 169° , $\text{SbI}_3 \cdot \text{Me}_3\text{SI}$, m. p. 194° , $\text{SbBr}_3 \cdot \text{Et}_3\text{SBr}$, m. p. 68° , $\text{SbCl}_3 \cdot \text{Et}_3\text{SI}$, m. p. 156° , $\text{SbCl}_3 \cdot \text{Me}_3\text{SI}$, m. p. 189° , and $\text{SbI}_3 \cdot 3\text{Et}_3\text{SBr}$, m. p. 182 — 183° . From conductivity data it appears that these compounds have the constitution $[\text{Et}_3\text{S}]\text{SbX}_4$ (X=halogen). R. CUTHILL.

Purification of protoactinium fixed on tantalum oxide with a view to the determination of protoactinium in radioactive minerals. CHENG DA-CHANG (Compt. rend., 1931, 193, 167—168).—To separate Ra (and Io) from the Ta_2O_5 ppt. carrying the Pa this is melted with 25% (on the wt. of the Ta_2O_5) of BaSO_4 and 10% of KHSO_4 . The mass is treated with H_2O , filtered, washed, and the insol. portion treated with aq. HF, which dissolves only the Ta_2O_5 with the Pa. Subsequent treatment is then as previously described (cf. this vol., 1026).

C. A. SILBERRAD.

Action of hydrogen sulphide on potassium chromate solution. H. B. DUNNICLIFF and C. I. SONI (Proc. XV Indian Sci. Cong., 1928, 167).—In solutions containing 2.15% K_2CrO_4 the Cr is recovered as hydroxide and the K as K_2S_5 and $\text{K}_2\text{S}_2\text{O}_3$.

CHEMICAL ABSTRACTS.

Interaction of sulphur dioxide and ammonia. G. SAMBAMURTI and M. N. L. NARASIMHAM (Proc. XV Indian Sci. Cong., 1928, 169).—The dry gases form the compounds $\text{NH}_2 \cdot \text{SO} \cdot \text{ONH}_4$ and $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{NH}_4$.

CHEMICAL ABSTRACTS.

Molybdenum-blue. C. R. ZINZADZÉ (Bull. Soc. chim., 1931, [iv], 49, 872—877).—Mo-blue is prepared

in a pure state by boiling MoO_3 with dil. H_2SO_4 and adding powdered Mo. The Mo-blue may be separated from H_2SO_4 by means of BuOH . The blue colour depends on both the concentration and the acidity of the solution. Dilution causes the solution to become yellow, but the change is reversible, the blue colour reappearing when H_2SO_4 is added or when the solution is evaporated. The blue colour is probably due to the compound $\text{MoO}_2 \cdot 4\text{MoO}_3 \cdot x\text{H}_2\text{O}$, which on dilution dissociates into the colourless MoO_2 and MoO_3 .

E. S. HEDGES.

Oxidations with fluorine. XVIII. Action of fluorine on cerous sulphate and on iodates. F. FICHTER and V. ARNAL (Helv. Chim. Acta, 1931, 14, 862—867; cf. A., 1930, 1537).—Gaseous F oxidises a solution of $\text{Ce}_2(\text{SO}_4)_3$, but a large concentration of H_2SO_4 (about 8*N*) is necessary to prevent the precipitation of Ce_2F_3 , and this reduces the solubility of the $\text{Ce}_2(\text{SO}_4)_3$. This limitation and the unavoidable formation of H_2O_2 with its reducing action combine to give poor yields of $\text{Ce}(\text{SO}_4)_2$. The optimum temp. is 2—4°. The F acts indirectly through the formation of unstable SO_4 . No HIO_4 could be obtained by passing F into a solution of either HIO_3 alone, or HIO_3 and H_2SO_4 , owing to the formation of H_2O_2 ; the presence of HIO_3 favours the formation of H_2O_2 (cf. A., 1929, 526). It is supposed that a peroxide, I_2O_6 , is first formed, which is decomposed by H_2O into HIO_3 and a true peracid, O_2IOOH , the latter in turn reacting with H_2O to give H_2O_2 and HIO_3 . In alkaline solution (about 2*N*), KIO_3 may be oxidised to KIO_4 , the most favourable yield obtained being 48.5%.

N. H. HARTSHORNE.

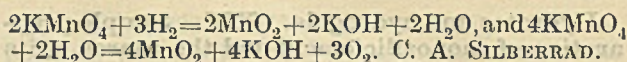
Polyhalides. I. Methods of preparation. H. W. CREMER and D. R. DUNCAN (J.C.S., 1931, 1857—1866).—Methods of prep. of the polyhalides have been improved. The following new compounds are described: KClBrI , m. p. 40°; NH_3Me , m. p. 71°, NH_2Me_2 , m. p. 136°, NHMe_3 , m. p. 67—68°, NH_3Et , m. p. 49°, NH_2Et_2 , m. p. 46—47°, NHEt_3 , NH_3Pr^a , NH_3Pr^s , m. p. 54°, and NMe_3Et , m. p. 145°, dibromiodides. $\text{NH}_4\text{Br}_2\text{I}$ has m. p. 198°. Evidence for the existence of the acids HIBr_2 , HIBrCl , and HICl_2 in aq. solution is adduced.

F. J. WILKINS.

Working up iodine residues. II. Oxidation of cuprous iodide with chromic acid. III. Conversion of cuprous iodide into potassium iodide. F. T. VAN VOORST (Chem. Weekblad, 1931, 28, 440—441, 442—443; cf. this vol., 448).—II. No HIO_3 is formed during the oxidation, and losses of I are very low.

III. Cu_2I is treated with sufficient KOH and the filtrate freed from Cu and evaporated. S. I. LEVY.

Action of hydrogen on potassium permanganate. (MLLE.) M. L. DELWAULLE (Compt. rend., 1931, 192, 1736—1738; cf. A., 1925, ii, 51).— H_2 passed into acid solution of KMnO_4 ppts. MnO_2 , the velocity increasing with acidity to a limit. In a neutral solution the result is the same save that the MnO_2 remains in colloidal solution. In alkaline solution reduction to K_2MnO_4 first occurs, and finally, after a long time, precipitation of MnO_2 . Agitation with H_2 gives the same results except as regards the acid solution, from which there is evolution of O_2 , due to the reactions:



Phosphates of trivalent manganese and of aluminium. A. YAKIMACH (Compt. rend., 1931, 192, 1652—1653).—On evaporating the solution whence $\text{NH}_4\text{Mn}^{\text{III}}\text{P}_2\text{O}_7$ (cf. A., 1903, ii, 151) has separated rose lamellæ of $\text{NH}_4\text{H}_2\text{Mn}^{\text{III}}(\text{PO}_4)_2$ are obtained. $\text{NH}_4\text{H}_2\text{Al}(\text{PO}_4)_2$ is prepared by heating 2 parts of $\text{Al}(\text{NO}_3)_3$ and 1 part of H_3PO_4 until evolution of nitrous fumes ceases, adding more H_3PO_4 , and then gradually $(\text{NH}_4)_2\text{HPO}_4$ with continued heating; the substance which separates differs from Cohen's product (cf. A., 1907, ii, 552), which could not be obtained (cf. A., 1924, ii, 677). Similarly are obtained $\text{KH}_2\text{Al}(\text{PO}_4)_2$ and $\text{Ca}[\text{H}_2\text{Al}(\text{PO}_4)_2]_2$, but no corresponding Na compound.

C. A. SILBERRAD.

Hydroxy-acid complexes of iron. C. MORTON (Pharm. J., 1931, 127, 85).—Mixtures of the FeCl_3 -Na salicylate- NaHCO_3 type contain Fe partly as a violet crystalloid complex, $\text{Fe}(\text{OH})_2[\text{C}_6\text{H}_4(\text{OH})\text{CO}_2]$, and partly as a red basic hydrosol, in proportions depending on the *pH*. Similar complexes, which are hydrolysed to more basic salts in dil. solution, exist in "Fe and NH_4 citrate," viz., $\text{Fe}_2(\text{OH})_3\text{C}_6\text{H}_5\text{O}_7$, and "Fe and K tartrate," $\text{Fe}_2(\text{OH})_4\text{C}_4\text{H}_4\text{O}_6$. The stability of such mixtures in alkaline solution is due to the peptising and protecting action of the hydroxy-acid anion on the hydrosol. Complexes are formed with glyceric, malic, glycollic, lactic, and mandelic acids, but not with formic, acetic, phthalic, or tricarballic acid, which contain no OH group.

E. HOPKINS.

Arsenides of platinum metals. L. WÖHLER and K. F. A. EWALD (Z. anorg. Chem., 1931, 199, 57—64).—The arsenides IrAs_2 , RhAs_2 , RuAs_2 , PtAs_2 , and PdAs_2 have been prepared by heating a mixture of the chloride with excess of As in a current of H_2 .

R. CUTHILL.

Significance of chemical reactions in chemical analysis. A. SCHLEICHER (Z. anal. Chem., 1931, 84, 401—406).

H. F. GILBE.

Accurate titration. I. W. PONNDORF (Z. anal. Chem., 1931, 84, 289—335).—The technique of accurate volumetric analysis as applied to delicate work, such as at. wt. determinations, is discussed in great detail with especial reference to the titration of NaCl and HI with AgNO_3 .

A. R. POWELL.

Identification of solids by means of b.p. elevation in saturated solutions. J. O. HALFORD (J. Amer. Chem. Soc., 1931, 53, 2640—2645).—The b. p. of a saturated solution is unaffected by the addition of more of the saturating solute, but is raised by the addition of another solute. This principle has been applied to the identification of substances and the detection of impurities in cases where the m. p. procedure is inapplicable owing to decomp.

J. G. A. GRIFFITHS.

Method for increasing sensitivity of certain chemical test reactions. I. STONE (Ind. Eng. Chem. [Anal.], 1931, 3, 325).—The sensitivity of colour tests may be increased by shaking the aq. solution with an immiscible liquid, whereupon the colour concentrates at the liquid-liquid interface.

E. S. HEDGES.

Sources of error in organic elementary analysis VIII. J. LINDNER.—See this vol., 1078.

Use of wide-range indicators for determination of p_H . F. R. MCCRUMB (Ind. Eng. Chem. [Anal.], 1931, 3, 233—235).—An investigation of the errors which may occur in the determination of p_H by wide-range indicators has shown that the so-called universal indicators can be used with safety only on well-buffered solutions or when it is known that the p_H of the indicator is close to that of the sample. In general, the wide-range indicator is useless for H_2O , soil extracts, pure sugar liquors, sewage effluents, evaporator water, laundry rinses, etc. Although fairly accurate results can be secured by using a number of solutions of a wide-range indicator adjusted in steps of 1.0 p_H according to the isohydric method, this procedure has no advantage over the use of several short-range indicators and has the disadvantage that the colour changes are not so distinct.

E. S. HEDGES.

Determination of water by drying. M. DOLCH and K. BÜCHE (Pflanzenbau, 1930, 4, 64—73; Chem. Zentr., 1931, i, 973).—Errors are discussed. Alternatively, the water is extracted by repeated treatment with EtOH, the aq. EtOH being mixed with petroleum and the temp. of separation compared with the curve given by control mixtures.

A. A. ELDRIDGE.

Determination of small amounts and traces of water and carbonic acid in silicates. II. E. DITTLER and H. HÜBER (Z. anorg. Chem., 1931, 199, 17—27).—By means of the method previously described (this vol., 325) determinations of H_2O in various minerals have been made. H_2O and CO_2 may be determined simultaneously by igniting the mineral with powdered quartz and after treatment of the gas evolved with α -naphthylxychlorophosphine passing it into 0.01N-Ba(OH)₂, titration of which with standard acid then gives the sum of the amount of CO_2 and the amount of HCl formed by the H_2O . To determine the CO_2 , a known excess of standard acid is then added and after boiling to expel CO_2 the solution is titrated with Ba(OH)₂. With minerals containing sulphides the SO_3 formed on ignition must be retained with PbO_2 or $PbCrO_4$ to prevent it passing into the Ba(OH)₂. The above method is suitable for micro-determinations and has been used for the determination of C and H in diamond.

R. CUTHILL.

Application of methyl alcohol in the ebullioscopic method of determination of water. A. BAKOWSKI (Rocz. Chem., 1931, 11, 490—504).—The ebullioscopic method gives accurate results using MeOH, except in those cases in which the substance examined is sol. in EtOH. The time required for a determination is 30 min., as compared with 62 min. for the xylene method.

R. TRUSZKOWSKI.

Determination of moisture by distillation. G. MIDDLETON (Pharm. J., 1931, 127, 86—87).—A suitable quantity (usually 10 g.) of the substance is boiled with 50 c.c. of tetrachloroethylene or CCl_4 and the vapour condensed in a graduated receiver with a flow-back for the solvent. After 15—20 min. all

the H_2O has collected in the receiver, and its vol. may be read to within 0.02 c.c. The method is rapid, and especially suitable for substances containing carbohydrates or volatile oils.

E. HOPKINS.

Direct iodine-silver determinations. P. FLEURY and J. COURTOIS (Bull. Soc. chim., 1931, [iv], 49, 860—872; cf. B., 1931, 630).—An investigation of the conditions under which the reciprocal determination of I and $AgNO_3$ can be carried out in the presence of starch paste.

E. S. HEDGES.

Determination of fluorine. P. MOUGNAUD (Compt. rend., 1931, 192, 1733—1735).—Pure CaF_2 is stable when heated at 800° in a covered crucible; the loss of wt. and production of CaO sometimes observed in determinations by Rose's method are due to decomp. of $Ca(OAc)_2$ not removed (cf. A., 1916, ii, 47). Precipitation of CaF_2 in NH_3 solution (cf. A., 1930, 180) gives on centrifuging the ppt. an excess, on calcination some CaO. The solubility of CaF_2 (precipitated and dried at 100°) at 18° in H_2O is 18.3 mg. per litre (of calcined CaF_2 , 15.1); in AcOH 30.8(0.083N)—58.6(1.66N); (NH_4Cl 20.8(0.25N)—27.8(1.66N); NH_4OAc 20.3(0.333N)—25.5(1.66N); NH_3 17.6(N)—17.5(1.66N). By evaporation in contact with AcOH some HF is evolved.

C. A. SILBERRAD.

Determination of small quantities of oxygen in gases. J. WIERCINSKI.—See B., 1931, 756.

Determination of sulphur [in iron and steel] by the evolution method. F. JUNGLUT.—See B., 1931, 762.

Standardisation of volumetric sulphuric acid solution. J. L. MAYER (J. Amer. Pharm. Assoc., 1931, 20, 651—653).—The $BaSO_4$ method is preferred to the Na_2CO_3 and KH tartrate methods (U.S.P.) for the standardisation of H_2SO_4 .

E. H. SHARPLES.

Potentiometric titration of Caro's acid and hydrogen peroxide. E. MÜLLER and G. HOLDER (Z. anal. Chem., 1931, 84, 410—416).—Caro's acid may be determined by potentiometric titration with As_2O_3 solution in presence of $NaHCO_3$. In presence of H_2O_2 the acid may be determined potentiometrically or visually by adding a few drops of KI solution; the I is alternately oxidised by the acid and reduced by the As_2O_3 . Potentiometric titration with KI in acid solution is also satisfactory, but the I which separates should be prevented from depositing on the electrode by addition of C_6H_6 . The subsequent determination of the H_2O_2 may be effected by potentiometric or visual titration with KBr—Br solution after addition of NaOAc.

H. F. GILLBE.

Distillation of free ammonia-nitrogen from buffered solutions. M. S. NICHOLLS and M. E. FOOTE (Ind. Eng. Chem. [Anal.], 1931, 3, 311—313).—For the quant. recovery of free NH_3 from aq. solutions of NH_4Cl and $(NH_4)_2SO_4$ a const. p_H of 7.4 or above is necessary. A phosphate buffer of p_H 7.4 is recommended. If Na_2CO_3 is used to adjust the p_H , either the recovery is incomplete or an appreciable quantity of org. N is included in the free NH_3 determination.

E. S. HEDGES.

Use of boric acid in micro-Kjeldahl determination of nitrogen. N. M. STOVER and R. B. SANDIN (Ind. Eng. Chem. [Anal.], 1931, 3, 240—242).—Accurate results can be obtained in the determination of N by Pregl's micro-method by the use of H_3BO_3 for absorbing the NH_3 . The distillate containing the NH_3 does not require boiling before titrating. A mixed indicator containing Me-red and tetrabromophenol-blue gives good results in H_3BO_3 solution.

E. S. HEDGES.

Micro-Kjeldahl method of nitrogen determination. W. F. ALLEN (Ind. Eng. Chem. [Anal.], 1931, 3, 239—240).—The simple apparatus described gives accurate results rapidly with samples requiring as much as 10 c.c. of conc. H_2SO_4 in the digestion mixture, as well as with samples containing as little as 0.1 mg. N.

E. S. HEDGES.

Modification of Pregl's method of determining nitrogen. J. J. RUTGERS (Compt. rend., 1931, 193, 51—53).—By widening the portion of the combustion tube containing the permanent charge of Cu and CuO from 8 to 20 mm. diameter, and using a larger and more finely divided charge, the period of contact of the gases and surface of contact are increased, and the time of a determination is reduced to 1 hr.

C. A. SILBERRAD.

Bromometric determination of ammonia-nitrogen. I. B. LEVY. II. M. TSCHPELE-VETZKY and S. POSDNIKOVA [with R. FEIN] (Z. anal. Chem., 1931, 84, 98—106, 106—118).—I. Addition of Br solution to solutions of NH_4 salts containing an excess of $NaHCO_3$ effects complete oxidation of the NH_3 to N without any side-reaction occurring. Excess of Br can then be determined iodometrically.

II. The oxidation is quant. in solutions of p_n 7.5—9.5, but in more alkaline solutions $NaNO_2$ is formed. In the presence of Fe^{+++} salts NH_4 may be determined bromometrically after addition of a phosphate buffer (see also B., 1931, 756).

A. R. POWELL.

Volumetric determination of nitrites in presence of nitrates. A. WINOGRAD (Chemist-Analyst, 1931, 20, No. 3, 15).—I is liberated from KI and H_2SO_4 by CO_2 which has been passed through the liquid.

CHEMICAL ABSTRACTS.

Use of aluminium and stannous chloride in the Gutzeit test for arsenic. J. P. MAYRAND (J. Amer. Pharm. Assoc., 1931, 20, 637—643).—The U.S.P. Gutzeit method is modified in that 1 g. Al replaces 8—10 g. Zn, 50 c.c. of 5% HCl replaces 25 c.c. of 20% H_2SO_4 , 0.8 c.c. of acid $SnCl_2$ is used instead of 0.25 c.c., and a 100-c.c. reduction bottle is employed. "Granular powder" As-free Al (20-mesh) is used and 0.0000004 g. As can be detected. E. H. SHARPLES.

Elimination of carbon dioxide from pyruvic acid. II. **Determination of carbon dioxide in kinetic investigations.** U. BOKLUND (Biochem. Z., 1931, 233, 478—483).—An apparatus and method for the determination of CO_2 are described. The process is a modification of that of Westerberg (Svensk Tekn. Tidsk., 1910, 40, 49).

W. MCCARTNEY.

Purification and analysis of alkali cyanides. M. R. THOMPSON (Bur. Stand. J. Res., 1931, 6, 1051—

1059).—Work on the purification and analysis of KCN and NaCN is reviewed. Pure (99.32—99.85%) KCN may be prepared by neutralising HCN with alcoholic KOH or KOEt solution, but NaCN so prepared contains Na_2CO_3 and other impurities; the use of NaOEt is preferable to that of NaOH. The salts are more sol. in MeOH than in EtOH, but recrystallisation is not recommended for prep. of the pure salts.

H. F. GILLBE.

Irregularities in sodium determination by sodium sulphate method. G. W. COLLINS (Ind. Eng. Chem. [Anal.], 1931, 3, 291).—The direct sulphate method gives low results in the presence of the side-chain 5-carbon derivatives of barbituric acid. No explanation is given. The method gives accurate results after removing the barbituric acid derivatives by acidification followed by extraction with Et_2O .

E. S. HEDGES.

Rapid volumetric method for determination of potassium. L. CLARKE and J. M. DAVIDSON (Ind. Eng. Chem. [Anal.], 1931, 3, 324—325).—A procedure for determining K in a solution of K_2SO_4 and $MgSO_4$ depends on the precipitation and titration of K H tartrate. A modification is proposed for solutions containing K^+ , Na^+ , Cl^- , and NO_3^- .

E. S. HEDGES.

Determination of free alkali and carbonate in alkaline hypochlorites. KERNY.—See B., 1931, 717.

Determination of calcium by alkalimetric titration. I. C. H. FISKE and E. T. ADAMS (J. Amer. Chem. Soc., 1931, 53, 2498—2501).—0.2 mg. of Ca is determined to 1% by precipitation as oxalate which is transferred to a Pt dish with HNO_3 . The nitrate is dried, treated with 0.5 c.c. of 2.5% $H_2C_2O_4$, and ignited. The resultant CaO dissolves easily in excess of 0.02N-HCl, which is titrated back.

J. G. A. GRIFFITHS.

Gravimetric determination of beryllium and its separation from aluminium by means of guanidine carbonate. A. JÍLEK and J. KOŤA (Coll. Czech. Chem. Comm., 1931, 3, 336—353).—In presence of NH_4 tartrate, guanidine carbonate ppts. Be salts in the form of a basic carbonate, whilst Al salts are not precipitated. Be can be determined in the ppt. by igniting and weighing as BeO .

E. S. HEDGES.

Determination of zinc with pyridine and ammonium thiocyanate. C. F. MILLER (Chemist-Analyst, 1931, 20, No. 3, 8—9).—Details are recorded.

CHEMICAL ABSTRACTS.

Determination of a very small quantity of cadmium in a rich zinc ore. J. G. FAIRCHILD (Chemist-Analyst, 1931, 20, No. 3, 5—7).—Precipitation of CdS in 3N- H_2SO_4 is recommended; the ppt. is dissolved and reprecipitated twice, the Cd being weighed as $CdSO_4$.

CHEMICAL ABSTRACTS.

Determination of lead with sodium carbonate. S. KOMARETZKY (Z. anal. Chem., 1931, 84, 407—410).—Pb may be titrated with Na_2CO_3 in neutral solution, using phenolphthalein as indicator. If free acid is present it is determined by titration with Na_2CO_3 and Me-orange, and a second portion of the solution is then

neutralised and heated for 30 min. to remove CO_2 prior to determination of the Pb. The results are satisfactory at the b. p. and at room temp., but at lower temp. are high probably because of diminished hydrolysis.

H. F. GILLBE.

Polarographic studies with the dropping mercury cathode. XX. Simultaneous determination of copper, bismuth, lead, and cadmium.

K. SUCHÝ (Coll. Czech. Chem. Comm., 1931, 3, 354—366).—When a solution of the sulphides of Cu, Bi, Pb, and Cd in HNO_3 is neutralised with NaOH , with the addition of 10% Na K tartrate, and electrolysed with the dropping Hg cathode, the current-potential curves show the presence of these metals by breaks at the following cathodic potentials: Cu -0.14 , Bi -0.34 , Pb -0.60 , Cd -0.80 volt. The tartrate prevents the simultaneous deposition of Cu and Bi. It is advantageous to use the solutions less conc. than 0.001N. Traces of these metals down to 10^{-3} g.-equiv. per litre can be determined, 2 c.c. of the solution being sufficient. If the amounts increase in the series $\text{Cu} < \text{Bi} < \text{Pb} < \text{Cd}$, any proportion may be determined, but if the nobler metals prevail, the less noble can be determined only if they constitute more than 2% of the nobler metals. The accuracy of determination of each component is about 5%.

E. S. HEDGES.

Determination of copper in cyanide solutions. E. H. SMITH (Chemist-Analyst, 1931, 20, No. 3, 10).— CN' is destroyed with HNO_3 ; the solution is evaporated, acidified with AcOH , treated with KI, and titrated with $\text{Na}_2\text{S}_2\text{O}_3$.

CHEMICAL ABSTRACTS.

Quantitative separation of copper and cadmium by reduction of their salts with potassium formate. E. I. FULMER (Ind. Eng. Chem. [Anal.], 1931, 3, 257—258).—When solutions of Cu salts are treated with HCO_2K , the solution evaporated to dryness and heated at $155-160^\circ$, spongy Cu is produced and may be determined as such. If Cd is also present, it is not reduced and may be determined in the filtrate.

E. S. HEDGES.

Determination of very small quantities of mercury and its importance. A. STOCK (Naturwiss., 1931, 19, 499—502).—The method of Bodnár and Szép (A., 1929, 614) is improved.

A. J. MEE.

Inaccuracy in determination of mercury by direct precipitation as mercuric sulphide from acid solution. E. P. FENIMORE and E. C. WAGNER (J. Amer. Chem. Soc., 1931, 53, 2453—2456).—The ppt. is too heavy, and this effect is increased by the presence of iodides or excess of other salts. Volhard's method is accurate in the absence of iodides or large quantities of other salts.

J. G. A. GRIFFITHS.

Anhydrous distillation method for determination of certain metals in organic compounds.

I. Mercury. E. P. FENIMORE and E. C. WAGNER (J. Amer. Chem. Soc., 1931, 53, 2468—2475).—The sample containing 0.15 g. of Hg is decomposed by gently heating with 20 c.c. of conc. H_2SO_4 and 10 g. of NH_4SO_4 . The Hg is distilled as HgCl_2 by heating in a stream of gaseous HCl. SO_2 is oxidised by Br. 5 c.c. of 6N-HCl are added to the previously diluted and neutralised distillate; $\text{ZnHg}(\text{SCN})_4$ is precipitated

by adding 25 c.c. of reagent (73 g. of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + 125$ g. of KSCN per litre) and determined by titration with iodate (A., 1919, ii, 248). If I is present, the Hg in the distillate, diluted with aq. KI, is precipitated with Zn dust after oxidation of SO_2 with I_2 . The excess of Zn is removed by HCl, the residual amalgam is dissolved, and the Hg is determined (*loc. cit.*). Halogens and S do not interfere.

J. G. A. GRIFFITHS.

Oxide content of aluminium and its determination. H. LÖWENSTEIN (Z. anorg. Chem., 1931, 199, 48—56).—Hahn's results for the amount of Al_2O_3 in samples of Al (B., 1930, 512) are too high owing to the Al being heated in a boat of siliceous material, some of which is volatilised as SiCl_4 . Using a boat of pure Al_2O_3 , however, Hahn's method gives the same results as Jander's method (A., 1928, 860). The Al_2O_3 in Al is formed solely by surface oxidation and its amount does not depend on the origin of the metal.

R. CUTHILL.

Analytical chemistry of rhenium. III. Dry reactions of rhenium. W. GEILMANN and F. W. WRIGGE. **IV. Microchemical reactions of rhenium.** W. GEILMANN and K. BRÜNGER. **V. Separation of rhenium by distillation with hydrogen chloride.** W. GEILMANN and F. WEIBKE (Z. anorg. Chem., 1931, 199, 65—76, 77—90, 120—128; cf. this vol., 328).—III. The results of the usual dry tests when applied to Re compounds are described. By a combination of dry tests and microchemical tests 0.05% Re can be detected in 10 mg. of material.

IV. Re may be detected microchemically by formation of K, Rb, and Cs per-rhenates, this test not being affected by presence of Mo compounds. In pure solutions of Re compounds the formation of the per-rhenates of various org. bases may also afford a delicate reaction.

V. If an aq. solution of HCl is distilled into H_2SO_4 containing dissolved KReO_4 at $175-200^\circ$ the Re distils over quantitatively. Separation of Re from Mo in this manner is possible, but not convenient.

R. CUTHILL.

Determination of ferric oxide and magnetic oxide in presence of iron and ferrous oxide. E. W. CHESBROUGH (Chemist-Analyst, 1931, 20, No. 3, 14—15).—Fe is determined by treating 1 g. with 100 c.c. of 20% CuSO_4 solution, filtering, acidifying with H_2SO_4 , and titrating with KMnO_4 . The residue is treated in a stoppered flask with 50 c.c. of 7N- H_2SO_4 , filtered, and FeO in the solution determined with KMnO_4 . Fe_3O_4 is separated magnetically and weighed.

CHEMICAL ABSTRACTS.

Potentiometric determination of ferric and dichromate ions. E. H. DUCLOUX (Rev. fac. cienc. quim., La Plata, 1930, 7, II, 97—139).— Fe^{+++} is determined potentiometrically in HCl solution by reduction with 0.05—0.1N- $\text{U}(\text{SO}_4)_2$ in 3N- H_2SO_4 ; Al, Cr, Ti, Mn, Zn, Ni, or Co salts may be present. $\text{Cr}_2\text{O}_7^{--}$ can be determined accurately and simultaneously.

CHEMICAL ABSTRACTS.

Determination of traces of nickel and cobalt in steel without destruction of the sample. R. JIRKOVSKY.—See B., 1931, 762.

Volumetric determination of chromium and nickel in the same solution. L. H. JAMES (Ind. Eng. Chem. [Anal.], 1931, 3, 258—259).—The procedure is a combination of known methods for the volumetric determination of Cr and Ni, utilising the oxidation of Cr salts by HClO_4 . The method is suitable for the analysis of stainless steels, but the cyanide titration of Ni cannot be carried out in presence of appreciable quantities of Cu or Co.

E. S. HEDGES.

Volumetric determination of uranium. Potentiometric titration of reduced uranium solutions with ceric sulphate, or with potassium permanganate. Application of differential method. N. H. FURMAN and I. C. SCHOONOVER (J. Amer. Chem. Soc., 1931, 53, 2561—2571; cf. this vol., 927).—The cold solution of U is reduced and the 25—40% of U^{III} produced is easily oxidised by air to U^{IV} before titration of the hot solution with $\text{Ce}(\text{SO}_4)_2$ (cf. B., 1925, 1016). Cl^- , but not OAc^- , interferes. Previous results (A., 1922, ii, 661) with KMnO_4 are confirmed.

J. G. A. GRIFFITHS.

Potentiometric titration of uranium by potassium permanganate. M. A. LUYCKX (Bull. Soc. chim. Belg., 1931, 40, 269—283).—The electrolytic reduction of the U^{VI} ion has been studied in detail; fall of temp. or increase of acidity favours the reduction. Both U^{III} and U^{IV} are produced at the commencement of the reduction, and the former is then oxidised by the excess of U^{VI} to U^{IV} ; when the U^{VI} is entirely reduced an equilibrium is set up between U^{III} and U^{IV} . In practice the reduction is usually incomplete, and it is recommended that the electrolysis should be prolonged for 12—14 min. at 80° , with a current of 1 amp., for a solution containing, e.g., 0.195 g. UO_2SO_4 and about 2% free acid.

H. F. GILLBE.

New reaction of polonium. M. HAÏSSINSKY (Compt. rend., 1931, 192, 1645—1647).—On electrolysis a HNO_3 solution of Po to which pyrogallol has been added some time previously, deposition of Po on the cathode ceases; also the Po can be separated almost completely by centrifuging such a solution. It is inferred that the Po is first reduced to the trivalent condition (cf. this vol., 697), and then forms an insol. compound with pyrogallol similar to the insol. $\text{C}_6\text{H}_3\text{O}_3\text{Bi}$ (cf. A., 1893, i, 643; 1925, ii, 442). A similar solution of Te gives no such compound.

C. A. SILBERRAD.

Separation of polonium and protoactinium fixed on tantalum pentoxide. F. REYMOND and CHENG DA-CHANG (Compt. rend., 1931, 192, 1723—1724).— Ta_2O_5 containing Po and Pa, in a state of jelly (0.1545 g.), is dissolved in 6.3% HF (60 c.c.); 0.1 g. H_2SeO_3 is added with a few drops of H_2SO_4 and 3 c.c. of aq. NaHSO_3 , *d* 1.332, and the whole boiled. On cooling, a few drops more aq. NaHSO_3 are added and the Se carrying all the Po is collected. The Ta_2O_5 with all the Pa is then quantitatively precipitated with NH_3 and $(\text{NH}_4)_2\text{SO}_4$ (cf. this vol., 1021).

C. A. SILBERRAD.

Determination of precious metals in Transvaal platinum ores and concentrates. H. R. ADAM and R. J. WESTWOOD.—See B., 1931, 763.

Micro-determination of platinum in alloys. R. STREBINGER and H. HOLZER.—See B., 1931, 722.

Calibrating thermocouples for low temperatures. A. J. MONACK (Chem. Met. Eng., 1931, 38, 416).—The m. p. of ice, transition point of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to Na_2SO_4 , b. p. of H_2O and of const.-boiling mixtures of C_6H_6 and MeOH , C_6H_6 and AcOH , amyl alcohol and iodide, butyric acid and PhBr , and dil. HNO_3 may be used for calibration.

D. K. MOORE.

Calibration of the Beckmann thermometer. I. Corrected Eucken's method. M. MATSUI, S. KAMBARA, K. MYAMURA, and A. MIYOSHI. II. Precise calibration of graduation scale. M. MATSUI and K. MYAMURA (J. Soc. Chem. Ind. Japan, 1931, 34, 197—200B, 200—202B).—I. A modification of Eucken's method ("Physikalisch-chemische Praktikumsaufgaben," 1928, 36) of calibrating the bore and fundamental interval of a Beckmann thermometer is described.

II. The methods of Gay-Lussac, Neumann and Thiesen, Eucken, and the least square method of Marck, Broch, and Hansen for calibrating the scale of a Beckmann thermometer are compared.

N. H. HARTSHORNE.

Thermostats. III. Time lag of various thermometers. S. KAMBARA and M. MATSUI (J. Soc. Chem. Ind. Japan, 1931, 34, 167—172B).—An apparatus for determining the time lags of various thermometers and thermocouples is described. The results obtained varied from zero with a bare Cu-constantan couple to 8.7 sec. with a Beckmann thermometer having a scale graduated to 0.002° .

A. R. POWELL.

Apparatus for rapid drying of solutions. W. W. EWING (Science, 1931, 74, 74—75).—15 c.c. of 40% aq. $\text{Sr}(\text{NO}_3)_2$ were evaporated to dryness without loss in 24 hr.

L. S. THEOBALD.

Photo-electric polarimetry. I. L. EBERT and G. KORTUM (Z. physikal. Chem., 1931, B, 13, 105—133).—The construction and manipulation of an apparatus suitable for measurements of absorptive and rotatory power with light of wave-length down to $254 \text{ m}\mu$ are described. The essential feature of the apparatus is the comparison of light intensities by means of two coupled photo-electric cells.

R. CUTHILL.

Error in spectrophotometric determinations. M. SCHLESINGER (Biochem. Z., 1931, 235, 70—78).—A systematic error appearing in these determinations with high extinction is critically examined.

P. W. CLUTTERBUCK.

Simple cell for conductometric titrations. J. M. PRESTON (J.C.S., 1931, 1827—1828).—The cell, made from a conical flask, is robust and easy to clean.

F. J. WILKINS.

Nomograph for evaluating electrometric p_{H} determinations. D. S. DAVIS (Chem. Met. Eng., 1931, 38, 416).

D. K. MOORE.

Electrical drop counter. S. E. OWEN (Science, 1931, 74, 19—20).—An electrical device for recording drop flow over extended periods of time is described.

L. S. THEOBALD.

Glass colour standards for determination of phosphorus by Denigès' colorimetric method. H. D. CHAPMAN (Ind. Eng. Chem. [Anal.], 1931, 3, 282—284).—The frequent prep. of new standards is obviated by the use of permanent glass colours. The technique described demands little sacrifice in accuracy. E. S. HEDGES.

All-glass steam-distillation apparatus for analytical purposes. V. E. WELLMAN (Ind. Eng. Chem. [Anal.], 1931, 3, 281).—The simple apparatus described is useful for distillates which act on cork or rubber, and is adapted for quant. work. E. S. HEDGES.

Dry method of micro-analysis of gases. F. E. BLACET and P. A. LEIGHTON (Ind. Eng. Chem. [Anal.], 1931, 3, 266—269).—The apparatus described employs samples of 25—100 cu. mm. No liquid reagents are used, O₂ being removed by yellow P, CO₂ by fused KOH, and H₂O vapour by fused P₂O₅. The accuracy of the method is of the same order as that ordinarily attained in the macro-analysis of gases. E. S. HEDGES.

Marking chemical glassware. K. H. MORKERT and W. D. HATFIELD (Ind. Eng. Chem. [Anal.], 1931, 3, 242).—For the permanent lettering or numbering of glass apparatus 30% aq. Na₂SiO₃ is applied by means of a steel pen and allowed to dry. The markings are heated for about 1 min. in a Bunsen or blow-pipe flame, when a permanent frosting occurs. E. S. HEDGES.

Extraction apparatus with two-way tap. E. THIELEPAPE (Chem. Fabr., 1931, 293—294, 302—303).—By fitting a two-way tap between the reaction vessel and the flask the ordinary continuous-flow apparatus may be employed for solvent recovery, recrystallisation, the rapid prep. of dry solvents, dialysis, extraction, and for sampling the extract. H. F. GILLBE.

Apparatus for the extraction of large volumes of liquids. J. FRIEDRICH (Chem.-Ztg., 1931, 55, 519—520).—A 7-litre extraction flask gives best extraction of one liquid by another if provided with a relatively small glass frit for diffusion of the extracting liquid together with a stirrer. Large filter plates are unsuitable, as some pores are inevitably larger than others and unequal distribution follows. Two types of apparatus are given for easy and difficult extractions. C. IRWIN.

Large-scale Soxhlet extraction. S. A. LOUGH (Ind. Eng. Chem. [Anal.], 1931, 3, 344).—A modified apparatus is described. E. S. HEDGES.

Simple, automatic pressure regulator for filtration. E. LEIFSON (Science, 1931, 73, 707—709).—An apparatus for filtration under controlled pressures is described. L. S. THEOBALD.

Vitreosil gas ejector pump. B. MOORE (Ind. Chem., 1931, 7, 282—283).—A fused SiO₂ filter pump, suitable for use with hot and cold corrosive gases, is described. The calculation of its dimensions is discussed. C. W. GIBBY.

Surface leakage of pyrex glass. W. A. YAGER and S. O. MORGAN (J. Physical Chem., 1931, 35, 2026—2042).—A method of measuring the surface leakage

of glass is described; results are given and the nature of the process is discussed. The variation of the surface conductivity with the relative humidity resembles the corresponding variation of the thickness of the adsorbed H₂O film. An observed variation with the frequency of the applied voltage is probably due to electrode polarisation. H. F. GILLBE.

Method of winding helical quartz springs and of constructing glass sorption buckets. A. E. CAMERON (J. Amer. Chem. Soc., 1931, 53, 2646—2648; cf. A., 1926, 493).—The quartz fibre is attached by wire to a horizontal quartz tube which is rotated while the fibre is heated with a small air-O₂-gas flame. Pyrex buckets 1 cm. diameter and weighing less than 0.1 g. are made from bulbs blown on the end of capillary tubes. J. G. A. GRIFFITHS.

Cellophane covers for Petri dishes for keeping out contaminations and studying the effects of ultra-violet light. F. H. JOHNSON (Science, 1931, 73, 679—680). L. S. THEOBALD.

Modified Engler distillation flask. W. SWIEN-TOSELAWSKI (Rocz. Chem., 1931, 11, 543—544).—The vapours from the distillation flask enter the middle part of the condenser, instead of at the bottom; in this manner, partial evaporation of the condensate by the hot vapours is avoided. R. TRUSZKOWSKI.

Modified vacuum regulator. A. A. SUNIER and C. M. WHITE (Ind. Eng. Chem. [Anal.], 1931, 3, 259).—The regulator described permits a set of predetermined pressures to be maintained in rotation in an apparatus. E. S. HEDGES.

Continuously operating diffusion vacuum pump. P. ANSIAU (Bull. Soc. chim. Belg., 1931, 40, 330—332).—When using the Hg-vapour pump described it is unnecessary to remove corrosive or easily condensable gases from the vessel to be evacuated; the pump need not be dried after cleaning. H. F. GILLBE.

Diaphragm valve. J. Y. YEE and J. REUTER (J. Amer. Chem. Soc., 1931, 53, 2645—2646).—The valve is greaseless and specially adapted for regulating low rates of gas flow. The edge of the circular Al diaphragm is held against the flange of a glass cup fitted with an outlet, and the centre of the diaphragm is pressed by means of a screw against the ground surface of the capillary inlet situated axially in the cup. J. G. A. GRIFFITHS.

Bubble counter for measurement of gas evolution. E. A. BUDGE (J. Amer. Chem. Soc., 1931, 53, 2451—2453).—Bubbles are formed under H₂O in the cup fused to the shallow capillary U-tube which communicates with the source of gas and a capillary U-tube containing Hg and two Pt contacts. Contact is broken as each bubble breaks away and is restored before each bubble develops. J. G. A. GRIFFITHS.

Simple ultra-centrifuge. J. W. BEAMS and A. J. WEED (Science, 1931, 74, 44—46). L. S. THEOBALD.

Determination of specific gravity of semi-solids. W. MAASS (Chem. Fabr., 1931, 318).—The *d* of such materials as bitumen is best determined by the Westphal balance using a Sn foil crucible in which the material to be tested is first dried and then main-

tained at 70—100° above its m. p. for 1 hr. to remove air inclusions. C. IRWIN.

Laboratory furnace with low gas consumption. R. HOEVERS (Chem. Weekblad, 1931, 28, 460—461).—

The gas-air mixture burns in an annular space surrounding the furnace tube; the temp. of the latter attains 1100° within 10—15 min., and is const. throughout the length of the tube. H. F. GILLBE.

Geochemistry.

Universal presence of oxides of nitrogen. D. VORLÄNDER and W. GOHDES (Ber., 1931, 64, [B], 1776—1784).—The assumption that the presence of oxides of N in the atm. is due mainly to lightning and other electrical discharges is inadequate. It is shown that the N₂ and O₂ of moist air yield oxides of N under the influence of ultra-violet irradiation. Moist N₂ and ozonised, electrolytically prepared O₂ do not yield oxides of N at 18—20° in the absence of light during 14 days; irradiation of such mixtures causes conversion of NO₂' into NO₃', probably in the gaseous phase. Oxides of N in crude air are therefore formed during irradiation from N₂ and O₂ or O₃, and this is the permanent source. It is uncertain whether the formation of NO or of O₃ is the primary action.

NO₂' is determined colorimetrically by a solution of α -naphthylamine hydrochloride, sulphanilic acid, and tartaric acid. Moist November air at +5° to +8° contains as an average 22×10^{-6} g. N₂O₃ per cu. m. In the depth of winter N₂O₃ is not present in measurable amount and NO₂ can scarcely be detected. H. WREN.

Hydrogen-ion concentration of the lake water in Japan. S. YOSHIMURA (Proc. Imp. Acad. Tokyo, 1931, 7, 195—197).—Types of lake water are classified, data tabulated for 40 lakes, and conclusions reached. N. M. BLYTH.

Radioactivity of Teano water. P. MISCIATTELLI (Atti III Cong. Naz. Chim., 1929, 582—583; Chem. Zentr., 1931, i, 2187).—The activity is due to accompanying radioactive substances; that of most radioactive Italian springs is due to emanation. A. A. ELDRIDGE.

Mbosi meteoric iron, Tanganyika Territory. D. R. GRANTHAM and F. OATES (Min. Mag., 1931, 22, 487—493).—A wedge-shaped mass of meteoric Fe measuring 10×4×3 feet and estimated to weigh 12—15 tons was found in October, 1930, near Mbosi between Lakes Tanganyika and Nyasa. A polished and etched surface shows well-marked Widmanstätten figures, the structure being that of a medium octahedrite. Analysis by F. OATES gave Fe 90.45, Ni 8.69, Co 0.66, Cu trace, S 0.01, P 0.11, insol. 0.03, total 99.95; and a partial analysis by M. H. HEY gave Fe 90.65, Ni 8.53, Co 0.62, Cu trace, total 99.80; *d* 7.64—7.84. A separate determination of C gave 0.073%. L. J. SPENCER.

Formation of diamond. F. STÖBER (Chem. Erde, 1931, 6, 440—452).—In Moissan's experiment (1893) for the production of diamond, the temp. was about 3000°, the pressure very high, and the time very short, whereas in those of Friedländer (1898) and of Hasslinger and Wolf (1903), the temp. was much lower (about 1400°), the pressure normal, and the time long. There thus appears to be a contra-

diction, which the author attempts to explain by his theory of crystallisation. L. J. SPENCER.

Glauconite in fossil foraminiferal shells. A. L. DRYDEN, jun. (Science, 1931, 74, 17).—Foraminiferal shells in material from the Oligocene Vicksburg group of Mississippi bear glauconite which evidently has been formed in the shell itself. L. S. THEOBALD.

Three minerals new for Långban [Sweden]. G. AMINOFF (K. Svensk. Vetén. Handl. Stockholm, 1931, [iii], 9, no. 5, 49—51).—The three new records for this locality are domeykite, native arsenic, and phenakite. Analysis by K. JOHANSSON of the domeykite gave Cu 71.45, As 27.98, insol. 0.28, total 99.71, agreeing with Cu₃As. L. J. SPENCER.

Pyroaurite. G. AMINOFF and B. BROOMÉ (K. Svensk. Vetén. Handl. Stockholm, 1931, [iii], 9, no. 5, 23—43).—A new analysis by K. JOHANSSON of pyroaurite from Långban, Sweden, gave Fe₂O₃ 23.19, Al₂O₃ 0.11, FeO 0.10, MnO 0.28, MgO 35.44, H₂O 33.62, CO₂ 7.01, SiO₂ 0.41, total 100.16; neglecting the CO₂ as due to secondary alteration, this agrees with the formula Fe(OH)₃.3Mg(OH)₂.3H₂O. The crystals are of two types: (1) larger six-sided plates giving hexagonal X-ray pattern and cell dimensions *a* 3.097, *c* 15.56 (*c/a* 5.024); (2) smaller rhombohedral crystals with basal plane, giving trigonal X-ray patterns, *a* 3.089, *c* 23.23 (*c/a* 7.520). L. J. SPENCER.

Mineral deposit of Långban [Sweden] from a chemical point of view. G. AMINOFF (K. Svensk. Vetén. Handl. Stockholm, 1931, [iii], 9, no. 5, 4—13).—The relative abundance of the 30 elements that have been detected from this locality is calc. There is a special concentration of Fe, Mn, Pb, Ba, and As. The 96 recorded minerals are listed with their chemical composition. L. J. SPENCER.

Arsenoklasite, a new arsenate from Långban [Sweden]. G. AMINOFF [with R. BLYTH] (K. Svensk. Vetén. Handl. Stockholm, 1931, [iii], 9, no. 5, 52—57).—This new mineral occurs as cryst. films with sarkinite (which it resembles in appearance) along fissures in dolomite impregnated with hausmannite. It is orthorhombic with perfect (010) cleavage; X-ray analysis gives the cell dimensions *a* 9.19, *b* 18.01, *c* 5.795 (*a* : *b* : *c* = 0.510 : 1 : 0.313), containing 4 mols. of Mn₃(AsO₄)₂.2Mn(OH)₂. Analysis gave As₂O₅ 36.96, MnO 55.01, FeO trace, MgO 0.87, BaO 0.11, CaO 0.57, H₂O 5.86, H₂O (hygr.) 0.04, total 99.42; *d* 4.16. L. J. SPENCER.

Origin of tectites of Indo-China. A. LACROIX (Compt. rend., 1931, 192, 1685—1689; cf. this vol., 60).—From an examination of several thousand more specimens the theory of their meteoric origin in the neolithic period is strengthened. C. A. SILBERRAD.

Diffusion of silica in formation of jasper in Corsica. P. JODOT (Compt. rend., 1931, 192, 1740—1742).—The schists of N. E. Corsica are interstratified with bands of jasper the middle portions of which are original limestone. The SiO_2 is derived from radiolaria in the limestone, and has first, in the form of unstable α -chalcedony, replaced the purest calcite, and then passed into the stable β -form; where the SiO_2 is not pure it is isotropic. Metamorphism of the more impure calcite has occurred more slowly, and has been further retarded where it touches the phyllites of the schists. C. A. SILBERRAD.

Deposits of serpentine and chromite in Togoland. N. KOURIATCHY (Compt. rend., 1931, 192, 1669—1672).—The gneissic peneplain in French Togoland contains many intrusions of peridotite, gabbro, norite, eclogite, orthoamphibolite containing clinzoisite, parameters III. 4(5). 4'. (4)5. [2. '4. 1(2). 2'], and massive serpentine. In the last named at Mt. Ajito and Goudéwé occurs chromite associated with kotschubeite. Analyses of the orthoamphibolite, chromite (4), and serpentine show (in this order): SiO_2 39.36, 0.74—5.54, 39.08; Al_2O_3 16.38, 16.04—24.61, 2.10; Fe_2O_3 3.86, 3.77—7.28, 6.21; Cr_2O_3 0.05, 39.14—49.88, 0.29; FeO 10.61, 7.37—10.99, 2.99; MnO 0.19, trace—0.05, 0.12; MgO 12.36, 14.70—16.19, 37.23; CaO 11.08, 0.22—0.62, 0; Na_2O 1.71, trace, 0.06; K_2O 0.30, trace, 0.11; TiO_2 1.42, 0.16—0.44, 0.09; P_2O_5 0.08, 0, 0; Cl 0.06, 0, 0; SO_3 0.22, 0, 0; NiO 0, 0, 0.04; $\text{H}_2\text{O} + 2.18$, 0.29—1.50, 11.87; $\text{H}_2\text{O} - 0.17$, 0—0.23, 0.12. C. A. SILBERRAD.

Stannite ore from Oonah Mine, Zeehan, Tasmania. F. L. STILWELL (Proc. Austral. Inst. Min. Met., 1931, 1—7).—The ore contains pyrite, mispickel, cassiterite, stannite, chalcopyrite, tetrahedrite, bismuthinite, and galena in a quartz gangue containing some siderite and fluorite. Of these minerals pyrite, mispickel, cassiterite, and quartz belong to an older generation than the others. The mode of occurrence of the individual minerals is described with reference to a number of photographs of polished sections. A. R. POWELL.

Granite of Dhoon, Isle of Man: a study in contamination. S. R. NOCKOLDS (Min. Mag., 1931, 22, 494—509).—The rock is a biotite-granodiorite-porphry and is abnormal in containing clots of biotite associated with zoisite, ilmenite, sphene, epidote, and garnet. These clots represent the remnants of a basic igneous rock (greenstone) which has been absorbed by the granitic magma. The original magma was of an alkali-granite type similar to the quartz-porphry dikes associated with the mass. Chemical analyses of the granite, quartz-porphry, and greenstone show that there has been an extensive interchange of oxides between the original magma and the basic igneous rock. L. J. SPENCER.

Pink epsomites and fauserite. M. H. HEY (Min. Mag., 1931, 22, 510—518).—The existence of the fauserite, $(\text{Mn}, \text{Mg})\text{SO}_4 \cdot 6\text{H}_2\text{O}$, of Breithaupt (1865) from Hungary is doubtful. Analyses of seven pink specimens from Hungary (now Slovakia) all show a preponderance of Mg with usually less than 1% MnO (but in one case 14.70%); these are really epsomites,

and the colour is largely due to cobalt (CoO to 3.16%). Solubility curves of the system $\text{MnSO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ at 17—19° show that solutions containing up to 25 mol.-% MgSO_4 deposit crystals of $(\text{Mn}, \text{Mg})\text{SO}_4 \cdot 5\text{H}_2\text{O}$, isomorphous with chalcantite, and containing a much smaller proportion of Mg than the solution. Solutions richer in Mg deposit crystals of $(\text{Mg}, \text{Mn})\text{SO}_4 \cdot 7\text{H}_2\text{O}$, isomorphous with epsomite, and containing a much higher proportion of Mg than the solution. L. J. SPENCER.

Detection of pyro-electricity. A. J. P. MARTIN (Min. Mag., 1931, 22, 519—523).—The crystal, suspended by a glass fibre, is cooled by immersion in liquid air, and if it develops a pyro-electric charge it is attracted to a metal plate. Dioptase, nepheline, thomsonite, etc. become pyro-electric. This is not in agreement with the degree of symmetry usually ascribed to dioptase. L. J. SPENCER.

Clouded feldspars and thermal metamorphism. A. G. MACGREGOR (Min. Mag., 1931, 22, 524—538).—A special type of cloudiness seen in micro-sections of plagioclase is due to the presence of minute inclusions, which have developed as a result of contact thermal metamorphism acting after the consolidation of the igneous rock. Metamorphosed lavas in Scotland and some other rocks showing this effect are described. L. J. SPENCER.

Apatite from China. G. CAROBBI (Atti III Cong. Naz. Chim., 1929, 338—340; Chem. Zentr., 1931, i, 2186).—The apatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot [\text{CaO}, \text{Ca}(\text{OH})_2, \text{CaCl}_2, \text{CaF}_2]$, contains small quantities of La, Sa, Eu, Er, Y, and possibly of Dy, Nd, and Pr; Ba, Sr, Pb, and As are present. A. A. ELDRIDGE.

Vesuvian lithidionite. G. CAROBBI (Rend. Accad. Sci. fis. mat. Napoli, 1930, 36, 21—31; Chem. Zentr., 1931, i, 2186—2187).—The blue lithidionite is identical with neocyanite. The formula is $\text{RO} \cdot 3\text{SiO}_2$ ($\text{RO} = \text{CuO}, \text{CaO}, \text{MgO}, \text{PbO}, \frac{1}{3}\text{Fe}_2\text{O}_3, \text{K}_2\text{O}, \text{Na}_2\text{O}$). Similar glasses can be obtained artificially. A. A. ELDRIDGE.

Japanese acid clay. VI. X-Ray studies. K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1931, 34, 244—247B).—X-Ray diffraction patterns of Japanese acid clay are similar to those of English fuller's earth and German activated clay and samples from different localities give similar results. No trace of quartz, feldspar, mica, etc. can be detected in the clay by X-ray examination, but a kaolinite clay from Formosa which is formed by the decomp. of liparite gives identical patterns. Clay which is extracted with dil. NaOH loses SiO_2 but retains its diffraction patterns. It is therefore concluded that the clay is a mixture of a microcryst. Al silicate and amorphous SiO_2 . C. IRWIN.

Thermal decomposition of synthetic hydrargillite (=gibbsite). H. ACHENBACH (Chem. Erde, 1931, 6, 307—356).—Artificially prepared gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), with α and β 1.577, γ 1.595, commences to lose H_2O at about 170°, and at about 200° (varying slightly with the v. p. and the time) it passes into the orthorhombic "boehmite" ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), with n 1.624. Most of the H_2O is lost at 350° (but a small amount remains up to 1000°) and

the product is then γ - Al_2O_3 , with n 1.693. At 1100° this changes into corundum. X-Ray data are given for each of these products.

L. J. SPENCER.

Chamosite from Schmiedefeld, Thuringia. H. JUNG (Chem. Erde, 1931, 6, 275—306).—The oolitic chamosite ore was cleaned in Clerici's solution from admixed chalybite and magnetite, and gave SiO_2 26.65, TiO_2 trace, Al_2O_3 16.14, Fe_2O_3 6.69, FeO 34.43, MgO 4.47, $\text{H}_2\text{O} +$ 11.42, $\text{H}_2\text{O} -$ 0.08 = 99.88; formula, $5\text{Al}_2\text{O}_3 \cdot 15(\text{Fe}, \text{Mg})\text{O} \cdot 11\text{SiO}_2 \cdot 16\text{H}_2\text{O}$. d 3.180—3.205, n 1.63, birefringence 0.005. Most of the H_2O is lost at about 400° . These characters, as well as the X-ray patterns, show that chamosite is distinct from, although closely related to, thuringite (A., 1930, 733).

L. J. SPENCER.

"Crystallised sandstone." F. STÖBER (Chem. Erde, 1931, 6, 357—367).—Crystals of calcite from Fontainebleau enclose 57—83% of sand. This is imitated in NaNO_3 by the author's method of growing large single crystals (Z. Krist., 1925, 61, 299). In the Ni bowl containing 400 g. of NaNO_3 a single crystal is produced in 12 hr., but with the addition of 600 g. of fine quartz sand a single crystal of NaNO_3 enclosing sand is produced in 18 min. An elaborate explanation, based on the rapid growth of acicular crystals, is given of this remarkable difference in the rate of growth.

L. J. SPENCER.

Volcanic ash from Guatemala. E. DEGER (Chem. Erde, 1931, 6, 376—380).—Eight chemical analyses are given of the ash from the 1929 eruption of the Santa Maria volcano. In the ash are nodules of salt crusts containing NaCl 95.50, CaSO_4 3.01, MgSO_4 0.90, SiO_2 0.30%.

L. J. SPENCER.

Origin of salt deposits. H. ERLÉNMEYER (Chem. Erde, 1931, 6, 390—401).—Based on his observations on the "creeping of crystals" (A., 1929, 503), the author's suggestion is that certain types of salt deposits, e.g., NaNO_3 and Na_2CO_3 , are due to surface efflorescence by capillarity in arid regions.

L. J. SPENCER.

Relation between the chemical composition and the optical properties in the chlorite group.

G. L. DSCHANG (Chem. Erde, 1931, 6, 416—439).—Eight new analyses with optical and density data are given of chlorites of various types. These and earlier analyses are plotted against the optical data in the following mixed series: I, serpentine ($\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$)—amesite ($\text{H}_4\text{Mg}_2\text{Al}_2\text{SiO}_9$); serpentine+amesite-ferroamesite ($\text{H}_4\text{Fe}^{\text{II}}\text{Al}_2\text{SiO}_9$); III, amesite-kämmererite ($\text{H}_4\text{Mg}_2\text{Cr}_2\text{SiO}_9$); ferroamesite-cronstedtite ($\text{H}_4\text{Fe}^{\text{II}}_2\text{Fe}^{\text{III}}\text{SiO}_9$).

L. J. SPENCER.

Structure of analcite. W. HARTWIG (Z. Krist., 1931, 78, 173—207).—Analcite from the Lipari Is., d 2.267, analysis: SiO_2 53.79, TiO_2 0.03, Al_2O_3 23.31, Fe_2O_3 0.53, CaO 0.77, MgO 0.24, K_2O 0.57, Na_2O 13.14, H_2O (below 115°) 0.16, (above 115°) 8.11, has a body-centred cubic lattice, a 13.684 ± 0.020 Å., and contains 16 mols. of $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$. Its symmetry, although approximating to, must be regarded as a non-cubic sub-group of O_h^h (cf. A., 1930, 1099; this vol., 550).

C. A. SILBERRAD.

Red-earth of Mediterranean countries. E. BLANCK and A. MUSIEROWICZ (Chem. Erde, 1931, 6, 381—389).—Further chemical analyses are given of red-earth (terra rossa) (A., 1930, 732, 1398). The samples now described are from the Yugoslavian-Dalmatian coast.

L. J. SPENCER.

Limestone bitumen and molasse at Pyrimont (Ain). J. J. PITTARD (Arch. Sci. Phys. Nat., 1931, [v], 13, 143—152).—Their genesis is discussed.

C. W. GIBBY.

Natural Italian gases. II. Higher hydrocarbons. M. G. LEVI, C. PADOVANI, and M. BUSI (Annali Chim. Appl., 1931, 21, 245—258).—Analyses of natural gases from various parts of Italy and, in some cases, determinations of the content of condensable hydrocarbons (gasoline) have been made. The methods of analysis are described.

T. H. POPE.

Base exchange and the formation of coal. II. W. H. A. PENSELER (N.Z. J. Sci. Tech., 1931, 12, 363—375; cf. this vol., 931).—The work of Taylor is further criticised and his theory of coal formation is regarded as untenable.

A. G. POLLARD.

Organic Chemistry.

Direct oxidation of hydrocarbons by air. P. MONDAIN-MONVAL and B. QUANQUIN.—See this vol., 1015.

Peroxidation of hydrocarbons during combustion in air. E. MARDLES (Nature, 1931, 128, 116—117).—The presence of MeOH in the oxidation products of CH_4 can be explained satisfactorily by the Engler-Bach peroxide theory (cf. this vol., 598).

L. S. THEOBALD.

Slow combustion of methane and ethane. W. A. BONE (Nature, 1931, 128, 188—189).—No evidence of initial "peroxidation" has yet been discovered and initial "hydroxylation" is the best interpretation of known facts.

L. S. THEOBALD.

Transformation of methane. I. Pyrogenic decomposition. C. PADOVANI and F. MAGALDI

(Atti III Cong. Naz. Chim. pura appl., 1929, 730—739; Chem. Zentr., 1931, i, 1742).—Rise of temp. from 1000° to 1250° increases the rate of decomp. of CH_4 in a SiO_2 tube and (at first) the quantity of unsaturated hydrocarbons produced; the latter value thereafter falls. The decomp. is accelerated by filling the tube with fragments of porous porcelain. When the CH_4 is mixed with H_2 the amount of unsaturated hydrocarbons formed at lower rates is greater than with CH_4 alone, but at higher rates the reverse holds.

A. A. ELDRIDGE.

Synthesis of β -dimethyldodecane and β - γ -dimethyleicosane. S. LANDA and A. KEJVAN (Coll. Czech. Chem. Comm., 1931, 3, 367—376).—Et sebacate and MgMeBr give β - γ -dimethyldodecane- β -diol, converted by distillation into mainly β - γ -

methyl- $\Delta^{\alpha 1}$ -dodecadiene (I), b. p. 239—241°/760 mm. (*tetrabromide*) (oxidation products, COMe₂ and sebacic acid), which is reduced catalytically (Pt-black) in Et₂O to β -*dimethyldodecane* (II), b. p. 117°/13 mm., m. p. -8.5°. Similarly, Et hexadecane- α -dicarbonylate and MgMeBr afford β -*dimethyleicosane- β - τ -diol*, dehydrated to a mixture of β -*dimethyleicosadienes* (III), b. p. 239.5—240.5°/21 mm., m. p. 0°, which is reduced to β -*dimethyleicosane* (IV), m. p. 41°.

The viscosities of (I) and (II) at 0—99°, of (III) at 10—99°, and of (IV) at 41—90° have been determined.

H. BURTON.

Knowledge of the double linking. E. BERGMANN (J. pr. Chem., 1931, [ii], 131, 68—70).—Polemical. A reply to Petrenko-Kritschenko (A., 1930, 1017).

H. A. PIGGOTT.

Highly-polymerised compounds. LI. Polymerisation and autoxidation. H. STAUDINGER and L. LAUTENSCHLAGER (Annalen, 1931, 488, 1—8).—The velocity of autoxidation is measured by heating the substance (trimethylethylene, styrene, isoprene, dimethylbutadiene, cyclopentadiene, tetrahydrobenzene, myrcene, limonene, terpinene, pinene, and menthene) with O₂ in sealed flasks at 80° and determination of the O₂ absorbed. The rate of polymerisation is determined by heating 10 g. of the material in a distillation flask in presence of CO₂ or O₂ for one or more days and removal of all matter volatile below 80°/vac. In all cases polymerisation occurs more rapidly in O₂ than in CO₂, but the differences in the rates are small in the case of terpenes. Since all the substances are autoxidisable, it must be admitted that the process of autoxidation accelerates that of polymerisation. Addition of benzoyl peroxide or of the peroxides of *as*-diphenylethylene, cyclohexene, or phellandrene causes polymerisation to occur more rapidly than in CO₂, but not so quickly as in O₂. It is therefore concluded that the isolated peroxides are not the actual catalysts and that primary peroxides with more pronounced accelerating action are formed during autoxidation. A unimol. peroxide has not been isolated. In presence of a little O₂, styrene gives the polymeride accompanied by small amounts of polymeric peroxide. With larger amounts of O₂ a homogeneous polymeric peroxide is never formed, since the action is always accompanied by polymerisation. Inseparable mixtures of polystyrene and its peroxide are invariably produced which yield styrene and PhCHO when heated. With *as*-diphenylethylene polymerisation is so little pronounced that the polymeric peroxide can be isolated.

H. WREN.

Direct reaction between oxygen and ethylene. S. LENHER (J. Amer. Chem. Soc., 1931, 53, 2420—2421).—At 300—525° the primary reactions between C₂H₄ and O₂ are the formation of ethylene oxide and CH₂O; dihydroxymethyl peroxide is isolated. Above 500° the polymerisation of C₂H₄ becomes marked. The formation of H₂O₂ has been observed.

H. A. PIGGOTT.

Preparation of unsymmetrical dialkylethylene derivatives. C. C. SCHMITT and C. E. BOORD (J. Amer. Chem. Soc., 1931, 53, 2427—2428).—The preparation of β -*methyl- Δ^{α} -pentene*, b. p. 61.5—62°/

760 mm., γ -*methylene-pentane*, b. p. 66.2—66.7°/760 mm., and β -*dimethyl- Δ^{α} -butene*, b. p. 56.0—56.5°/760 mm., by methods previously described (cf. this vol., 709) is reported.

H. A. PIGGOTT.

Dimerisation of isoprene. T. WAGNER-JAUREGG (Annalen, 1931, 488, 176—186).—The hydrocarbon obtained together with caoutchouc and dipentene by heating isoprene by itself or with AcOH and regarded by Harries as β -*dimethyl- $\Delta^{\alpha\gamma}$ -octatriene* contains only two double linkings and when hydrogenated in presence of PtO₂ affords *m*-menthane. A *m*-menthadiene obtained by auto-polymerisation of isoprene and described by Aschan as diprene is very similar to Harries' hydrocarbon in physical properties and, like it, affords carvestrene dihydrochloride when acted on by HCl in AcOH. The identity of the hydrocarbons is regarded as established. β -Myrcene, obtained by Ostromisslenski by heating isoprene at 80—90° for several days, is identical with diprene and is the sole dimeride of isoprene formed under these conditions. It appears to be a mixture of very similar hydrocarbons. The formation of aliphatic polymerides of low mol. wt. from isoprene is effected in AcOH containing H₂SO₄. Hydrocarbons and acetates are produced from which geranyl acetate has been isolated; the geraniol, obtained by hydrolysis, is identified as the diphenylurethane.

H. WREN.

Explosion limit of crude acetylene mixed with oxygen and nitrogen. S. TAGI and K. TAKEOTA.—See this vol., 1015.

Explosibility of acetylene-steam mixtures. REINARSKI and others.—See this vol., 1015.

Addition of hydrogen bromide to vinyl bromide. G. N. BURKHARDT and W. COCKER (Rec. trav. chim., 1931, 50, 837—847).—Determinations of the proportions of $\alpha\alpha$ - (I) and $\alpha\beta$ -dibromoethanes (II) in mixtures formed during the addition of HBr to vinyl bromide are effected by treatment with cold MeOH-KOH; (II) is readily hydrolysed, whilst (I) is stable. (I) is always the major isomeride when aq. HBr is used, but the amount decreases with increase in concentration of the aq. HBr and temp. With conc. solutions of HBr in AcOH at 17° (II) is the main product; at 100°, formation of (I) is favoured. Theoretical considerations are discussed and some of Wibaut's assumptions (this vol., 598) criticised.

Large amounts of C₂H₂ are produced from (I) or (II) and PhSNa in EtOH. $\alpha\beta$ -*Dipiperidinoethane* has b. p. 130—132°/15 mm., 140—142°/20 mm.

H. BURTON.

Preparation of cyclopropyl cyanide and trimethylene chlorobromide. J. B. CLOKE, R. J. ANDERSON, J. LACHMANN, and G. E. SMITH (J. Amer. Chem. Soc., 1931, 53, 2791—2796).—Trimethylene chlorobromide, prepared in 94% yield from trimethylene chlorohydrin and PBr₃, is converted into γ -chlorobutyronitrile, which with NaNH₂ in liquid NH₃ and Et₂O gives 75—90% yields of cyclopropyl cyanide.

H. BURTON.

Dimethylisobutylcarbinol. Preparation and dehydration. H. DE GRAEF (Bull. Soc. chim. Belg., 1931, 40, 315—329; cf. A., 1924, i, 1025).—Action of MgBu ^{β} Br (from Bu ^{β} Br purified with 2% NaOH) on

COMe₂ gives dimethylisobutylcarbinol (yield 35—48%), diisobutyl, mesityl oxide, phorone, isophorone, diacetone alcohol, βζ-dimethyl-Δ^ε-hepten-β-ol-δ-one (A., 1928, 396), βδζ-trimethylheptane-βδ-diol, b. p. 116—118°/12 mm., 231—234°/760 mm. (also obtained from MgBu^δBr and diacetone alcohol), and a *decadiene*, b. p. 152—154°/760 mm. (also obtained by dehydration of the above trimethylheptanediol). Et isovalerate (from isovaleric acid obtained by oxidation of synthetic isoamyl alcohol) and MgMeBr give dimethylisobutylcarbinol (yield 86%), which cannot be freed from Et isovalerate. Reduction of mesityl oxide and purification through the hydrogen sulphite compound gives dimethylisobutylcarbinol, b. p. 42—44°/12 mm., 133.1°/760 mm. (yield 90—94%) [bromide, b. p. 83—84°/100 mm. (cf. A., 1914, i, 369)], and βθ-trimethylnonan-δ-ol-ζ-one (A., 1928, 396), dehydrated to βθ-trimethyl-Δ^δ-nonen-ζ-one. Dehydration of dimethylisobutylcarbinol by various methods gives βδ-dimethyl-Δ^γ-pentene, b. p. 82.6°, reduced to βδ-dimethylpentane, b. p. 80.6°, and oxidised to COMe₂, isobutyric acid, and βδ-dimethylpentan-β-ol-γ-one, which readily isomerises to βγ-dimethylpentan-γ-ol-δ-one (cf. A., 1928, 866). A. A. LEVI.

Cetyl alcohol and its derivatives. (MLLE.) Y. DELCOURT (Bull. Soc. chim. Belg., 1931, 40, 284—294).—The prep., purification, and physical consts. of cetyl alcohol, m. p. 49.10°, cetyl iodide, m. p. 21.15°, and dotriacontane, m. p. 70°, are recorded.

A. A. LEVI.

Highly-polymerised compounds. LII. Polyvinyl acetates and polyvinyl alcohols. H. STAUDINGER and A. SCHWALBACH (Annalen, 1931, 488, 8—56).—Irradiation of vinyl acetate in CHCl₃ yields compounds of the type

Me·CH(OR)·[CH₂·CH(OR)]_x·CH₂·CHCl₂, the mol. wt. of which in freezing C₆H₆ corresponds with that calc. from the Cl content. The products can be separated into more and less sparingly sol. fractions in which all the mols. have the same terminal groups. Treatment of a product (about 30 units) with P and HI gives a paraffin hydrocarbon containing P, which is removed by distillation in a high vac. over soda-lime, giving a normal paraffin, mol. wt. about 930. Polymerisation of vinyl acetate occurs by union of many individual mols. to a long chain by normal valencies. The viscosity of polyvinyl acetate (*n*>50) is similar to that of ordinary org. compounds. Polymerisation of vinyl acetate at low temp. leads to more complex compounds the solutions of which do not obey the Hagen-Poiseuille law. Rise of temp. decreases the viscosity of such solutions independently of the concentration; the effect is reversed by cooling. The dissolved particles must therefore undergo a uniform reversible transformation, thus establishing the presence of mols., not micelles. Solvent mols. become attached to reactive positions, e.g., CO groups, of the polyvinyl acetate and the co-ordinative linkings are partly ruptured by rise of temp. The dissolved mols. hence experience a change in diameter which is expressed in alteration of viscosity. The increase of η_{sp.} with concentration is ascribed to the mutual interference of the long mols.; with increase in concentration the sphere of activity rapidly becomes

greater than the available vol. of the solution. It is concluded that the mol. wt. of the products can be calc. from the viscosity provided that the relationship between the η_{sp.}/*c* values and mol. wt. has been determined at a definite temp. and all observations are made at that temp. Solutions of polyvinyl alcohols behave similarly to those of polyvinyl acetates. The behaviour of polysaccharides and their acetates is analogous.

Polymerisation of heated vinyl acetate is accelerated by O₂, in the absence of which the process does not occur below 180°. In quartz vessels under the influence of light, polymerisation takes place more rapidly in N₂ or CO₂ than in O₂ or air. The degree of polymerisation of vinyl acetate can be controlled by the experimental conditions within the degree *n*=20—900, the most complex products being obtained by cold photopolymerisation in N₂. The impossibility of preparing the longest chains in O₂ is probably due to attachment of the terminal valencies of the element, whereby further growth of the mol. is inhibited. Polymerisation in solution takes place more slowly, but leads to products of lower mol. wt. than those obtained from the undiluted material under similar conditions. The polyvinyl acetates are readily hydrolysed by KOH or HCl in EtOH to polyvinyl alcohols, complex or less complex products being derived from the acetates of differing mean mol. wt. It has not been found possible to convert a given acetate into the alcohol and thence into the acetate with the original properties. The simplest alcohols are readily sol. in H₂O, formamide, ethylene glycol, and glycerol, whereas the most complex dissolve only in the heated solvent, possibly with slight degradation. The relation between mol. wt. and viscosity of the alcohols is based on the assumption that an acetate of known mean mol. wt. can be hydrolysed to the alcohol without alteration of the length of the C chain. The non-cryst. nature of the polyvinyl alcohols and acetates is ascribed to the presence of asymmetric C atoms which render possible the occurrence of diastereoisomerides and hence an unsymmetrical structure of the thread mols. H. WREN.

Derivatives of aliphatic glycols. III. G. M. BENNETT and A. N. MOSSES (J.C.S., 1931, 1697—1701).—Polymethylene chlorohydrins, prepared from the glycols and conc. HCl at 95° in presence of petroleum (b. p. 90—120°) under conditions suitable for continuous removal are converted by PhSNa into the hydroxy-sulphides OH·[CH₂]_n·SPh, and thence by SOCl₂ in NPhEt₂ and CCl₄ into the chloro-sulphides. The following are described: η-chloroheptyl, b. p. 150°/20 mm., m. p. 10—11° (phenylurethane, m. p. 76°), θ-chlorooctyl, b. p. 125—140°/18 mm. (phenylurethane, m. p. 77°), ι-chlorononyl, b. p. 140—145°/20 mm., m. p. 28° (phenylurethane, m. p. 67°), and κ-chlorodecyl, m. p. 10—11° (phenylurethane, m. p. 72°), alcohols; phenyl η-hydroxyheptyl, m. p. 49°, θ-hydroxyoctyl, m. p. 55°, ι-hydroxynonyl, m. p. 60°, and κ-hydroxydecyl, m. p. 66.5°, sulphides; phenyl η-chloroheptyl, θ-chlorooctyl, m. p. 16°, ι-chlorononyl, m. p. 5°, and κ-chlorodecyl, m. p. 27.5°, sulphides. Hexamethylene glycol and AcCl at 100° give ζ-chlorohexyl acetate, b. p. 113—116°/17 mm., convertible into phenyl ζ-hydroxyhexyl,

m. p. 43°, and ζ -chlorohexyl, m. p. 7—8°, sulphides. Improvements in the prep. of tetra- to deca-methylene glycols are recorded. H. BURTON.

Oxidisability of glycerol. J. KRÉPELKA and O. TOMIČEK (Časopis Českoslov. Lék., 1930, 10, 266—267; Chem. Zentr., 1931, i, 2034).—Glycerol is oxidised to CH_2O by NaBO_3 at 20° in a few days.

A. A. ELDRIDGE.

Styracitol. II. Y. ASAHINA and H. TAKIMOTO (Ber., 1931, 64, [B], 1803—1805).—Styracitol [1:5-anhydrosorbitol] (isolation from *Styrax Obassia* described) is converted by boiling PhCHO into *dibenzylidenestyracitol*, m. p. 163—165°, $[\alpha]_D^{25} - 148.73^\circ$ in CHCl_3 , and m. p. 192—193°, $[\alpha]_D^{25} - 80.47^\circ$ in CHCl_3 , and by boiling COMe_2 containing 1% of HCl into *diisopropylidenestyracitol*, m. p. 96—97°, $[\alpha]_D^{17} - 115.24^\circ$ in EtOH . Successive treatment of styracitol with KOH and MeSO_4 and Ag_2O and MeI lead to *styracitol tetramethyl ether*, b. p. 143—144°/16 mm., $d_4^{18} 1.1092$, $[\alpha]_D^{18} - 35.63^\circ$, oxidised by HNO_3 ($d 1.42$) to oxalic and *d*-dimethoxysuccinic acids. H. WREN.

Condensations of polyhydric alcohols, sugars, and hydroxy-acids with aldehydes and ketones by means of phosphoric oxide. J. W. PETTE (Ber., 1931, 64, [B], 1567—1568).—Tribenzylidenemannitol, m. p. 224°, is most readily prepared by addition of P_2O_5 to a well-stirred mixture of PhCHO and mannitol. H. WREN.

Preparation and properties of divinyl ether. W. L. RUGH and R. T. MAJOR (J. Amer. Chem. Soc., 1931, 53, 2662—2671).—Divinyl ether (I), b. p. 28.3° \pm 0.2°/760 mm., is best prepared (yield about 25%) from $\beta\beta'$ -dichlorodiethyl ether and KOH at 200—240° in a slow stream of NH_3 ; by-products are H_2 , C_2H_2 , MeCHO , ethylene oxide, dioxan, and β -chloroethyl vinyl ether. Catalytic reduction (Adams) of (I) in BuOH gives 15% of Et_2O . (I) is only partly polymerised by benzoyl peroxide; polymerisation is inhibited by NH_3 . Traces of (I) were obtained from $\beta\beta'$ -dichloro- and -di-iodo-diethyl ethers and NaNH_2 , but (I) could not be prepared from $\beta\beta'$ -dihydroxydiethyl ether and Al_2O_3 or P_2O_5 . The quaternary *di-iodide* from $\beta\beta'$ -di-iododiethyl ether and NPhMe_2 has m. p. 220—230° (decomp.). H. BURTON.

Ether-like compounds. V. Synthesis of monoethers of higher diprimary glycols. M. H. PALOMAA and R. JANSSON (Ber., 1931, 64, [B], 1606—1610; cf. this vol., 710).— δ -Methoxy-*n*-butyl alcohol, b. p. 63—64°/7 mm., $d_4^{20} 0.9286$, is obtained in 36.5% yield by the action of $\text{Me } \gamma$ -chloropropyl ether on Mg , trioxymethylene, and a little ZnCl_2 in Et_2O ; with PCl_3 and pyridine it gives δ -methoxy-*n*-butyl chloride, b. p. 142.5—142.8°/751 mm., $d_4^{20} 0.9875$. $\text{Et } \gamma$ -chloropropyl ether and gaseous CH_2O similarly give δ -ethoxy-*n*-butyl alcohol, b. p. 72 $\frac{5}{8}$ /8 mm., $d_4^{20} 0.9079$, whence δ -ethoxy-*n*-butyl chloride, b. p. 157—157.5°/760 mm., $d_4^{20} 0.9603$. ϵ -Methoxy-*n*-amyl alcohol, b. p. 83—84°/9 mm., $d_4^{20} 0.9215$, ϵ -methoxy-*n*-amyl chloride, b. p. 41°/5 mm., $d_4^{20} 0.9714$, and ϵ -ethoxy-*n*-amyl alcohol, b. p. 89—91°/9 mm., $d_4^{20} 0.9067$, are described. H. WREN.

Soya-bean lecithins. Y. YOKOYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, 7, 226—229; cf. this vol., 401, 600).—Lecithins of the β -series were

brominated and fractionated by successive solvents: *palmito-oleo-*, *dioleo-*, *oleolinoleo-*, *palmitolinoleo-* (bromide, m. p. 85°), and *palmitolinoleo-* (bromide, m. p. 105°)- β -lecithins were isolated in the form of their bromo-derivatives. E. LEWKOWITSCH.

Copper mercaptides and their reaction with carbon disulphide. W. E. DUNCAN, E. OTT, and E. E. REID (Ind. Eng. Chem., 1931, 23, 381—383).— $\text{Cu}^I \text{ Et, Bu, hexyl, nonyl, Pr}^\beta$, isobutyl, isoamyl, isohexyl, and isononyl sulphides have been prepared from the mercaptans with $\text{Cu}(\text{OAc})_2$. Cu^{II} is reduced to Cu^I and an equiv. amount of the disulphide is obtained. On treatment with S , CuS and the alkyl disulphide are obtained. Basic mercaptides are not obtained when the compounds are treated with NaOH and no hydrolysis was observed. With CS_2 thiocarbonates more sol. in org. solvents than the original mercaptides are formed. Additive products of Cu mercaptide, alkyl disulphide, and CS_2 have also been obtained. Double compounds of Cu^I and Na thiocarbonates can also be obtained. T. A. SMITH.

Action of phenyl methionate [methanedisulphonate] on hydrazine hydrate. H. J. BACKER and P. L. STEDEHOUDER (Rec. trav. chim., 1931, 50, 931—935).— Ph methionate and aq. N_2H_4 at 130° give PhOH , Ph methanesulphonate (I), the N_2H_4 salt, m. p. 148—149° (decomp.) [corresponding *Na* and *Ba* (+ H_2O) salts], of *Ph H* methionate (+ H_2O), and N_2H_4 methionate; at 155°, NH_4 *Ph* methionate (II), m. p. 217°, NH_4 methionamate, m. p. 230° (corresponding *Ba* salt), and NH_4 methionate (III), not melted at 300°, are produced. Ph methionate and N_2H_4 in EtOH give (I), (II), and (III). *Ph Me* methionate has m. p. 63°.

Ph ethane- $\alpha\alpha$ -disulphonate and N_2H_4 at 130° afford the N_2H_4 salt [corresponding *Ba* (+5 H_2O)], *Tl*, m. p. 130.5°, and *brucine*, decomp. about 270°, salts of Ph H ethane- $\alpha\alpha$ -disulphonate. H. BURTON.

Action of β -bromoethanesulphonyl chloride on amines. E. RIESZ (Ber., 1931, 64, [B], 1895—1896).—Aniline is converted by β -bromoethanesulphonyl chloride in Et_2O into a substance $\text{C}_8\text{H}_9\text{O}_2\text{NS}$, m. p. 53°, which dissolves readily in alkali hydroxide and decolorises alkaline KMnO_4 ; it has the constitution $\text{NPh} \left\langle \begin{array}{l} \text{SO}_2 \\ \text{CH}_2 \end{array} \right\rangle \text{CH}_2$ or $\text{NPh} \cdot \text{SO}_2 \cdot \text{CH} : \text{CH}_2$.

H. WREN.

Energy transformations at surfaces. I. Reduction of carboxylic acids by induced, intramolecular transformation of siloxen-acid derivatives. H. KAUSKY and A. HIRSCH (Ber., 1931, 64, [B], 1610—1622).—Reaction between siloxen and gaseous HCO_2H follows the course $:\text{SiH} + \text{HCO}_2\text{H} = :\text{Si} \cdot \text{O} \cdot \text{CHO} + \text{H}_2$; it is greatly facilitated by slight rise of temp. or irradiation. The product is hydrolysed to intensely yellow hydroxysiloxens, HCO_2H , and traces of CH_2O . SO_2 acts as acceptor for the liberated H_2 and the product when hydrolysed yields small amounts of $\text{H}_2\text{S}_2\text{O}_4$. Reaction between siloxen and SO_2 in indifferent media containing a little H_2O follows the course $:\text{SiH} + \text{H}_2\text{SO}_3 = :\text{Si} \cdot \text{SO}_3\text{H} + \text{H}_2$; $\text{H}_2 + 2\text{SO}_2 = \text{H}_2\text{S}_2\text{O}_4$. Hydroxysiloxens, readily obtained by hydrolysis of the bromosiloxens, are converted by acids into the siloxen-acids; acid chlorides cause

replacement of almost all OH groups. Bromo- and bromoacetato-siloxens are transformed by NH_3 into aminosiloxens, gaseous NH_3 giving intermediate products of the type $\text{Si}_3\text{O}_3\text{H}_5 \cdot \text{NH}_3 \cdot \text{Br}$; in liquid NH_3 the compound passes into aminosiloxen and NH_4Br , which is readily removed by repeated washing. All aminosiloxens react readily with acids according to the scheme $:\text{Si} \cdot \text{NH}_2 + 2\text{HX} = :\text{SiX} + \text{NH}_4\text{X}$. Tribromo-siloxen in EtOH is converted by gaseous NH_3 into triaminosiloxen, converted by CO_2 into the carbamido-compound stable in the dark, but slowly yielding HCN if irradiated. Cautious treatment of the product with O_2 causes reduction of the CO_2 with formation of HCN. The O atom of the CO_2 is absorbed by the Si-Si linking. H_2O liberated in the production of HCN hydrolyses the unchanged Si-O-CO-NH₂ and the newly-formed Si-CN groups, so that NH_3 is simultaneously produced; extraneous H_2O operates markedly in this direction. *Triformiatosiloxen* under similar conditions affords CH_2O . Quant. experiments with monoformiatosiloxen indicate the production of CH_2O in about 5% yield. AcOH and BzOH are similarly reduced to the corresponding aldehydes, the change being particularly marked with the highly-substituted Bz compounds.

H. WREN.

Catalysis in organic chemistry. IV. Decompositions of esters and acids by anhydrous zinc chloride. H. W. UNDERWOOD, jun., and O. L. BARIL (J. Amer. Chem. Soc., 1931, 53, 2200—2202).—The decomps. described below were observed when the substance (1 mol.) was heated with anhyd. ZnCl_2 (cf. A., 1930, 321). $\text{Cl} \cdot \text{CO}_2\text{Et}$ gives C_2H_4 , EtCl, and HCl (at room temp.); $\text{Cl} \cdot \text{CO}_2\text{Pr}^a$ behaves similarly, but less C_3H_6 is formed; $\text{Bu}^a \cdot \text{CO}_2$ gives BuOH (95%) and a little Δ^a -butene; $\text{Pr}^b \cdot \text{OBz}$ gives C_3H_6 , C_6H_6 , BzOH, and Pr^bCl ; Bu^a phthalate gives Δ^a -butene, phthalic acid and anhydride, BzOH, and Bu^bOH ; *iso*amyl salicylate gives γ -methyl- Δ^a -butene and its dimeride, and PhOH; Me and Et anthranilates give *o*-toluidine (75%) and *o*-aminoethylbenzene (66%), respectively; Et methylmalonate gives C_2H_4 and Et propionate; and $\text{CH}_2\text{Ph} \cdot \text{OAc}$ gives AcOH and tar; in all cases except the last CO_2 is generated. Et *m*-nitrobenzoate, Et_2CO_3 , HCO_2H , AcOH, and propionic and *n*-butyric acids were recovered unchanged. BzOH, salicylic and cinnamic acids are decomposed to the corresponding hydrocarbon and CO_2 .

H. A. PIGGOTT.

Formic acid from hydrolysis of cellulose oxalate. J. P. MONTGOMERY (J. Amer. Chem. Soc., 1931, 53, 2700—2701).—Details are given for the prep. of formic acid from cryst. oxalic acid, absorbent cotton, and conc. HCl.

H. BURTON.

Separation of glycerides. XIX. B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, 7, 230—233; cf. A., 1929, 1271; this vol., 602).—Previous results are summarised and discussed. Fatty acids occur in almost all possible combinations as glycerides; these, however, appear to be selectively distributed in the various organisms, few glycerides occurring in more than 1 or 2 different oils.

E. LEWKOWITSCH.

Thermal transformation of olefines. Cracking of oleic acid under high pressure. A. D. PETROV (Ber., 1931, 64, [B], 1827—1834).—The

gaseous products obtained when oleic acid is heated with H_2O and Al_2O_3 at 380—400° for 3—4 hr. contain H_2 48%, CO_2 20%, $\text{C}_n\text{H}_{2n+2}$ 18%, and C_nH_{2n} 0.0%. The aromatic products (PhMe, $\text{C}_6\text{H}_4\text{Me}_2$) in the liquid fractions cannot therefore be formed in accordance with Davidson's scheme and dehydrogenation of naphthenes of the 6-membered type cannot occur under these conditions as shown by experiments with dimethylcyclohexane. They arise most probably from cyclohexenes derived from diethylenic hydrocarbons formed by pyrolysis of liquid olefines of high mol. wt. The presence of naphthenes of the 3- and 4-membered type in the liquid products is highly probable. The paraffins of the fractions of lower b. p. have preponderatingly the *iso*-structure.

H. WREN.

Migration of the double linking of oleic acid during hydrogenation. K. H. BAUER and M. KRALLIS (Chem. Umschau, 1931, 38, 201—203).—Oleic acid heated in contact with Al_2O_3 at 250° in a stream of N_2 yielded a semi-solid product containing 9.2% of (Twitchell) "solid" acids; Δ^a -oleic acid m. p. 41—42°, was identified. Thus the migration of the double linking observed during hydrogenation at 180—220° by Hilditch and Vidyarthi (A., 1929, 423) and by Steger and Scheffers (this vol., 711) is a result of the high temp., and the non-formation of it in the low-temp. experiments of Bauer and Ermann (A., 1930, 1271) is explained. When a reduced Ni- Al_2O_3 catalyst was used, some stearic acid was produced, attributed to the presence of adsorbed H_2 not displaceable by N_2 .

E. LEWKOWITSCH.

Couepic acid, a new isomeride of elæostearic acid. J. VAN LOON and A. STEGER (Rec. trav. chim., 1931, 50, 936—942).—Details are given for the isolation of *couepic acid*, $\text{C}_{18}\text{H}_{30}\text{O}_2$, m. p. 74—75°, from the total fatty acids of the oil from *Couepia grandiflora*, Benth. The acid is reduced to stearic acid and oxidised by O_3 to valeric and azelaic acids. Et *couepate* is oxidised to valeric acid and Et H azelate, indicating that the acid is a geometrical isomeride of α - and β -elæostearic acids.

H. BURTON.

[Composition of linseed oil and the terminology α - and β -linoleic and α - and β -linolenic acids.] H. P. KAUFMANN and M. KELLER (Chem. Umschau, 1931, 38, 203—205).—Van der Veen's criticism (this vol., 822) of the thiocyanometric determination of linolenic acid is refuted. The abnormally high thiocyanogen val. for linseed oil found by van Loon (Diss., Delft, 1928) might be due to the excessively long reaction period (4 days) used, which may lead to untrustworthy figures.

E. LEWKOWITSCH.

Kolbe's synthesis with β -isoamyloxypropionic acid. F. FICHTER and A. SHNIDER (Helv. Chim. Acta, 1931, 14, 857—861).—The electrolysis of β -isoamyloxypropionic acid is closely paralleled by the thermal decomp. at 300° of its peroxide to *isovaleraldehyde*, *isoamyl β -isoamyloxypropionate*, b. p. 122—125°/12 mm., $\alpha\delta$ -diisoamyloxybutane (73% of theory), and CO_2 , the main reaction being

$$[\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{O}]_2 \rightarrow$$

$$[\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2]_2 + 2\text{CO}_2$$
 affording a confirmation of the peroxide theory of the Kolbe synthesis. β -isoAmyloxypropionyl chloride, b. p. 82°/12 mm., pre-

pared from the acid and PCl_5 , is converted by H_2O_2 in pyridine into its *peroxide*, which with NH_3 gives the *amide*, m. p. 65° .
H. A. PIGGOTT.

Partition principle applied to structures of enolic sodium derivatives of 1:3-diketones and β -keto-esters. A. MICHAEL and J. ROSS (J. Amer. Chem. Soc., 1931, 53, 2394—2414).—In presence of 1 equiv. of NaOEt Et malonate reacts more rapidly than the acetoacetate both with MeI and with EtBr in EtOH ; with EtBr the abs. velocities are less and the difference is greater, and the acetoacetate reaction then slower instead of faster than that with NaOEt alone. The interaction in EtOH at 0° of equimol. amounts of NaOEt , Et acetoacetate, and Et malonate with MeI results in almost exclusive methylation of the acetoacetate, but with EtBr the malonate alone is ethylated. It is considered that the Na is attached mainly to the acetoacetate, and that during the slow reaction with EtBr transference of the metal to the malonate occurs.

Et γ -ketobutane- $\alpha\beta$ -tricarboxylate, b. p. $147^\circ/5$ mm. (*semicarbazone*, m. p. 76°), is obtained, accompanied by Et ethanetetra-carboxylate, by the action of Et sodioacetoacetate on Et chloromalonate; it is converted by MeI and NaOEt (1 equiv.) into the α -*Me* derivative, b. p. 144 — $152^\circ/2$ mm., hydrolysed by aq. $\text{Ba}(\text{OH})_2$ to α -carboxy- α -methylsuccinic, α -methyl-lævulic, and 1:3-diketo-4:5-dimethylcyclopentane-4:5-dicarboxylic, m. p. 295 — 300° , acids. Bromoacetone and Et sodiomethylmalonate interact in EtOH to give *Et* α -carbethoxy- α -methyl-lævulate, b. p. $133^\circ/5$ mm. (*semicarbazone*, m. p. 102°), hydrolysed by $\text{Ba}(\text{OH})_2$ to the acid (syrup), which on distillation gives α -methyl-lævulic acid. The action of NaOEt , suspended in EtOH - Et_2O , on *Et* γ -ketobutane- $\alpha\beta\beta$ -tricarboxylate gives a mixture of *liquid*, b. p. $149^\circ/2$ mm. (with partial conversion into the solid isomeride) [*disemicarbazone*, m. p. 220° ; *semicarbazide* derivative (pyrazole?), $\text{C}_{11}\text{H}_{14}\text{O}_4\text{N}_2$, m. p. 76°], and *solid*, m. p. 86° , enolates; as the former, but not the latter, gives a coloration with FeCl_3 the respective constitutions of Et 1:4-dihydroxy- $\Delta^{1:3}$ -cyclopentadiene-2:3-dicarboxylate and 1:4-dihydroxy-1:4-endomethylene- Δ^2 -cyclobutene-2:3-dicarboxylate are assigned. It is considered that enolisation should occur most readily at the keto-group of *Et* γ -ketobutane- $\alpha\beta\beta$ -tricarboxylate, and that the direction of methylation with MeI is a consequence of the greater reactivity of Na attached to the malonic residue in this compound.

Me chloroformate and sodiobenzoylacetone interact in cold Et_2O to give a mixture of *solid*, m. p. 57° , and *liquid*, b. p. $164^\circ/2$ mm., *O*-carbomethoxy-derivatives. By treatment with NH_3 , K_2CO_3 , NH_2OH , or NH_2Ph under various conditions either benzoylacetone or a derivative of it with these reagents is formed. The solid ester forms two *semicarbazones*, $\text{CH}_3\text{ON}_3\text{:CPh}\cdot\text{CHAc}\cdot\text{CO}_2\text{Me}$, m. p. 166° , and $\text{CH}_3\text{ON}_3\text{:CPh}\cdot\text{CH}\cdot\text{CMe}\cdot\text{O}\cdot\text{CO}_2\text{Me}$, m. p. 183° , the former of which alone gives a coloration with FeCl_3 . The latter is converted into the former by treatment with acids. The final product in dil. aq. AcOH is *Et* 5-phenyl-3-methylpyrazole-4-carboxylate, m. p. 62° ; an unidentified substance, m. p. 202° , is also formed. The liquid ester does not give definite products with

semicarbazide. Both liquid and solid esters give propiophenone when reduced catalytically, but benzoylacetone under the same conditions gives α -phenylbutane- $\alpha\gamma$ -diol, b. p. 129 — $131^\circ/2$ mm. (*diacetate*, b. p. $140^\circ/2$ mm.). They are therefore regarded as geometrical isomerides of the ester $\text{CHBz}\cdot\text{CMe}\cdot\text{O}\cdot\text{CO}_2\text{Me}$, and benzoylacetone therefore reacts in the enolic form corresponding with this in accordance with the partition principle. CH_2Bz_2 under similar conditions gives an *O*-carbethoxy-derivative, m. p. 90° , and considerable unidentified liquid material.

Benzoylacetone and semicarbazide acetate in EtOH give the *mono*-, m. p. 127 — 128° , and *di-semicarbazone*, m. p. 242° ; the former is converted into 5-phenyl-3-methylpyrazole-1-carboxylamide by AcOH or HCl in warm EtOH .
H. A. PIGGOTT.

Acetoacetic ester condensation. III. Rôle of sodium in the condensation. J. M. SNELL and S. M. McELVAIN (J. Amer. Chem. Soc., 1931, 53, 2310—2316).—Interaction of finely-divided Na with an excess of carefully purified AcOEt produces EtOH and Et acetoacetate in the ratio 1:7:1 when the EtOH is removed during the reaction, and 2:1 where it is not; the yield of H_2 is only about 0.08—0.09 mol. per atom Na . Allowing for the EtOH produced by reduction, its yield (88%) is thus approx. the same as with NaOEt as condensing agent (93%). Also, under comparable conditions, approx. the same yield of ketonic ester is obtained with NaOEt as with Na . Assuming that AcOEt is reduced by direct addition of Na to the $\text{C}=\text{O}$ linking (otherwise the argument fails), the mechanism of the condensation consists in the reduction of AcOEt by Na with formation of NaOEt , which then brings about the acetoacetic ester condensation. The sum of the proposed reactions is $9\text{AcOEt} + 4\text{Na} \rightarrow 4\text{ONa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et} + 6\text{EtOH}$, the H_2 observed being produced by secondary interaction of Na and EtOH .
H. A. PIGGOTT.

Lævulic acid. I. Preparation from carbohydrates by digestion with hydrochloric acid under pressure. R. W. THOMAS and H. A. SCHUETTE (J. Amer. Chem. Soc., 1931, 53, 2324—2328).—A yield of 42% of lævulic acid is obtained by heating sucrose with 2.4 times its wt. of 6.5% aq. HCl at 162° in an autoclave for 1 hr. Comparable results are obtained with dextrose, lævulose, and starch.
H. A. PIGGOTT.

Determination of the hydroxyl content of organic compounds: determination of castor oil. S. MARKS and R. S. MORRELL (Analyst, 1931, 56, 428—429).—The method of Bölsing, as modified by Peterson and West (cf. A., 1927, 1100), gives the most concordant results. Immersion in boiling H_2O for 15 min., as originally suggested by Verley and Bölsing (cf. A., 1902, ii, 54), is rapid and simple, and gives satisfactory results with substances not decomp. at that temp., e.g., castor oil, β naphthol, vanillin, and guaiacol.
T. McLACHLAN.

Structures of the oxalates of sexavalent molybdenum. H. M. SPITTLE and W. WARDLAW (J.C.S., 1931, 1748—1753).—Salts of the type $\text{B}_2[\text{MoO}_2(\text{C}_2\text{O}_4)_2]$, where B =quinoline, 2-methylquinoline, or strychnine,

are obtained when the bases are added to a solution of MoO_3 (1 mol.) in aq. oxalic acid (2—3 mols.). The salts may occur in 3 forms, 2 of which should be optical isomerides; the strychnine salt could not, however, be resolved. When the ionic concentration of 2-methylquinolinium oxalate is decreased relatively to the Mo concentration, 2-methylquinolinium hydrogen molybdenum trioxymonoxalate, $(\text{C}_{10}\text{H}_{10}\text{N})\text{H}[\text{MoO}_3\text{C}_2\text{O}_4\text{H}_2\text{O}]$, results. New formulæ are suggested for the salts $\text{MoO}_3\cdot\text{R}_2\text{C}_2\text{O}_4\cdot x\text{H}_2\text{O}$ and $(\text{MoO}_3)_2\cdot\text{R}_2\text{C}_2\text{O}_4\cdot x\text{H}_2\text{O}$.

H. BURTON.

Supposed isomerism of cyclic oxalic esters. W. H. CAROTHERS and F. J. VAN NATTA (Ber., 1931, 64, [B], 1755—1759).—Repetition of the work of Bergmann and Wolff (A., 1930, 912) gives a product, m. p. 100—110°, rising to 125—130° after crystallisation, which is shown to be a polymeric ethylene oxalate by its cryst. form. The monomeric variety, m. p. 143°, has been isolated only after distillation, never as a primary product. Bergmann's product, m. p. 166°, from methoxalyl chloride and ethylene glycol is not methyl β -hydroxyethyl oxalate, which is prepared from Me oxalate and ethylene glycol at 160—185°; it has b. p. 103—105°/0.6 mm., m. p. 32—33°, d_{20}^{20} 1.2830.

H. WREN.

Interaction of sulphuryl chloride with substances containing the reactive methylene group.

II. K. G. NAIK and N. T. TALATI (J. Indian Chem. Soc., 1931, 8, 203—207; cf. A., 1927, 758).—The reactivity of the CH_2 group increases with increasing negative character of the adjoining groups, e.g., in substances $\text{CH}_2(\text{COR})_2$, in the order $\text{R}=\text{NH}_2 < \text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 < \text{OEt}$. The following substances were obtained by treatment of the corresponding unchlorinated compounds with SO_2Cl_2 , nuclear chlorination not taking place in these cases: dichloromalondi-o-, m-, p-nitroanilides, m. p. 152°, 166°, and 178°, respectively; dichloromalondiethylamide, m. p. 131°; dichloromalondiisobutylamide, m. p. 84°; dichloromalondiheptylamide; dichloromalondi-p-3-xylylide; dichloromalonamide; monochloromalontetraphenylamide; monochloromethylmalondiethylamide, m. p. 108°; monochloromethylmalondiisobutylamide, m. p. 102°; monochloromethylmalondibenzylamide, m. p. 159°. Malondi-m- and p-nitroanilides, m. p. 196° and 243°, respectively, were prepared from $\text{CH}_2(\text{CO}_2\text{Et})_2$ and the nitroanilines, but o-nitroaniline did not react even at 200°. The o-compound, m. p. 182°, was obtained by condensing the base with $\text{CH}_2(\text{CO}_2\text{H})_2$ in presence of POCl_3 . Methylmalondiethylamide and -isobutylamide, m. p. 151° and 133°, respectively, were obtained from $\text{CHMe}(\text{CO}_2\text{Me})_2$ and the respective bases.

R. S. CAHN.

Polymorphism of malonic, succinic, and glutaric acids as a function of temperature.

F. D. LA TOUR (Compt. rend., 1931, 193, 180—182; cf. A., 1930, 1100).—The above acids are dimorphous, the curve of transition points following a similar course to that of the m. p. X-Ray measurements are recorded for some of the substances.

A. A. LEVI.

Rotation and configuration in the Walden inversion. W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1931, 35, 1624—1647).—A discussion. Rotations and configurations of optically active com-

pounds can be correlated by means of criteria outlined by van 't Hoff. These show that *l*-(—)-malic, *l*-(—)-chlorosuccinic, *l*-(+)-aspartic, *l*-(+)-lactic, *l*-(+)-alanine, and *l*-(—)-chloropropionic acids are all of the same configuration. (The signs in parentheses indicate actual rotations in H_2O , and *l* indicates that lævrotatory salts and esters are produced.) In the two series thus determined HNO_3 , Ag_2O , and NOCl act by replacement, whilst PCl_5 , SOCl_2 , KOH , and NH_3 produce a Walden inversion. The hydroxy-acids can be correlated by this method, which shows that *l*-(+)-lactic, *l*-(—)-mandelic, *l*-(—)-malic, and *l*-(—)-tartaric acid have the same configuration.

L. S. THEOBALD.

Identification of mesaconic acid. H. H. MOTTEN and G. L. KEENAN (J. Amer. Chem. Soc., 1931, 53, 2347—2349).—Micro-crystallographic data are given for the hydrazide, m. p. 217—218° (corr.), and *p*-nitrobenzyl ester, m. p. 134° (corr.), of mesaconic acid, and for the acid itself, m. p. 204.5°. The Et₂ ester has b. p. 93—95°/10 mm.

H. A. PIGGOTT.

Cork. V. Phloionic acid. VI. Phloionolic acid. VII. Phellogenic acid. P. ZETSCHE and M. BÄHLER (Helv. Chim. Acta, 1931, 14, 846—849, 849—851, 852—856).—V. Phloionic acid (*Me* ester, m. p. 77—78°), when purified by repeated crystallisation from MeOH, or by means of its Pb salt, has m. p. 124°, is dibasic, and appears to have the formula $\text{C}_{18}\text{H}_{31}\text{O}_6$. It does not form an anhydride.

VI. Phloionolic acid, dimorphic, m. p. 104° (stable) and 95° (*Me* ester, m. p. 77°), is isolated from fraction K_6 (this vol., 713), and purified by repeated crystallisation from MeOH, AcOEt, or 80% EtOH. It is monobasic, has the formula $\text{C}_{18}\text{H}_{26}\text{O}_5$, and therefore is probably a trihydroxystearic acid. Its properties closely resemble those of an acid, m. p. 107—108°, isolated from cutin (A., 1925, i, 1025).

VII. The conversion of phellonic acid into phellogenic acid by fusion with KOH at 350° occurs with loss of CO_2 , giving nonadecanedicarboxylic acid. The same product is similarly obtained from α -hydroxy-arachidic acid, and margaric acid from α -hydroxy-stearic acid.

H. A. PIGGOTT.

Synthesis of agaric acid. M. PASSERINI and G. BANTI (Atti III Cong. Naz. Chim. pura appl., 1929, 343—346; Chem. Zentr., 1931, i, 1432—1433).—The Na derivative of Et acetonedicarboxylate was heated with cetyl iodide; the cetyl derivative was treated with phenylcarbimide and AcOH in Et₂O during 40 days, the product being hydrolysed with alcoholic KOH. The product afforded Me heptadecyl ketone, m. p. 81—83°, methylcetylmaleic anhydride, m. p. 33°, and *r*-cetylcitric (agaric) acid (+1.5 H_2O), m. p. 130—132°.

A. A. ELDRIDGE.

Pyranoid structure of glycuronic acid and of theophyllinearabioside. J. PRYDE and R. T. WILLIAMS (Nature, 1931, 128, 187).—Methylation, followed by esterification and oxidation with HNO_3 , of bornyl-*d*-glycuronide gives a mixture of *d*-dimethoxysuccinic acid and *r*-xylotrimethoxyglutaric acid showing that the glycuronic acid in bornylglycuronide possesses a pyranoid structure. Methylation of *d*-glycurone yields two stereoisomeric cryst. trimethylglycurones. The main oxidation product (with HNO_3)

of the pentose residue of trimethyltheophylline-*l*-arabinoside is *d*-arabotrimethoxyglutaric acid, indicating that theophyllinearabinoside is a pyranoid compound. The purine residue of this arabinoside has been isolated as a yellow cryst. compound, $(C_7H_7N_4O_2 \cdot NO_2)_2 \cdot H_2O$, m. p. 275°, presumably 8-nitrotheophylline. L. S. THEOBALD.

Muconic and hydromuconic acids. V. Ester-addition to ethyl muconate. E. H. FARMER and T. N. MEHTA (J.C.S., 1931, 1762—1764).—Ethyl Δ^{α} -butene- $\alpha\delta$ -dicarboxylate- γ -malonate, b. p. 175—180°/2 mm. (oxidation products, oxalic and tri-carballylic acids), and a trace of an isomeric ester are formed when Et muconate is condensed with Et malonate in presence of a little NaOEt; cyclisation and isomerisation are inhibited (cf. J.C.S., 1922, 121, 2015; 1923, 123, 3324). H. BURTON.

Synthesis of ethyl thioacetoacetate. P. C. RAY (Nature, 1931, 128, 189).—Et thioacetoacetate has been synthesised as indicated by $CMeCl:CH \cdot CO_2Et$ ^{alcoholic} \xrightarrow{KSH} $SH \cdot CMe:CH \cdot CO_2Et \rightleftharpoons CSMe \cdot CH_2 \cdot CO_2Et$. This ester behaves like Et acetoacetate towards hydrazines, NH_2OH , aromatic amines, etc., undergoes Grignard, Reformatsky, and Michael reactions, and in Knoevenagel's reaction yields thioaldehydes.

L. S. THEOBALD.
Photosynthesis of formaldehyde and carbohydrates. G. G. RAO and N. R. DHAR.—See this vol., 920.

Formose. P. KARRER and E. VON KRAUSS (Helv. Chim. Acta, 1931, 14, 820—831).—The solution obtained by polymerising aq. CH_2O with $Ca(OH)_2$ contains pentoses, hexoses, and presumably some heptoses, that can be fractionated by distillation of the crude mixture of their isopropylidene compounds, by which means fractions corresponding either with pentoses or with hexoses are obtained. Without exception the individual fractions after hydrolysis reduce Fehling's solution only very feebly, but interact with I, and therefore probably contain $\cdot CHO$ groups. In an attempt to fractionate the isopropylidene compounds, b. p. 110—120°/0.6 mm., by means of phenylhydrazine, an osazone, m. p. 156—158°, was obtained in small amount. H. A. PIGGOTT.

Reactions of acetaldehyde over zinc chromite under a pressure of 210 atmospheres. H. ADKINS, K. FOLKERS, and M. KINSEY (J. Amer. Chem. Soc., 1931, 53, 2714—2720).—A more detailed account of work previously reviewed (A., 1930, 1559).

H. BURTON.

Reactions of ortho-derivatives of aldehydes and ketones. W. COCKER, A. LAPWORTH, and A. T. PETERS (J.C.S., 1931, 1382—1391).—A generalisation according to electronic theories of the Pinner-Kötz theory regarding the action of KCN on $CCl_3 \cdot CHO$ (A., 1913, i, 1309) is discussed, being supported by the ready loss of HCl from 2-chloro-1-cyanocyclohexane, b. p. 138°/15 mm., and the formation of BzOEt from BzCN and cold NaOEt. It explains the conversion of $CCl_3 \cdot CHO$ in EtOH into Et dichloroacetate. The arguments of Chattaway and Irving (A., 1929, 795) are refuted. Chloral alcoholate and HCN in cold EtOH

in the presence of NPr_3 form chloralcyanohydrin exothermally. The generalised theory is applied to the conversion of cyanohydrins into aminonitriles, which proceeds by way of the free aldehyde or ketone, and to the reversible formation of acetals. HCl is removed from 6-nitro-2:4-bis(trichloromethyl)-1:3-benzdioxin not only by KCN, but also by NaOH. *cyclo*Hexanone in ligroin shaken with KCN in aq. NH_3 gives 1-aminocyanocyclohexane, the hydrochloride of which [m. p. 233° (decomp.)] with dil. H_2SO_4 at 115—120° yields 1-aminocyclohexanecarboxylic acid, m. p. 350° (decomp.). MeCHO, aq. KCN, and NH_2Et_2 give diethylaminopropionitrile. R. S. CAHN.

Purported addition of magnesium benzyl chloride to the ethylenic linking in citronellal. H. GILMAN and W. F. SCHULZ (J. Amer. Chem. Soc., 1931, 53, 2799—2801).—Polemical against Kharasch (Ann. Survey of Amer. Chem., 1930, 5, 193).

H. BURTON.

Modern chemistry of the sugars. H. PRINGSHEIM (Z. angew. Chem., 1931, 44, 677—682).—The natural occurrence of individual sugars is discussed. H. WREN.

Synthesis of *d*-threose. J. R. MENDIVE (Chemia, 1930, 7, 321—331; Chem. Zentr., 1931, i, 1596—1597).—*d*-Threose (phenylhydrazone, m. p. 164—165°) has been obtained ash-free by degradation of *d*-xylose by Wohl's method; cryst. derivatives were not obtained. Tetra-acetylxylo-nitrile, m. p. 83°; diacetylamido-*d*-threose, m. p. 166°.

A. A. ELDRIDGE.

Decarboxylation of *d*-galacturonic acid with special reference to the hypothetical formation of *l*-arabinose. C. M. CONRAD (J. Amer. Chem. Soc., 1931, 53, 2282—2287).—*l*-Arabinose could not be isolated from the syrupy products of decarboxylation of Ba *d*-galacturonate and Ehrlich's tetra-acid "*a*" (A., 1929, 1273) with boiling 4% H_2SO_4 . It was, however, obtained by similar treatment of apple and lemon pectins, in the former case in more than twice the yield that could have formed by decarboxylation of galacturonic acid (measured by CO_2 evolution). It is therefore concluded that the hydrolysis of galacturonic acid to furfuraldehyde does not proceed by way of arabinose, and that arabinose units are present in the plant materials in cases where it is isolated by their hydrolysis. H. A. PIGGOTT.

Reactivity of methylated sugars. IV. Action of dilute alkali on trimethylxylose. C. E. GROSS [with W. L. LEWIS] (J. Amer. Chem. Soc., 1931, 53, 2772—2784).—The equilibrium solution from xylose and dil. $Ca(OH)_2$ contains xylose (52.9%), lyxose (8.3%), and a condensation product (9.8%) derived from 4 mols. of the expected 2-ketoxxylose. Evidence of a stable, intermediate enol could not be obtained. Under similar conditions, 2:3:4-trimethylxylose is transformed partly into trimethyl-lyxose; evidence of a stable enol is obtained. Acidification of the equilibrated solution gives some furfuraldehyde, and the gum isolated contains trimethyl-lyxose (70%), trimethylxylose (26%), and partly demethylated products (4%). The conversion of trimethylxylose into trimethyl-lyxose confirms the identity of their ring structures. H. BURTON.

Oxidation of sugars. I. Electrolytic oxidation of aldoses in presence of a bromide and calcium carbonate. H. S. ISBELL and H. L. FRUSH (Bur. Stand. J. Res., 1931, 6, 1145—1152).—Details are given of the electrolytic oxidation of various aldoses in presence of a bromide as catalyst, whereby the monocarboxylic acids are produced in almost quant. yield; in presence of CaCO_3 the Ca salts are readily isolated by crystallisation from the reaction products. The anode efficiency is 80—99%, and the process is economically practicable on a technical scale. H. F. GILLBE.

Determination of small quantities of biologically important sugars with the exclusion of non-carbohydrate reducing substances. O. LEHMANN (Planta [Z. wiss. Biol.], 1931, 13, 575—642).—A comprehensive scheme for sugar analysis is based on the method of Hagedorn and Jensen (A., 1923, ii, 673). Lævulose-dextrose mixtures are examined before and after differential decomp. with HCl, and sucrose, maltose, and starch after hydrolysis with acid or fermentation. In pentose-hexose mixtures the total reducing value is obtained by the Hagedorn-Jensen reagent, hexoses are removed by fermentation, and pentoses determined by a modified furfuraldehyde method (A., 1924, ii, 876). A. G. POLLARD.

Identity of the saccharals of epimeric sugars. M. GEHRKE and F. OBST (Ber., 1931, 64, [B], 1724—1729).—The configurative difference between epimeric sugars is destroyed by the introduction of a double linking between the 1- and 2-C atoms. As predicted, *d*-glucal is found to be identical with *d*-mannal and *d*-xylal with *d*-lyxal. Acetobromoglucose or acetobromolyxose is converted by Zn and 50% AcOH into *d*(-)-*xylal* (*lyxal*) diacetate, b. p. 79—82°/0.2—0.3 mm., m. p. 39—40°, $[\alpha]_D^{20} -314.2^\circ$ in CHCl_3 , hydrolysed by $\text{Ba}(\text{OH})_2$ in MeOH to *d*(-)-*xylal* (*lyxal*), b. p. 91—92°/0.2—0.3 mm., m. p. 49—50°, $[\alpha]_D^{20} -254.6^\circ$ in H_2O . The diacetate is hydrogenated in MeOH in presence of Pd-asbestos to *d*(-)-*dihydroxylal* (*lyxal*) diacetate, b. p. 82—83°/0.2—0.3 mm., $[\alpha]_D^{20} -38.8^\circ$ in EtOH, which does not add Br or show reducing properties. *d*(-)-*Dihydroxylal* (*lyxal*), b. p. 97—99°/0.2—0.3 mm., m. p. 67—68°, $[\alpha]_D^{20} -44.9^\circ$ in H_2O , is oxidised by perbenzoic acid in AcOEt to *d*(-)-lyxose, identified as the phenylbenzylhydrazone. The prep. of *d*(-)-lyxose from penta-acetyl-galactonitrile is described. Acetobromomannose is transformed into *d*(-)-glucal triacetate, m. p. 54—55°, $[\alpha]_D^{20} -15.5^\circ$ in EtOH, and thence into *d*(-)-mannal, *d*(+)-dihydro-mannal triacetate, and *d*(+)-dihydromannal, identical with the series of compounds derived from acetobromoglucose. H. WREN.

Action of sulphite and hydrogen sulphite solutions on sugars at high temperatures. E. HÄGGLUND (Fenno-Chem., 1930, 2, 49—54; Chem. Zentr., 1931, i, 2040).—If dextrose is heated with NaHSO_3 solution in a closed vessel at 135°, the cold product treated with H_2SO_4 , the Na_2SO_3 removed with EtOH, and the filtrate neutralised with BaCO_3 , a Ba sulphonate is obtained of which part is hydrolysed by boiling H_2O to BaSO_3 . A disulphonate (Ba 35.5, S 12.4%) was isolated; prolonged hydrolysis of this gave *d*-gluconic acid. The sulphonic acid contains a

CO_2H group and is stable towards boiling dil. acid and alkali. A. A. ELDRIDGE.

Determination of hexoses in the hydrolytic products of polysaccharides. E. SCHMIDT, M. ATTERER, and H. SCHNEGG (Cellulosechem., 1931, 12, 235—242).—The hexose content of the hydrolytic products (Clark's method, B., 1922, 339A) of pentosan-free polysaccharides, including viscose-silk and mannan, is 84.1—84.5% as determined by fermentation with *Schizosaccharomyces Pombe* or *Sacch. Vordermannii*. The presence of Ba inhibits fermentation. One ClO_2 treatment of the hydrolytic products is more effective than an animal charcoal treatment in converting humin substances into products which do not retard fermentation. Even dil. Cl_2 (0.1%) oxidises dextrose and should not be used for bleaching. The activity of the yeasts decreases quickly during use, but can be restored by growing in wort. *d*-Galactose can be determined by *S. Vordermannii* only in presence of a phosphate-containing nutrient. *S. Pombe* does not ferment *d*-galactose. The agreement between the fermentation values of hemicellulose hydrolytic products (cf. A., 1929, 1113; B., 1929, 937) points to the absence therein of *d*-galactose. A. RENFREW.

Reaction between dextrose and potassium permanganate in acid solution. S. L. RIDGWAY (J. Physical Chem., 1931, 35, 1985—2004).—Gluconic acid could not be isolated from the products of oxidation of dextrose in acid solution by KMnO_4 or by HBr and KMnO_4 . The velocity of the former reaction increases very slowly with increase of the total concentration, but fairly rapidly with increase of the KMnO_4 or the acid concentration. The first stage of the process is very rapid, but the point at which the velocity diminishes is not const.; the KMnO_4 is at this point almost entirely reduced to MnO_2 , which then oxidises the remaining dextrose relatively slowly. Dextrose cannot be determined by oxidation with KMnO_4 in acid solution. H. F. GILLBE.

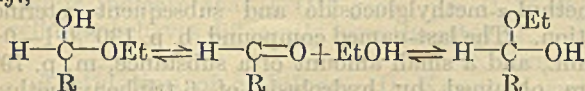
Compounds of carbohydrates with acetaldehyde; ethylideneglucose. B. HELFERICH and H. APPEL (Ber., 1931, 64, [B], 1841—1847).—Dextrose is converted by paracetaldehyde containing a little conc. H_2SO_4 into a mixture of 4:6-ethylidene- α - and - β -*d*-glucose from which the homogeneous α -compound, m. p. 179—182° (corr.), $[\alpha]_D^{20} +66.4^\circ$ to $[\alpha]_D^{20} -2.36^\circ$ in H_2O , is obtained by repeated crystallisation from aq. COMe_2 . It reduces boiling Fehling's solution. The 6-position is occupied, since it fails to react with CPh_3Cl . The osazone, $\text{C}_{20}\text{H}_{24}\text{O}_4\text{N}_4$, has m. p. 185—186°, $[\alpha]_D^{20} -79.57^\circ$ in CHCl_3 . β -Methyl-*d*-glucoside is converted similarly into 4:6-ethylidene- β -methyl-*d*-glucoside, m. p. 189—190° (corr.), $[\alpha]_D^{20} -79.1^\circ$ in H_2O , transformed by Ac_2O and NaOAc at 100° into 4:6-ethylidene- β -methyl-*d*-glucoside 2:3-diacetate, m. p. 180.5—182°, $[\alpha]_D^{20} -65.9^\circ$ in CHCl_3 , also obtained by treating ethylideneglucose with Me_2SO_4 and NaOH and subsequently with Ac_2O in pyridine. Methylation of ethylideneglucose or ethylidene- β -methyl-*d*-glucoside affords ethylidene- β -methyl-*d*-glucoside 2:3-dimethyl ether, m. p. 109.5—111°, $[\alpha]_D^{20} -47.8^\circ$ in CHCl_3 , obtained in smaller yield from 3-methylglucose and paracetaldehyde. The substance is converted by PhCHO and ZnCl_2 into benzylidene- β -

methyl-*d*-glucoside 2 : 3-dimethyl ether, m. p. 133.5—134°, $[\alpha]_D^{20}$ —60.0° in EtOH. H. WREN.

Condensation products of dextrose and *p*-toluidine. M. AMADORI (Atti R. Accad. Lincei, 1931, [vi], 13, 72—77).—When heated together in 95% EtOH, *p*-toluidine (7 g.) and dextrose (10 g.) yield the (?)glucosidic compound C₁₃H₁₉O₅N, m. p. 115°, moderately stable in alkaline solution, but decomp. into the original components in acid solution. If the toluidine and dextrose, in the above proportions, are heated at 80—90° until molten, they give an isomeric compound, m. p. 154°, which is stable in neutral or acid, but decomposes, apparently with formation of dextrose, in alkaline, solution, and is analogous to Schiff's bases. T. H. POPE.

Rotatory dispersion of aldehydo-sugar acetates. M. L. WOLFROM and W. R. BRODE (J. Amer. Chem. Soc., 1931, 53, 2279—2281).—The values of $1/M[\alpha]_\lambda$ in the visible region for the aldehydo-acetates of *d*-galactose and *l*-arabinose in CHCl₃ lie on a straight line when plotted against λ^2 . In the case of dextrose a slight deviation is observed in the violet region. H. A. PIGGOTT.

Mutarotation of the alcoholate and aldehydrol of aldehydogalactose penta-acetate. M. L. WOLFROM (J. Amer. Chem. Soc., 1931, 53, 2275—2279).—The rotation of the cryst. alcoholate (A., 1930, 1023) of aldehydogalactose penta-acetate, $[\alpha]_D + 1.5^\circ$ in EtOH-free CHCl₃, falls rapidly to a min. and then increases, rather less rapidly, to a value higher than the original. The form of the curve is regarded as pointing to reversible decomp. of the semi-acetal into aldehyde ($[\alpha]_D - 25^\circ$) and EtOH, and formation from these of a semi-acetal with a new configuration, e.g.,



The aldehydrol, on the other hand, under like conditions, shows only a steady fall in rotation along an exponential curve, indicating a simple unimol. decomp. into free aldehyde and H₂O, and favouring the aldehydrol structure assigned. No mutarotation is shown by the aldehyde itself. H. A. PIGGOTT.

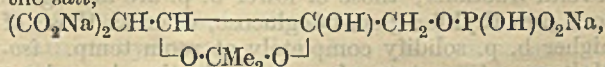
Ring structure of β -methylgalactoside. A. MÜLLER (Ber., 1931, 64, [B], 1820—1826).— β -Galactose penta-acetate is converted by HBr in AcOH into α -acetobromogalactose, m. p. 81—82°, $[\alpha]_D^{20} + 235.2^\circ$ in C₆H₆, transformed by Ag₂CO₃ in MeOH into acetomethylgalactose, m. p. 94°, which is hydrolysed by NaOMe to β -methylgalactoside, m. p. 174°. The last-named compound is transformed by CPh₃Cl in pyridine into β -methylgalactoside 6-triphenylmethyl ether, m. p. 167—169° after softening at 80°, $[\alpha]_D^{20} - 39.48^\circ$ in CHCl₃ (2 : 3 : 4-triacetate, m. p. 138°, $[\alpha]_D^{20} - 50.29^\circ$ in CHCl₃). The corresponding B₂ compound, m. p. 95°, $[\alpha]_D^{20} + 77.73^\circ$ in CHCl₃, is converted by HBr in AcOH into the non-cryst. β -methylgalactoside 2 : 3 : 4-tribenzoate, converted by *p*-toluenesulphonyl chloride into 2 : 3 : 4-tribenzoyl- β -methylgalactoside 6-*p*-toluenesulphonate, m. p. 194° after softening at 190°, $[\alpha]_D^{20} + 148.7^\circ$ in CHCl₃, transformed by NaI in COMe₂ at 100° into 2 : 3 : 4-tribenzoyl- β -methylgalactoside-6-iodo-

hydrin, m. p. 145°, $[\alpha]_D^{20} + 169.3^\circ$ in CHCl₃ (also +COMe₂, m. p. 140°). With AgI⁺ in pyridine the iodohydrin yields 2 : 3 : 4-tribenzoyl- β -methyl- Δ^5 -galactoseinide, which readily absorbs Br. After hydrolysis with KOH in EtOH it is inactive towards Fehling's solution, which it strongly reduces after acidification of the hydrolysate with HCl.

H. WREN.

Colorimetric determination of lævulose and its application to mixtures of various carbohydrates. H. BREDERECK (Ber., 1931, 64, [B], 1730—1732).—1 c.c. of the solution, mixed with 10 c.c. of 4% (NH₄)₂MoO₄ and 0.25 c.c. of 4*N*-HNO₃, is heated in a closed tube for 2½ min. at 65° and cooled for 3 min. at 0°. The colour is matched against that produced by standard lævulose solutions. Lævulose may be determined quantitatively in presence of 70—80% of dextrose, 80—90% of galactose, 60—70% of mannose, 80—90% of arabinose, and 80% of a mixture of the sugars cited above. Under the experimental conditions the hydrolysis of sucrose is so slight that lævulose can be accurately determined in presence of 80% of sucrose and of 70—80% of a mixture of sucrose and dextrose. H. WREN.

Model experiments based on the theory of alcoholic fermentation. IV. Preparation and oxidation of di- β -diisopropylidene-fructose-1-phosphoric acid. H. OHLE and F. GARCIA Y GONZALEZ (Ber., 1931, 64, [B], 1759—1765; cf. A., 1930, 70).— β -Diisopropylidene-fructose does not yield tri- β -diisopropylidene-fructose phosphate, m. p. 135—136°, $[\alpha]_D^{20} - 29.5^\circ$ in CHCl₃, under the action of POCl₃ in pyridine or in Et₂O or CHCl₃ in absence or presence of pyridine; it is obtained in small amount by aid of PCl₅ in Et₂O, readily by means of POCl₃ and PCl₅ in Et₂O. Hydrolysis of the ester with NaOH in aq. MeOH affords diisopropylidene-fructose hydrogen 1-phosphate (Na salt, $[\alpha]_D^{20} - 23.5^\circ$ in H₂O; non-cryst. K salt; Ag salt, m. p. 210° (decomp.); cinchonidine salt, m. p. 212—213° (decomp.), $[\alpha]_D^{20} - 66.06^\circ$ in MeOH; Me ester, m. p. 108—109°, $[\alpha]_D^{20} - 35.69^\circ$ in MeOH, from the Ag salt and MeI; Et ester, m. p. 113—114°, $[\alpha]_D^{20} - 34.77^\circ$ in MeOH, from the acid and Et orthoformate). The acid is very stable towards alkalis, whereas its hydrolysis with acids involves the :CMe₂ groups to a greater or smaller extent. Hydrolysis of the Me or Et ester with NaOH is accompanied by partial re-formation of di- β -diisopropylidene-fructose hydrogen 1-phosphate. Oxidation of Na di- β -diisopropylidene-fructose 1-phosphate by NaMnO₄ in initially neutral solution follows the same course as that of diisopropylidene-fructose 1-sulphate (*loc. cit.*), leading through the expected intermediate product to the salt,



which is decomposed by dil. mineral acids to H₃PO₄, CO₂, COMe₂, methylglyoxal, and glycollic acid. The yield of methylglyoxal is considerably less than that obtained from the sulphuric ester, due to partial conversion into acetol and pyruvic acid.

H. WREN.

Action of mercury salts on acetohalogeno-sugars. VI. Syntheses of gentiobiose- and

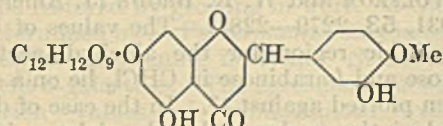
cellobiosido-6-glucose derivatives. G. ZEMPLÉN and A. GERECs [with J. ERDÉLYI] (Ber., 1931, 64, [B], 1545—1554).—Detailed descriptions are given of the conversion of starch successively into β -glucosan and its triacetate. The last-named substance is transformed by TiCl_4 in CHCl_3 into α -1-chloro-2:3:4-triacetyl-*d*-glucose, m. p. 124—125°, $[\alpha]_D^{20}$ -189.2° in CHCl_3 , and by TiBr_4 into α -1-bromo-2:3:4-triacetyl-*d*-glucose, decomp. 126—127°, $[\alpha]_D^{20}$ +217.4° in CHCl_3 (converted by MeOH and Ag_2CO_3 into β -1-methyl-2:3:4-triacetyl-*d*-glucose, m. p. 133—134°, $[\alpha]_D^{20}$ -16.0° in CHCl_3). Acetobromoglucose, 1-chloro-2:3:4-triacetylglucose, and $\text{Hg}(\text{OAc})_2$ in C_6H_6 afford *acetochlorogentiobiose*, $\text{C}_{26}\text{H}_{35}\text{O}_{17}\text{Cl}$, m. p. 136.5—137°, $[\alpha]_D^{20}$ -82.83° in CHCl_3 , transformed by Ag_2CO_3 in aq. COMe_2 and subsequent acetylation into gentiobiose octa-acetate, m. p. 166—167°, $[\alpha]_D^{20}$ +27.39° in CHCl_3 , which gives gentiobiose when hydrolysed. Acetobromocellobiose, 1-chloro-2:3:4-triacetylglucose, and $\text{Hg}(\text{OAc})_2$ yield 1-chloro-6- β -cellobiosidoglucose deca-acetate $\text{C}_{38}\text{H}_{51}\text{O}_{25}\text{Cl}$, decomp. about 223—224°, $[\alpha]_D^{20}$ +48.37° in CHCl_3 , the formation of an intermediate, halogen-free product being indicated. Interaction of 1-chloro-2:3:4-triacetylglucose, acetobromocellobiose, and $\text{Hg}(\text{OAc})_2$ in boiling C_6H_6 gives a mixture of α - and β -6-cellobiosidoglucose hendeca-acetate (identified by hydrolysis to the free sugar), from which 1-chloro-6- β -cellobiosidoglucose deca-acetate is obtained by treatment with TiCl_4 in C_6H_6 . α -1-Bromo-6- β -cellobiosidoglucose deca-acetate has decomp. 205°, $[\alpha]_D^{20}$ +69.91° in CHCl_3 . H. WREN.

Action of mercury salts on acetohalogeno-sugars. VII. Synthesis of 1- β -methylgentiobiose and 1- β -methyl-6- α -glucosidoglucose; isomaltose question. G. ZEMPLÉN and Z. BRUCKNER (Ber., 1931, 64, [B], 1852—1858).—The action of acetobromoglucose on 2:3:4-triacetyl-1- β -methylglucose in C_6H_6 in presence of $\text{Hg}(\text{OAc})_2$ readily affords 1- β -methylgentiobioside hepta-acetate, m. p. 82°, $[\alpha]_D^{20}$ -16.99° in CHCl_3 , when a considerable proportion of $\text{Hg}(\text{OAc})_2$ is used, but when less is used the corresponding α -derivative preponderates in the non-crystallisable product. Hydrolysis of the latter by NaOMe followed by treatment with BzCl in pyridine yields the non-cryst. 1- β -methyl-6- α -glucosidoglucose heptabenzoate, m. p. about 85° after softening at 75°, $[\alpha]_D^{20}$ +54.67° in CHCl_3 , whereas treatment of it with Me_2SO_4 and NaOH gives heptamethyl-1- β -methyl-6- α -glucosidoglucose, $[\alpha]_D^{20}$ +95.13° in EtOH, +93.1° in H_2O . 1- β -Methylgentiobioside heptabenzoate has m. p. 203°, $[\alpha]_D^{20}$ +2.0° in CHCl_3 .

The product of the methylation of Fischer's isomaltose is separated by distillation in a high vac. into several fractions; those of lower b. p. are analogous to 1- β -methyl-6- α -glucosidoglucose, whereas those of higher b. p. solidify completely at room temp. isomaltose octa-acetate after saponification has about 40% of the reducing power of dextrose, rising only to 80% after hydrolysis. It contains therefore considerable amounts of foreign matter of high mol. wt. in addition to the disaccharide or mixture of disaccharides. H. WREN.

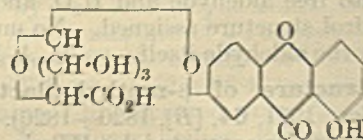
Natural glucosides. III. Position of the biose residue in hesperidin. F. E. KING and

A. ROBERTSON (J.C.S., 1931, 1704—1709).—The formula assigned to hesperidin ($\text{Ac}_{3(\text{or } 9)}$ derivative, m. p. 175—176°) by Asahina and Inubuse (J. Pharm. Soc. Japan, 1929, 49, 11) is confirmed. Hesperidin with Me_2SO_4 and dil. NaOH or MeI and K_2CO_3 in COMe_2 , gives products hydrolysed by dil. acid to 4-hydroxy-2:6-dimethoxyphenyl 3:4-dimethoxystyryl ketone (I), m. p. 194° (acetate, m. p. 175°), synthesised from 4-hydroxy-2:6-dimethoxyacetophenone and veratraldehyde. Catalytic reduction (Pd) of (I) affords 4-hydroxy-2:6-dimethoxyphenyl β -3:4-dimethoxyphenylethyl ketone, m. p. 109°, also obtained together with the 2-hydroxy-4:6-dimethoxy-isomeride by the Hoesch condensation of β -3:4-dimethoxyphenylpropionitrile and phloroglucinol Me_2 ether. By analogy with hesperitin (*ibid.*, 1928, 48, 207), hesperidin is considered to have the following structure:



H. BURTON.

Natural glucosides. IV. Constitution of euxanthic acid. A. ROBERTSON and R. B. WATERS (J.C.S., 1931, 1709—1714).—Euxanthic acid with MeI and Ag_2O gives *Me O-tetramethyleuxanthate*, m. p. 168°, hydrolysed by HCl in aq. MeOH to 7-hydroxy-1-methoxyxanthone, m. p. 235° (lit. 240°), and a trimethylglycuronic acid, apparently identical with that described by Challinor *et al.* (this vol., 465). Oxidation of the glycuronic acid with HNO_3 and esterification of the products formed afford a little *Me d*-dimethoxysuccinate and mainly *Me trimethyl- β -saccharolactonate*, m. p. 106°, also obtained by oxidation of 2:3:4-trimethyl- α -methylglucoside and subsequent esterification. The last-named compound, b. p. 130°/0.1—0.2 mm., and a small amount of a substance, m. p. 79°, are obtained by hydrolysis of 6-triphenylmethyl-2:3:4-trimethyl- α -methylglucoside, m. p. 166—167° (cf. A., 1925, i, 9), with HCl in MeOH. Euxanthic acid has the structure:



H. BURTON.

Highly-polymerised compounds. LIII. Constitution of compounds of high mol. wt., particularly cellulose. H. STAUDINGER (Ber., 1931, 64, [B], 1688—1697).—Mainly a reply to Hess and Sakurada (this vol., 828). The validity of applying measurements of viscosity to the determination of the mol. wt. of cellulose and its derivatives is justified by the complete analogy of the behaviour of these substances with that of synthetic highly polymerised compounds. With both synthetic and natural products, deviations from the Hagen-Poiseuille law become more marked with increase in mol. wt. and more noticeable in conc. than in dil. solution. They are not observed in very dil. solution (sol solution) in which the mols. have freedom of movement. Diminution of the viscosity of cellulose

solutions with increasing purification of the preps. is not due to the removal of incrusting matter, but to degradation of the sensitive macromols. The observation that the viscosity of a cellulose acetate solution is more dependent on pressure than that of a solution of the cellulose from which it was prepared is attributed to the greater diameter of the acetate mol. The applicability of the Bergmann-Machemer method to the determination of mol. wt. of materials belonging to the same polymeric homologous series is supported by the results of new measurements of the mol. wt. of highly-degraded cellulose acetates in dioxan. Hess' conception of the cellulose mol. is adversely criticised.

H. WREN.

Action of sodium on cellulose in liquid ammonia. P. C. SCHERER, jun., and R. E. HUSSEY (J. Amer. Chem. Soc., 1931, 53, 2344—2347).—Interaction of Na with cellulose in dry liquid NH_3 at its b. p./1 atm. proceeds rapidly to the monosodium-derivative ($1\text{Na} : 1\text{C}_6\text{H}_{10}\text{O}_5$), the theoretical amount of H_2 being evolved; further reaction is then slow, but yields eventually the Na_2 -derivative. The formation of NaNH_2 could not be detected. H. A. PIGGOTT.

Treatment of cellulose and oxidised cellulose with acetic-sulphuric acid mixtures. R. H. VAN DYKE, C. J. STAUD, and H. LEB. GRAY (J. Amer. Chem. Soc., 1931, 53, 2725—2732).—Cellulose (cotton linters) is oxidised with CrO_3 ($\equiv 0.5$ and 20 per $\text{C}_6\text{H}_{10}\text{O}_5$ unit) or KMnO_4 ($\equiv 0.5$ and 10) in $\text{N-H}_3\text{PO}_4$ (cf. A., 1930, 750). The oxidised and unoxidised celluloses are treated with AcOH and H_2SO_4 at 20 — 25° during 330 — 335 hr. and the Ac contents of the various products determined. The most vigorously oxidised celluloses give products with the smallest Ac content. The results indicate that 1 OH group per $\text{C}_{24}\text{H}_{40}\text{O}_{20}$ in cellulose behaves differently from the other 11.

H. BURTON.

Acetylation of cellulose. D. KRUEGER and E. TSCHIRCH (Ber., 1931, 64 [B], 1874—1878).—Under certain conditions HClO_4 is much more efficient than H_2SO_4 as catalyst for the acetylation of cellulose. Both acids are effective in concentration so small that the solubility of cellulose does not enter into the question, and the acceleration of the process must be attributed to a sp. property depending on the structure of the acids. The formation of mixed esters, observed on the acetylation of cellulose in presence of H_2SO_4 , is not a general property of acid catalysts; primary cellulose acetates obtained in homogeneous or heterogeneous systems in presence of HClO_4 are free from this acid. Acetylation of cellulose occurs at a lower temp. and with a rapidity not previously observed when HClO_4 is used as catalyst. H. WREN.

Modern organic solvents. I. Development of the solvents industry. New conception of the constitution of cellulose nitrate. Solvent action in dyeing [dry cleaning] and allied processes. E. CLAYTON and C. O. CLARK (J. Soc. Dyers and Col., 1931, 47, 183—191).—Historical review of industrial solvents manufacture. In the esterification of cellulose the primary OH external to the anhydro-glucoside ring is first attacked and the micellar structure is loosened. Entry of a second ester group possibly

produces a 5-ring chelated compound, in which all associating power has been lost. Further nitration breaks down the chelated structure and usually also (by oxidation) the chains themselves.

Solubility in COMe_2 persists so long as free OH remains, e.g., in all the nitrates, but not in the triacetate. Highly nitrated cellulose may, however, owe its solubility in COMe_2 to degradation by oxidation. The highest nitrates and the triacetate, being non-associated, have a natural solubility in the non-associated solvent, CHCl_3 . The degree of hydrolysis accompanying the esterification of cellulose is a measure of the breakdown of primary valencies of the intramolecular chains, and the increased area exposed to the solvent leads to accelerated solvation. A table is given showing the solvent effects of pyridine, EtOH , MeOH , glycol mono-ethyl and -butyl ethers, diacetone alcohol, and diglycol mono-ethyl and -butyl ethers on 15 acid, direct, and basic dyes. The presence of more than a certain, usually small, proportion of solvent leads to const. partition of dye between fibre and solvent mixture, and prevents exhaustion of the dye-bath unless solvent is removed during dyeing. The use of mixtures of solvents with wetting agents is discussed. The "benzine soap" used in dry-cleaning owes its solubility in the petroleum to the presence of excess of fat or fatty acid. NH_4 oleate, insol. in light petroleum, dissolves instantly on addition of oleic acid, the electrovalent (ionised) form passing into the covalent (co-ordinated) form. C. HOLLINS.

Pine-wood lignin. B. RASSOW and H. GABRIEL (Cellulosechem., 1931, 12, 227—235).—Wood cellulose appears to adsorb lignin superficially, since, by repeated extraction with ammoniacal CuO solution, followed by washing with dil. H_2SO_4 , the total extract, mostly lignocellulose, increases. Some lignin is also dissolved. The amounts of materials dissolved from wood-meal by glycerol or glycol decrease after repeated extractions. Lignin can be detected in the glycol extract. Extraction for 5—10 min. at 165 — 175° by glycerol containing about 0.15% of mineral acid gives a viscous solution rich in lignin. If glycol replaces glycerol the separation of lignin from cellulose is complete and takes place with little decomp., giving an easily-filtered solution from which glycol-lignin can be separated by precipitation with H_2O , dissolution in AcOH , and reprecipitation with H_2O . With HCl it gives lignin, OMe val. 17.3. The process is contrasted with that of Hibbert and co-workers (A., 1930, 1275). The OMe val. of a lignin is shown to be an index of its purity. A. RENFREW.

Sulphur derivatives of simple amines. I. Amine hydrogen sulphides. M. ACHTERHOFF, R. F. CONAWAY, and C. E. BOORD (J. Amer. Chem. Soc., 1931, 53, 2682—2688).—Amine hydrogen sulphides are prepared from the dry amine and an excess of dry H_2S usually in Et_2O below 0° in absence of air; the following are described (the m. p. in parentheses are those in closed tubes): NEt_2Me , m. p. 40 — 44° (90 — 92°); NEtMe_2 , m. p. 34 — 40° ; NMe_3 , m. p. 15 — 20° (28 — 30°); NEtEt , m. p. 50 — 55° (55 — 57°); NEt_2Et (55 — 62°); NEt_2Pr , m. p. 25 — 27° ; NEtPr , m. p. 38 —

42° (40—42°); NHPr_2 , m. p. 58—62° (76—78°); NH_2Bu , m. p. 18—20°; NHBu_2 , m. p. 25—30° (28—32°); *isoamylamine*, m. p. 62—67°; $\text{NH}(\text{CH}_2\text{Ph})_2$, m. p. 32—34°. The salts from the more volatile amines decompose in air giving S, whilst those from the less volatile amines are similarly oxidised to the corresponding thiosulphates.

H. BURTON.

Influence of poles and polar linkings on tautomerism in the simple three-carbon system. II. Prototropy in bisquaternary $\alpha\gamma$ -propenylenediammonium salts. C. K. INGOLD and E. ROTHSTEIN (J.C.S., 1931, 1666—1683; cf. A., 1929, 300).—Salts containing the isomeric ions

$[\text{Et}_3\text{N}^+\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NMeEt}_2]^{++}$ and

$[\text{Et}_3\text{N}^+\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{NMeEt}_2]^{++}$ are synthesised and shown to be interconvertible in presence of 0.1N-KOH or $-\text{NaOPr}^s$ at 30°. The interconversion is regarded as prototropic and not dependent on primary addition to the double linking, since β -hydroxy- and β -methoxy-trimethylenediammonium salts could not be converted into similar unsaturated substances.

Tetraethyl- β -chlorotrimethylenediamine (I), b. p. 109°/10 mm. (*dipicrate*, m. p. 153°), from the β -OH-derivative and POCl_3 in CHCl_3 , is converted through its dimethiodide into NNN-methyl-diethyl-N'N'N'-methyl-diethyl- β -chlorotrimethylenediammonium *dipicrate*, m. p. 215° (decomp.). Successive treatment of the dimethiodide from (I) and MeBr in MeNO_2 with EtOH-KOH, dil. HCl, and Na picrate, affords NNN-methyl-diethyl-N'N'N'-methyl-diethyl- $\alpha\gamma$ -propenylene-diammonium *dipicrate* (II), m. p. 234° (decomp.), reduced catalytically (Pt-black) to NNN-methyl-diethyl-N'N'N'-methyl-diethyl-trimethylenediammonium *dipicrate*, m. p. 282° (decomp.) [in this and similar experiments the original picrate is usually converted into the chloride, reduction (or oxidation etc.) carried out, and the new salt converted into the new picrate]. The last-named picrate is also prepared by way of the dimethiodide of tetraethyltrimethylenediamine, b. p. 81.9°/9 mm. (from trimethylene dibromide and NHEt_2 in MeNO_2). Oxidation of (II) with aq. 1% KMnO_4 gives NMeEt_2

(*picrate*, m. p. 185°) and the betaine $\text{NMeEt}_2\cdot\overset{\ominus}{\text{C}}\text{H}_2\cdot\overset{\oplus}{\text{C}}\text{O}_2$ [*picrate*, m. p. 146° (lit. 153—154°)]. Methyl-diethyl- β -chloro- γ -diethylamino-*n*-propylammonium bromide (corresponding *dipicrate*, m. p. 133°), from (I) and MeBr in MeNO_2 , eliminates HCl with hot EtOH-KOH forming, after treatment with Na picrate, methyl-diethyl- γ -diethylamino- Δ^α -propenyl- α -ammonium *dipicrate*, m. p. 198°. This is converted by Et_2SO_4 into $\text{N}^+\text{N}^+\text{N}^+$ -methyl-diethyl-N γ N γ N γ -triethyl- Δ^α -propenylene- $\alpha\gamma$ -diammonium *dipicrate* (III), m. p. 229—230° (decomp.), reduced catalytically to NNN-methyl-diethyl-N'N'N'-triethyl-trimethylenediammonium *dipicrate*, m. p. 263—264° (decomp.), and oxidised to the betaine $\text{NEt}_3\cdot\overset{\ominus}{\text{C}}\text{H}_2\cdot\overset{\oplus}{\text{C}}\text{O}_2$ (*picrate*, m. p. 193—194°). Triethyl- β -chloro- γ -diethylamino-*n*-propylammonium iodide, m. p. 213—214° (decomp.) (corresponding *picrate*, m. p. 184°), from (I) and EtI, is converted into triethyl- γ -diethylamino- Δ^α -propenyl- α -ammonium *dipicrate*, m. p. 167—168°, which with MeI gives $\text{N}^+\text{N}^+\text{N}^+$ -triethyl-N γ N γ N γ -methyl-diethyl- Δ^α -propenylene- $\alpha\gamma$ -diammonium *dipicrate* (IV), m. p. 230° (decomp.)

(oxidation product $\text{NMeEt}_2\cdot\overset{\ominus}{\text{C}}\text{H}_2\cdot\overset{\oplus}{\text{C}}\text{O}_2$). (III) and (IV) are interconvertible in presence of alkalis.

α -Chloro- γ -iodoisopropyl alcohol and NMe_3 in EtOH at 75—80° give trimethyl- γ -chloro- β -hydroxy-*n*-propylammonium iodide, m. p. 140—150°, converted by successive treatment with NEt_3 and Na picrate into NNN-trimethyl-N'N'N'-triethyl- β -hydroxy-trimethylenediammonium *dipicrate*, m. p. 230°. Tetraethyl- β -hydroxy-trimethylenediamine (*dipicrate*, m. p. 163°), from epichlorohydrin and NHEt_2 , when treated successively with MeI and Na picrate affords NNN-methyl-diethyl-N'N'N'-methyl-diethyl- β -hydroxy-trimethylenediammonium *dipicrate*, m. p. 259—260° (decomp.). Methyl-diethyl- γ -diethylamino- β -hydroxy-*n*-propylammonium picrate has m. p. 205° (decomp.).

$\alpha\gamma$ -Dichloro- β -methoxypropane and NHEt_2 at 100° afford tetraethyl- β -methoxy-trimethylenediamine, b. p. 98—101°/9 mm. [*dipicrate*, m. p. 110°; *chloroplatinate*, m. p. 215° (decomp.)], also formed from (I) and boiling MeOH-KOH. The following salts are prepared, usually by addition of 1 or 2 mols. of alkyl halide to this ditert. base and subsequent treatment with the requisite reagent: NNN-methyl-diethyl-N'N'N'-methyl-diethyl- β -methoxy-trimethylenediammonium *dipicrate*, m. p. 164—167° [corresponding *chloroplatinate*, m. p. 237—238° (decomp.)]; triethyl- γ -diethylamino- β -methoxy-*n*-propylammonium picrate, m. p. 220° [corresponding *chloroplatinate*, m. p. 224—225° (decomp.)]; methyl-diethyl-, benzyl-diethyl-, and *p*-bromobenzyl-diethyl- γ -diethylamino- β -methoxy-*n*-propylammonium *chloroplatinates*, m. p. 217—218° (decomp.), 201° (decomp.), and 210° (decomp.), respectively; NNN-triethyl-N'N'N'-triethyl-, NNN-benzyl-diethyl-N'N'N'-benzyl-diethyl- and NNN-*p*-bromobenzyl-diethyl-N'N'N'-benzyl-diethyl- β -methoxy-trimethylenediammonium *chloroplatinates*, m. p. 263° (decomp.), 195° (decomp.), and 156—160° (decomp.), respectively. 2:4:6-Trinitrophenyl *p*-bromobenzyl ether, from *p*-bromobenzyl bromide and Ag picrate, has m. p. 125°.

H. BURTON.

Oxidation of *N*-methylhydroxylamine by iodine. O. L. BRADY and M. D. PETERS (J.C.S., 1931, 1604—1605; cf. A., 1926, 1142).— CH_2O was isolated from the products of oxidation of *N*-methylhydroxylamine by I. The reactions are formulated: $\text{NHMe}\cdot\text{OH} + \text{I}_2 \rightarrow 2\text{HI} + \text{CH}_2\cdot\text{N}\cdot\text{OH} \rightarrow \text{CH}_2\text{O} + \text{NH}_2\text{OH}$.

R. S. CAHN.

Preparation of glycine. J. M. ORTEN and R. M. HILL (J. Amer. Chem. Soc., 1931, 53, 2797—2799).— $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ is treated with a large excess of aq. NH_3 during 48 hr. at room temp., the excess of NH_3 evaporated in a vac., and the glycine precipitated with MeOH. The yield of pure glycine is 60—64%.

H. BURTON.

Reactions of alanine. J. A. SÁNCHEZ (Semena méd., 1931, i, 651—653).—(a) Alanine (0.01 g.) is heated at 100° for 1 min. with KMnO_4 solution (1%); after cooling, oxalic acid (0.05 g.) is added, followed by EtOH (2 c.c.), *o*-nitrobenzaldehyde (0.02—0.03 g.), and NaOH (30% solution, 10 drops); indigotin is extracted by shaking with CHCl_3 . (b) CHI_3 is formed when alanine is heated with NaOCl, and NaOH and I in KI are added. (c) The products of dry distillation of alanine contain NH_2Et , which is detected with Bouchardat's, Dragendorff's, or Sanchez' reagents.

CHEMICAL ABSTRACTS.

Aminolysis of alanine. S. MOLINARI.—See this vol., 1015.

α -Cyano- β -methylbutyric acid. F. C. B. MARSHALL (J. Amer. Chem. Soc., 1931, 53, 2415—2416).—The isolation of α -cyano- β -methylbutyric acid (cf. A., 1913, i, 1038) in a cryst. form, m. p. 31°, is described.

H. A. PIGGOTT.

Rotatory power of ricinoleamide. E. ANDRÉ and C. VERNIER (Compt. rend., 1931, 193, 178—180).—Repeated treatment of castor oil with NH_3 in EtOH gives fractions of ricinoleamide of gradually increasing dextrorotatory power.

A. A. LEVI.

Hypoglycæmia-producing substances. II. ψ -Thiocarbamide, amidine, and carbamide derivatives. S. KAWAI, T. HOSONO, Y. SHIKINAMI, and S. YONECHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 16, 9—16).—Pentamethylene dichloride and thiocarbamide in boiling BuOH yield *pentamethylene α -di- ψ -thiocarbamide dihydrochloride* $[\text{CH}_2]_5[\text{SC}(\text{NH})\cdot\text{NH}_2]_2\cdot 2\text{HCl}$, m. p. 206° (+ H_2O), 210° (anhyd.), as well as a by-product, m. p. 144°. Decane- α -diol (improved prep.) is converted by SOCl_2 into *decamethylene dichloride* (I), b. p. 147—148°/11 mm., which does not react with thiocarbamide in boiling BuOH, but in a sealed tube at 175—190° gives NH_4Cl , a colourless solid, m. p. 53—53.5°, containing N but not S or Cl, and a liquid, b. p. 174—179°/14 mm. (I) with NaI in COMe_2 gives the crude di-iodide, which with thiocarbamide in boiling isoamyl alcohol, followed by treatment with AgCl, leads to *decamethylene- α -di- ψ -thiocarbamide dihydrochloride*, m. p. 186° (picrate, m. p. 112—112.5°). *Hexane-*, m. p. 230—231° (decomp.), and *octane-*, m. p. 185—186°, - $\omega\omega'$ -*di- ψ -thiocarbamide dihydrochlorides* are similarly prepared. *Hexane-*, decomp. 302—303°, *heptane-*, m. p. 214—215°, *octane-*, decomp. 191—192°, *nonane-*, decomp. 160—161°, and *decane-*, m. p. 175—175.5°, - $\omega\omega'$ -*di-amidine dihydrochlorides* are prepared from the corresponding polymethylene dicyanides through the crude di-imino-ether dihydrochlorides, decomp. 126—127°, 115—116°, 106—107°, 72—75°, and 112°, respectively. The polymethylenedi- ψ -thiocarbamide dihydrochlorides and polymethylenedi-amidine hydrochlorides have $\frac{1}{10}$ — $\frac{1}{15}$ the hypoglycæmic action of the corresponding diguanidine dihydrochlorides, but have the same toxicity; the corresponding dicarbamides are, however, less toxic, but not being H_2O -sol., they cannot be administered.

J. D. A. JOHNSON.

Oxycyanogen. I. H. HUNT (J. Amer. Chem. Soc., 1931, 53, 2111—2115; cf. A., 1925, ii, 568).—CNO cannot be obtained by the methods described by Lidov (A., 1913, i, 252, etc.), and the reactions and equations recorded have not been confirmed.

J. G. A. GRIFFITHS.

Organic gold compounds. II. Preparation and properties of gold-carbon compounds of the type R_2AuX and RAuX_2 . M. S. KHARASCH and H. S. ISBELL (J. Amer. Chem. Soc., 1931, 53, 2701—2713).—Compounds of the type AuR_2X cannot be prepared by the Grignard method when R is a strongly electronegative radical, e.g., Ph. The following gold dialkyl halides are prepared and converted into the cyanides by AgCN in Et_2O or C_6H_6 (the decomp. temps. of the compounds are given in parentheses): *Au diethyl chloride*, m. p. 48° (48°), bromide,

m. p. 58° (58°), and *cyanide*, m. p. 92° (92—160°); *Au di-n-propyl chloride*, an oil (107—120°), *bromide*, an oil (95°), and *cyanide*, m. p. 84° (128—147°); *Au diiso-propyl chloride* (95—120°), *bromide* (100—130°), and *cyanide*, m. p. 88—90° (121—123°); *Au di-n-butyl bromide*, an oil (65°), and *cyanide* (125—130°); *Au diisobutyl bromide and cyanide*, m. p. 112—113° (160°); *Au diisoamyl bromide and cyanide*, m. p. 70° (135—140°); *Au dicyclohexyl chloride* (180—190°), *bromide* (140—148°), and *cyanide*, m. p. 152° (slight decomp.) (155°); *Au dibenzyl chloride* (70—110°), *bromide* (77°), and *cyanide* (122°); *Au di- β -phenylethyl bromide*, m. p. 112—115° (105—115°), and *sulphate* (105—108°) (from the bromide and Ag_2SO_4). *Au dicyclohexyl thiosalicylate*, decomp. 173—180°, is prepared from the corresponding chloride and thiosalicylic acid in C_6H_6 and alcoholic KOH. The above β -phenylethyl derivatives are disulphonated (*Ca* salts isolated) by oleum in CHCl_3 . The cyanides are more stable than the halides, and all the above compounds are more stable towards reducing agents than Au^{III} salts. *Au β -phenylethyl*, decomp. 150—160°; *benzyl*, decomp. about 140°, and *cyclohexyl*, decomp. 150°, *dibromides*, prepared from the appropriate AuR_2Br and Br_2 in CHCl_3 , are very unstable towards reducing agents. Solutions of these dibromides in CHCl_3 are intensely coloured; the colour is discharged by unsaturated substances indicating addition to the double linking. Compounds of the type AuR_3 could not be prepared.

H. BURTON.

Magnesium cyclohexyl chloride and bromide. H. GILMAN and E. A. ZOELLNER (J. Amer. Chem. Soc., 1931, 1945—1948).—Details are given for the prep. of Mg cyclohexyl chloride and bromide in yields of 96.5 and 92%, respectively. Chlorides are preferred to other halides in the prep. of Grignard reagents.

H. BURTON.

Transformation of benzene into methane. A. MAILHE and CREUSOT (Compt. rend., 1931, 193, 60—63).—A quant. study of the formation of CH_4 on passing C_6H_6 and H_2 over heated Ni showed that the yield (1) depended on the mode of prep. of the catalyst, (2) was highest when the C_6H_6 was free from thiophen, and (3) commenced below 250°, reached a max. at 280°, then falling until 310°, and subsequently rising (sometimes to a max.). The activity of the catalyst decreases with time at 280°, owing to deposition of a yellow substance, sol. in COMe_2 , but is restored by raising the temp. to 320—330°, the yellow substance then disappearing. The max. yield obtained was 82.3%.

R. S. CAHN.

Conversion of toluene and [*m*]-xylene into methane. A. MAILHE and CREUSOT (Compt. rend., 1931, 193, 176—178).—Hydrogenation of PhMe and *m*-xylene gives a max. yield of CH_4 at two different temps., between which a waxy substance is also formed.

A. A. LEVI.

Photochemical oxidation of organic hydrocarbons. II. Toluene, and the oxidation of benzaldehyde. C. J. KOTHARI and H. E. WATSON.—See this vol., 1019.

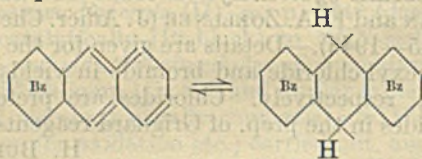
Addition of free radicals to unsaturated compounds. J. B. CONANT and H. W. SCHERP (J. Amer.

Chem. Soc., 1931, 53, 1941—1944).—Prolonged interaction of hexaphenylethane and isoprene in N_2 gives 45% of $\alpha\alpha\alpha\zeta\zeta$ -hexaphenyl- γ -methyl- Δ^7 -hexene, m. p. 166°, oxidised by O_3 to $\beta\beta\beta$ -triphenylpropionic acid and $\beta\beta\beta$ -triphenylethyl methyl ketone (I), m. p. 140.5°; (I) is synthesised from $\beta\beta\beta$ -triphenylpropionyl chloride and $ZnMeCl$. 1:4-Addition of CPh_3 occurs. $\beta\gamma$ -Dimethylbutadiene and CPh_3 afford a hydrocarbon, $C_{44}H_{10}$, m. p. 240° (decomp.), oxidised by O_3 to (I).

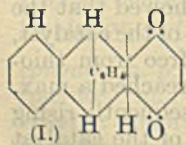
H. BURTON.

1-Ethyl-naphthalene and its hydrogenation products. G. LÉVY (Compt. rend., 1931, 193, 174—176; cf. this vol., 949).—Catalytic reduction of 1-acetylnaphthalene (A., 1897, i, 75) at 200° gives 1-ethyl-naphthalene, m. p. 15°, b. p. 256.5°/756 mm. (purified through the picrate, m. p. 98.5°), and a little 1-ethyltetrahydronaphthalene. Reduction of 1-ethyl-naphthalene with Na in amyl alcohol gives the dihydro-derivative, b. p. 246°/758 mm. With H_2 and Ni at 200° it gives the tetrahydro-derivative, b. p. 115°/17 mm., 237.5°/764 mm., whilst at 160° 1-ethyldecahydronaphthalene, b. p. 222°/760 mm., is obtained. Hydrogenation is more difficult than for the 2-isomeride, whilst the exaltation of the mol. refractivity is less for the 1- than for the 2-series. A. A. LEVI.

Polynuclear, aromatic hydrocarbons and their derivatives. IX. Constitution of anthracene. E. CLAR (Ber., 1931, 64, [B], 1676—1688).—Further evidence is adduced in favour of the view that anthracene is an equilibrium mixture,

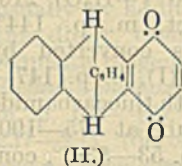


Anthracene is converted by *p*-benzoquinone in boiling $C_6H_4Me_2$ into *p*-benzoquinoneanthracene (I), decomp. 250° after darkening at 207°. It shows no tendency towards dissociation, does not react with picric acid, gives a normal mol. wt. in camphor, and is converted by excess of CrO_3 into anthraquinone. Its absorption spectrum is intermediate between those of anthracene and dihydroanthracene. Continuous oxidation with CrO_3 converts it into endo-9:10-*o*-phenylene-9:10-dihydro-1:4-anthraquinone (II), m. p. 289—294° (decomp.) according to the rate of heating, which yields an almost black quinhydrone with quinol. It is converted by phenylhydrazine or $Na_2S_2O_4$ into 1:4-dihydroxy-endo-9:10-*o*-phenylene-9:10-dihydroanthracene, m. p. 345° (decomp.) after darkening at 340° (diacetate, m. p. 253—254°), transformed by distillation with Zn into anthracene and quinol. It can also be obtained by the action of a trace of HBr on *p*-benzoquinoneanthracene. 2:3-Dichloro-9:10-*o*-phenylene-9:10-dihydroanthraquinone, m. p. 270° (partial decomp.), is prepared by chlorinating *p*-benzoquinoneanthracene or endo-9:10-*o*-phenylene-9:10-dihydro-1:4-anthraquinone in boiling AcOH or from anthracene and chloroanil in boiling AcOH or $C_6H_4Me_2$ or without solvent. With NH_2Ph in AcOH it affords

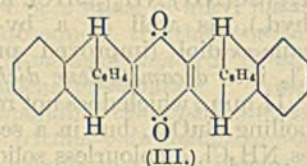


(I.)

2-chloro-3-anilino-endo-9:10-*o*-phenylene-9:10-dihydro-1:4-anthraquinone, m. p. 235—239° (decomp.) according to the rate of heating. 2:3-Dibromo-endo-9:10-*o*-phenylene-9:10-dihydro-1:4-anthraquinone, m. p. 320—325° (decomp.), is described. 9:10-Diphenylanthracene and *p*-benzoquinone in boiling $C_6H_4Me_2$ yield the corresponding quinhydrone, m. p. 195° after softening at 155°, which readily decomposes into its components. endo-9:10-*o*-Phenylene-9:10-dihydro-1:4-anthraquinoneanthracene, becoming brown at 265° and blackening without melting at 370°, prepared from its components in boiling $C_6H_4Me_2$, is converted by Br in boiling AcOH into endo-1:4:5:8-di-*o*-phenylene-2:3:6:7-dibenzanthraquinone (III), not molten below 370°, reduced by phenylhydrazine to endo-1:4:5:8-di-*o*-phenylene-2:3:6:7-dibenzanthraquinol, darkening without melting at 360—370°.



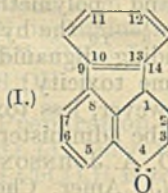
(II.)



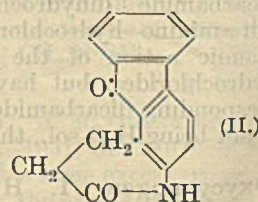
(III.)

The products obtained previously from 2:3:6:7-dibenzanthracene-9:10-diyl and *p*-benzoquinone or chloroanil are not quinol ethers, but 2:3:6:7-dibenzanthracene-benzoquinone or -chloranil, respectively. H. WREN.

Fluoranthene and its derivatives. III. J. VON BRAUN and G. MANZ (Annalen, 1931, 488, 111—126).—Under certain conditions mono-substitution in fluoranthene can be effected, the entering group being considered to occupy position 4 for the following reasons. Since the Br atom of bromofluoranthene is readily replaced by H, it is apparently attached to the $C_{10}H_8$ nucleus. 4-Keto-1:2:3:4-tetrahydrofluoranthene (I) is reduced in feebly acid solution to 4-hydroxy-



(I.)



(II.)

1:2:3:4-tetrahydrofluoranthene, m. p. 130—134°, apparently stereoisomeric with the product m. p. 136—139°, of the hydrogenation of 4-hydroxyfluoranthene and yielding the same phenylcarbamide, m. p. 274—275°. 4-Aminofluoranthene is reduced to 4-amino-5:6:7:8-tetrahydrofluoranthene, m. p. 114—116°, the Ac derivative, m. p. 224—225°, of which is oxidised to a ketocarboxylic acid; the deacetylated acid passes by spontaneous loss of H_2O into the lactam (II), m. p. 346—348°.

4-Bromofluoranthene, b. p. 205—207°/0.2 mm., m. p. 103°, prepared by adding 1 mol. of Br in CS_2 to a boiling solution of fluoranthene in CS_2 containing a little PBr_3 and irradiated with a quartz lamp, is separated from dibromo-compounds by means of its

picrate, m. p. 129—130°. It is very resistant towards alkali hydroxide, does not react with Mg, and is reduced by Na-Hg to 1:2:3:4-tetrahydrofluoranthene, m. p. 73—74°. It does not react with K phthalimide, but with CuCN at 260° yields 4-cyano-fluoranthene, m. p. 112°. Treatment of fluoranthene in CHCl_3 with ClSO_3H yields a mixture of isomeric monosulphonic acids which by successive treatment with NaCl, POCl_3 , and NH_2Et in C_6H_6 affords fluoranthene-4-sulphonethylamide, m. p. 167—168°, transformed by KCN and NaCN into 4-cyanofluoranthene. The nitrile is hydrolysed by conc. HCl at 130° to fluoranthene-4-carboxylic acid, decomp. 264—275° [*Et* ester, b. p. 250—253°/0.5 mm., m. p. 73—75°; corresponding amide (from the acid by means of SOCl_2 and NH_3), m. p. 271—273°]. 4-Hydroxyfluoranthene, m. p. 185—187°, obtained from the sulphonethylamide and KOH at 290—340°, is converted by NH_3 in EtOH at 300° into 4-aminofluoranthene, m. p. 111—112° (hydrochloride, m. p. 285—288°; *Ac* compound, 241—242°), which cannot be prepared from the sulphomethylamide and NaNH_2 . Treatment of fluoranthene with HNO_3 (*d* 1.42) in glacial AcOH affords 4-nitrofluoranthene, m. p. 159—160°, reduced by SnCl_2 and HCl to 4-aminofluoranthene, from which 4-hydroxyfluoranthene is prepared by the action of *N*-HCl at 230°. H. WREN.

Molecular compounds of the perylene series.

K. BRASS and E. TENGLER (Ber., 1931, 64, [B], 1650—1653).—Perylene and picric acid in C_6H_6 yield the compounds $\text{C}_{20}\text{H}_{12}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m. p. 221°, and $\text{C}_{20}\text{H}_{12}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_2$, m. p. 154—155°. The following substances are described: ($\text{R}=\text{C}_{20}\text{H}_{12}$); $2\text{R}\cdot\text{SbCl}_5$, $\text{R}\cdot 2\text{SnCl}_4$, $\text{R}\cdot\text{FeCl}_3$; ($\text{R}'=\text{perylenequinone}$) $\text{R}'\cdot\text{SbCl}_5$; $\text{R}'\cdot\text{SnCl}_4$; $2\text{R}'\cdot\text{FeCl}_3$; $2\text{R}'\cdot\text{AlCl}_3$. Dibromo-3:10-perylenequinone and bromodi-3:10-perylenequinone sulphide yield the compounds $\text{C}_{20}\text{H}_8\text{O}_2\text{Br}_2\cdot\text{SbCl}_5$ and $\text{C}_{40}\text{H}_{17}\text{O}_4\text{BrS}\cdot 2\text{SbCl}_5$. H. WREN.

Reduction of benzylideneaniline, benzophenoneanil, and benzilaniol by the system $\text{Mg}+\text{MgI}_2$. W. E. BACHMANN (J. Amer. Chem. Soc., 1931, 53, 2672—2676).—Benzylideneaniline, Mg, and MgI_2 in $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$ give the compound $(\cdot\text{CHPh}\cdot\text{NPh}\cdot\text{MgI})_2$, hydrolysed by dil. AcOH to dianilindibenzyl. Similarly, benzophenoneanil gives $\text{IMg}\cdot\text{CPh}_2\cdot\text{NPh}\cdot\text{MgI}$ (hydrolysed to benzhydriylaniline), whilst fluorenoneanil yields 9-fluorenylaniline. Benzilaniol is converted into (probably) $\text{IMgO}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{NPh}\cdot\text{MgI}$ (I), hydrolysed to desylaniline and converted by I or O_2 into benzilaniol. Hydrolysis of the product from (I) and CO_2 gives desylaniline and CO_2 . H. BURTON.

α -Phenylethylguanidine and α -phenylethyldiguanide. F. BOBECK (Annalen, 1931, 487, 294—300).—dl- α -Phenylethylguanidine (I), but not dl- α -phenylethyldiguanide (II), is resoluble by mandelic acid, and thus constitutes a readily accessible, optically active base, nearly as strong as KOH. dl-Phenylethylammonium chloride (III) and cyanamide at 120° gave (I), hygroscopic, cryst. No racemisation occurs with active material if the reaction is carried out at 100°, and the *l*-base has $[\alpha]_D -29.3^\circ$. The following

salts are described: *chloride*, *l*-, m. p. 177—178°; *sulphate*, *dl*-, m. p. 242°; *nitrate*, *dl*-, m. p. 123—124°; *carbonate*, *dl*-, m. p. 184° (sealed tube); *hydrogen carbonate*, *dl*-, m. p. 182° (sealed tube); *oxalate*, *dl*-, m. p. 240°, *d*- and *l*-, m. p. 250°; *acetate*, *l*-, m. p. 160—170°; *picrate*, *dl*-, m. p. 175.5°, *d*- and *l*-, m. p. 150°; *chromioxalate*, $\text{Cr}(\text{C}_2\text{O}_4)_3\cdot(\text{C}_9\text{H}_{13}\text{N}_3)_3\cdot 10\text{H}_2\text{O}$ (no loss of wt. at 105°). Mandelic acid is resolved by the active bases. The CuSO_4 compound ($+\text{H}_2\text{O}$) of (II) is obtained (*a*) from α -phenylethylamine, dicyanodiamide, and cryst. CuSO_4 kept at room temp. for several months, and (*b*) from (III) and dicyanodiamide at 120—140°, followed by ammoniacal CuSO_4 . The following derivatives of (II) are also described: NiSO_4 compound ($+3\text{H}_2\text{O}$); *hydrogen sulphate*, m. p. 220°. The nitrate of (I) has μ_x 101.5, whence $U_f=30.5$.

R. S. CAHN.

Quaternary ammonium salts from tertiary amines and benzenesulphonyl chloride. F. SCHLEGEL (Ber., 1931, 64, [B], 1739—1743).—Benzenesulphonyltrialkylammonium salts are formed from the sulphonyl chloride and strong tert. bases in presence of H_2O , but reaction does not take place with weak bases, e.g., pyridine and NPhMe_2 . The following are described: *benzenesulphonyldimethylethylammonium chloroplatinate*, incipient decomp. 211°, *chloride*, decomp. about 227°, *picrate*, m. p. 120—124°, *chloroaurate*, m. p. 167° after softening at 145°, *perchlorate*, m. p. 123—126° (decomp.); *dimethylethylammonium picrate*, m. p. 195°, and *chloroaurate*, m. p. 206° (decomp.); *benzenesulphonylbenzyltrimethylammonium chloroaurate*, m. p. 136—138° (decomp.); *benzyltrimethylammonium chloroaurate*, m. p. 142—143°, and *chloroplatinate*, m. p. 192°; *benzyltrimethylammonium benzenesulphonate*, m. p. 137°, or ($+\text{H}_2\text{O}$), m. p. about 75°, from benzyltrimethylamine and Me benzenesulphonate in anhyd. Et_2O , converted into the corresponding *chloroaurate*, m. p. 137—140° (decomp.), *chloroplatinate*, m. p. 233—236° (decomp.), and *perchlorate*, m. p. 126—127°; *benzylammonium benzenesulphonate*, m. p. 190°. H. WREN.

2:7-Diaminofluorene as reagent for zinc, cadmium, and copper. J. SCHMIDT and W. HINDERER (Ber., 1931, 64, [B], 1793—1796).—Fluorene is converted by HNO_3 (*d* 1.52) and glacial AcOH into 2:7-dinitrofluorene, m. p. 269° (decomp.), reduced by Sn and fuming HCl to 2:7-diaminofluorene hydrochloride (corresponding *chlorostannate*; 2:7-diaminofluorene, m. p. 165°). In about 1% solution in EtOH the base gives an immediate ppt. of the *sulphate* with H_2SO_4 or a sol. *sulphate*. The chlorides or nitrates must therefore be used in investigating its behaviour towards salts. With MgCl_2 , MnCl_2 , CoCl_2 , $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, CrCl_3 , $\text{Cd}(\text{OAc})_2$, or $\text{Zn}(\text{OAc})_2$ ppts. or colorations are not observed. Even in very dil. solutions ZnCl_2 and CdCl_2 or solutions of Zn or Cd salts in presence of NaCl yield white ppts. of $\text{C}_{13}\text{H}_{12}\text{N}_2\cdot\text{ZnCl}_2$ and $\text{C}_{13}\text{H}_{12}\text{N}_2\cdot\text{CdCl}_2$, respectively. CuCl_2 yields a dark blue ppt. $\text{C}_{13}\text{H}_{12}\text{N}_2\cdot\text{CuCl}_2$, appearing in very dil. solution as a blue to green colour; the reaction is more sensitive than that with NH_3 . As the base is readily precipitated from EtOH by H_2O the aq. solution of the salt should be diluted with twice its vol. of EtOH. H. WREN.

Reduction of aromatic nitro- and nitroso-compounds with sodium alkoxides. II. F. B. DAINS and W. O. KENYON (J. Amer. Chem. Soc., 1931, 53, 2357—2364).—The reducing action of a series of alkoxides and Na derivatives of ketones and ketonic esters on NO_2 -compounds, PhNO , and *p*-nitrosotoluene and -dimethylaniline is described. The reaction is, in the cases tried, catalysed by org. bases. In general, amines and azoxy-compounds are produced, but the polyhydric alcohols tend to give azo-derivatives. *p*-Nitrotoluene and its derivatives form considerable amounts of stilbenes, *m*-nitrobenzaldehyde gives *m*-nitrobenzoic acid almost quantitatively, and 3:4-dichloronitrobenzene gives 3:4:3':4'-tetrachloroazoxybenzene, m. p. 137—138°, with no evidence of the formation of 3-chloro-4-nitrophenyl ethers (cf. A., 1929, 54). Glycol and glycerol as reducing agents react more slowly than the monohydric alcohols, and are oxidised to oxalic and volatile org. acids; deoxybenzoin is converted into benzilic acid. Et sodioacetate, in contrast to benzoylactic and malonic esters, reduces *p*-chloronitrobenzene to NH_2Ph .

The formation of amino-acids appears to be confined to *o*-halogenonitrobenzenes (cf. A., 1928, 1366), and propyl or higher alcohols. The interaction of 2:5-dibromonitrobenzene with NaOPr^a gives α -2:5-dibromoanilinopropionic acid, m. p. 156°, also obtained from 2:5-dibromoaniline and α -bromopropionic acid; α -4-chloro-*m*-toluidinopropionic acid, m. p. 158°, is similarly prepared. Addition of aq. Br_2 to 2:5-dibromoaniline in dil. H_2SO_4 gives 1:2:3:5-tetrabromoaniline, m. p. 118°. H. A. PIGGOTT.

Constitution of a bromonitroazoxybenzene. D. BIGIARI [with C. ALBANESE and I. POGGI] (Gazzetta, 1931, 61, 392—396).—Bromo- α -*p*-nitroazoxybenzene (I), m. p. 135—137° (A., 1913, i, 1110), by reduction gives NH_2Ph and bromo-*p*-phenylenediamine (hydrochloride, blackens without melting at 250°; Bz_2 derivative, m. p. 235°), showing the Br atom to be in the same nucleus as the NO_2 group. *o*-Bromo-*p*-nitroaniline is oxidised by H_2SO_5 to *o*-bromo-*p*-nitronitrosobenzene, m. p. 123°, which, by condensation with NH_2Ph and oxidation with peracetic acid, gives (I), for which the formula $\text{Ph}\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_3\cdot\text{Br}\cdot\text{NO}_2$ is suggested. E. E. J. MARLER.

Diphenyl derivatives. J. FELDMANN (Helv. Chim. Acta, 1931, 14, 751—778).—Diphenyl-4:4'-disulphonic acid (dichloride, m. p. 203°) is converted by nitration into the 2:2'-dinitro-derivative [Na (+2 H_2O) and K salts; dichloride, decomp. 151°; dianilide, m. p. 104—104.5° (sinters 72—72.5°)], which is reduced by Fe and AcOH to 2:2'-diaminodiphenyl-4:4'-disulphonic acid (H_2O) [anilide dihydrochloride is obtained by reduction of the nitroanilide with $\text{Fe}(\text{OH})_2$], the constitution of which is proved by its conversion into carbazole by 20% HCl at 230°. 2:2'-Di-*p*-nitrobenzamidodiphenyl-4:4'-disulphonic acid is reduced by Fe and HCl to the di-*p*-aminobenzamidoderivative. The 2:2'-dihydrazine (dihydrochloride) may be prepared by reducing the diazotised diamino acid with SnCl_2 (but not with Na_2SO_3); it combines with Et acetoacetate to form a bispyrazolone (+2AcOH). The following new dyes are described (shades are on wool): from tetrazotised 2:2'-diaminodiphenyl-

4:4'-disulphonanilide and 2 mols. of: α -naphthol-4-sulphonic acid (brick-red); α -naphthol-3:8-disulphonic acid (brownish-red); 8-acetamido- α -naphthol-3:6-disulphonic acid (bordeaux); β -naphthol-6:8-disulphonic acid (brown to red; acid-coupled); from tetrazotised 2:2'-diaminodiphenyl-4:4'-disulphonic acid: β -naphthol (orange); 1-phenyl-3-methyl-5-pyrazolone (yellow); 8-acetamido- α -naphthol-3:6-disulphonic acid (reddish-violet); salicylic acid (orange-brown); and from tetrazotised 2:2'-di-*p*-aminobenzamidodiphenyl-4:4'-disulphonic acid and: β -naphthol (orange-brown); phenylmethylpyrazolone (yellow); 1:8-aminonaphthol-3:6-disulphonic acid (brownish-violet); α -naphthol-3:8-disulphonic acid (reddish-orange); 6-phenylamino- α -naphthol-3-sulphonic acid (yellowish-red); salicylic acid (orange); bispyrazolone (above) (yellow). The dye from 2 mols. of diazobenzene and the bispyrazolone is yellow. The majority of these dyes are characterised by poor affinity. H. A. PIGGOTT.

2:4:6-Trichlorophenylhydrazine. F. D. CHATAWAY and H. IRVING (J.C.S., 1931, 1740—1743).—2:4:6-Trichlorophenylhydrazine, m. p. 143—144° (decomp.) (β -Ac, m. p. 157°, β -Bz, m. p. 163.5°, and β -Bz- α -Ac, m. p. 156°, derivatives; hydrochloride, m. p. above 350°), is prepared by reduction of 2:4:6-trichlorobenzene diazonium chloride with $\text{SnCl}_2\cdot\text{HCl}$. Citraconyl-2:4:6-trichlorophenylhydrazide, m. p. 166—167° (decomp.), and cinnamaldehyde-, m. p. 104—105°; benzaldehyde-, m. p. 91—92°; salicylaldehyde-, m. p. 98.5—99.5°; 2:4-dinitrobenzaldehyde-, m. p. 109—110°; 2:4:6-trinitrobenzaldehyde-, m. p. 145—146°; acetone-, m. p. 58—59°; benzophenone-, m. p. 106—107°; mesoxalic acid-, m. p. 183° (decomp.), and pyruvic acid-2:4:6-trichlorophenylhydrazone, m. p. 126—127°, are described. H. A. PIGGOTT.

Isomerism of hydrazones. II. Molecular compounds of stereoisomeric hydrazones. M. BUSCH, L. WESELY, and O. KÜSPERT (Ber., 1931, 64, [B], 1589—1596; cf. A., 1925, i, 40).—The possibility that isomerism of hydrazones $\text{NHR}\cdot\text{N}:\text{CPh}\cdot\text{CH}_2\cdot\text{NHR}$ is due to the existence of a form $\text{R}\cdot\text{N}:\text{N}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NHR}$ is excluded by the production of isomerides with *as*-dialkylhydrazines. Since the compounds do not react with aldehydes, the possible existence of desmotropes, $\text{NHR}\cdot\text{NH}\cdot\text{CPh}:\text{CH}\cdot\text{NHR}$, is negated. The hydrazones form mol. compounds of the two isomerides, the relationships resembling somewhat those observed with optically active and racemic compounds. Phenacyl-*p*-toluidine and *as*-phenylbenzylhydrazine in CHCl_3 -EtOH in presence of AcOH give bimol. phenacyl-*p*-toluidinephenylbenzylhydrazone, m. p. 141°. Cautious crystallisation of the substance from CHCl_3 -EtOH leads to its separation into the unimol. *n*-form (? *anti*-form), m. p. 118°, and *h*-form (? *syn*-variety), m. p. 127°. Boiling AcOH causes partial isomerisation of the *n*- to the *h*-form. Addition of ligroin to a solution of equal amounts of the *n*- and *h*-varieties in C_6H_6 results in separation of the bimol. form. In EtOH the isomerides do not react with PhCHO or CH_2O in presence of AcOH or HCl. *n*-Phenacyl-*p*-toluidinephenylmethylhydrazone, m. p. 155.5°, is the sole product isolated from *as*-phenylmethylhydrazine and phenacyl-*p*-toluidine in CHCl_3 containing AcOH,

whereas in EtOH containing AcOH at 60—65° the *h*-hydrazone, m. p. 160—161°, is also produced. Partial isomerisation of the *n*- to the *h*-compound occurs in boiling AcOH. The *dimeride*, m. p. 176°, is obtained from the simpler isomerides in C₆H₆-ligroin. According to conditions, the action of phenacyl-*p*-phenetidide and *as*-phenylbenzylhydrazine affords the separate *n*-form, m. p. 119°, and *h*-variety, m. p. 126°, of phenacyl-*p*-phenetididephenylbenzylhydrazone or the bimol. substance, m. p. 134° (existing as its components in C₆H₆); the last-named substance is obtained from its components by the method described above. Partial isomerisation of the *n*-hydrazone occurs in boiling EtOH. The *h*-form, m. p. 121°, and *n*-variety, m. p. 93—94°, of phenacyl-*N*-methylanilinephenylbenzylhydrazone are described; the corresponding bimol. product could not be obtained. H. WREN.

Constitution of normal diazotates. A. ANGELI and Z. JOLLES (Gazzetta, 1931, 61, 397—404; cf. A., 1930, 1428).—A reply to Hantzsch (this vol., 614) refuting that author's arguments in favour of the stereoisomerism of diazohydroxides.

E. E. J. MARLER.

Bromination of 1-diazo-β-naphthol-4-sulphonic acid. P. RUGGLI and M. MICHELS (Helv. Chim. Acta, 1931, 14, 779—783).—The technical bromo-derivative of diazo-β-naphthol-4-sulphonic acid, prepared by bromination in ClSO₃H or H₂SO₄, is converted by Cu₂O in EtOH into 6-bromo-β-naphthol-4-sulphonic acid (*Na* salt), identified by its conversion by Na—Hg in feebly acidic solution into 6-bromo-β-naphthol and β-naphthol, and by its oxidation with alkaline KMnO₄ to 4-bromophthalic acid; it is therefore the 6-bromo-derivative. H. A. PIGGOTT.

Cyclic esters of sulphuric acid. I. Methylene sulphate. W. BAKER (J.C.S., 1931, 1765—1771).—Methylene sulphate (convenient prep. described) reacts with pyrocatechol and protocatechualdehyde (but not the acid) with formation of methylene ethers. With monohydric phenols the ethers CH₂(OAr)₂ are formed, of which the following are new: *di*-*o*-, m. p. 129°, *-m*-, m. p. 112°, and *-p*-nitrophenyl, m. p. 147°, *dianisyl*, m. p. 54°, and *di*-*p*-acetamidophenyl, m. p. 191—192°, *methylene ethers*; *di*-*p*-aminophenyl *methylene ether*, m. p. 103°, is prepared by alkaline hydrolysis of the last-named. Resorcinol Me ether did not give a definite product. Glycols give cyclic ethers, e.g., *pinacol methylene ether*, m. p. 12°, b. p. 125°/752 mm.; saligenin gives 1:3-benzdioxin and *di*-*o*-(*hydroxymethylphenoxy*)methane, m. p. 118°. H. A. PIGGOTT.

Catalytic reduction of mixtures of *p*-nitro- and -nitroso-phenols with ketones. R. T. MAJOR (J. Amer. Chem. Soc., 1931, 53, 2803—2804; cf. this vol., 837).—Catalytic reduction of a mixture of *p*-nitrosophenol and COMe₂ at room temp. gives *p*-isopropylaminophenol, which is not formed under similar conditions from *p*-aminophenol and COMe₂. *p*-Hydroxyphenylhydroxylamine is probably an intermediate in the first case (cf. *loc. cit.*).

H. BURTON.

Chlorine derivatives of benzylphenols. I. Dichloro-derivatives of *o*- and *p*-benzylphenols. R. C. HUSTON and E. F. ELDRIDGE (J. Amer. Chem. Soc., 1931, 53, 2260—2264).—Chlorination of 4-

hydroxydiphenylmethane in CHCl₃ gives the 3:5-dichloro-derivative, m. p. 58—58.5° (*benzoate*, m. p. 98—99°; *benzenesulphonate*, m. p. 93—94°; *p*-toluenesulphonate, m. p. 120—121°), also obtained, together with 2:6-dichlorophenyl benzyl ether, m. p. 39.5—40°, b. p. 194—196°/15 mm., by the Friedel-Crafts reaction with CH₂Ph·OH and 2:6-dichlorophenol. Chlorination of 2-hydroxydiphenylmethane in CHCl₃ yields 3:5-dichloro-2-hydroxydiphenylmethane, m. p. 77—77.5° (*benzoate*, m. p. 66—67°; *benzenesulphonate*, m. p. 110—110.5°; *p*-toluenesulphonate, m. p. 124.5—125°), also obtained, admixed with 2:4-dichlorophenyl benzyl ether, by interaction of CH₂PhCl and Na 2:4-dichlorophenoxide in PhMe. It was not found possible to chlorinate further these dichlorobenzylphenols. 2:4- and 2:6-Dichlorophenyl benzyl ethers are also obtained by interaction of the Na phenoxide and CH₂PhCl in MeOH. H. A. PIGGOTT.

Action of aromatic alcohols on aromatic compounds in presence of aluminium chloride.

VII. Condensation of benzyl alcohol with *p*-cresol. R. C. HUSTON and W. C. LEWIS (J. Amer. Chem. Soc., 1931, 53, 2379—2382).—The interaction of CH₂Ph·OH, *p*-cresol, and AlCl₃ in light petroleum below 30° gives 3-benzyl-*p*-cresol, m. p. 35—36° (previously described as a liquid) (*Bz*, m. p. 42—42.5°, b. p. 205—206°/5 mm., and 5-bromo-, m. p. 46—47°, derivatives; *benzenesulphonate*, b. p. 190—192°/2 mm., *p*-toluenesulphonate, m. p. 58—59°), and (presumably) 2:5-dibenzyl-*p*-cresol (*Bz* derivative, b. p. 243—245°/6 mm.). The same products are obtained from CH₂PhCl and Na *p*-tolylxide in PhMe (cf. A., 1925, i, 656). The orientation of the bromo-derivative is proved by its prep., together with a little of its benzyl ether, m. p. 40—41°, from 6-bromo-*p*-cresol, Na, and CH₂PhCl in PhMe. H. A. PIGGOTT.

Bromination of *m*-cresol. G. DARZENS and A. LÉVY (Compt. rend., 1931, 193, 292—294).—*m*-Cresol and Br in AcOH give 6-bromo-*m*-cresol, b. p. 135—137°/18 mm., m. p. 63° (*Ac*, b. p. 135—136°/17 mm., m. p. 10.5°, and *Bz*, m. p. 83°, derivatives; Me ether, b. p. 112°/14 mm., m. p. 9.5°, converted by the Grignard method into 5-methoxy-*o*-toluic acid). 5-Bromo-*m*-cresol could not be prepared by brominating either *m*-cresol or its acetate (cf. A., 1889, 389).

H. BURTON.

α-Naphtholsulphonic acids and derivatives. II. E. GEBAUER-FÜLNEGG and E. HAEMMERLE (J. Amer. Chem. Soc., 1931, 53, 2648—2653).—α-Naphthol-2:4:7-trisulphonyl chloride (A., 1929, 1440) is obtained from ClSO₃H and α-naphthol-2:4- or -4:7-disulphonic acid. Similarly, α-naphthol-4:6- and -6:8-disulphonic acids yield α-naphthol-4:6:8-trisulphonyl chloride, m. p. 217° (cf. *loc. cit.*), whilst the 3:8- and 4:8-disulphonic acids afford naphth-sultone-3-, m. p. 190—191°, and -4-sulphonyl chlorides, m. p. 195°, respectively. The α-naphtholtrisulphonyl chlorides, m. p. 203° and 140° (*loc. cit.*), are probably the 2:3:6- and 3 (or 2):5:7-derivatives, respectively. *O*-Carbethoxy-α-naphthol-3:8-, m. p. 180—181°, -4:8-, m. p. 177—179°, -3:6-, m. p. 95°, and -4:7-, m. p. 120°, -disulphonyl chlorides are prepared from the corresponding carbethoxynaphtholdisulphonic acids and PCl₅. H. BURTON.

Preparation of β -orcinol. A. SONN [with C. RIESZ and H. FISCHER] (Ber., 1931, 64, [B], 1847—1850).—2 : 5-Dimethyldihydroresorcinol, m. p. 175—176° after slight softening, is obtained by treatment of 5-methyldihydroresorcinol with MeI and 20% aq. KOH at 60—70°. Alternatively, *p*-xylylene is transformed, in 70% yield, by $\text{Na}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 followed by PbO_2 into *p*-xyloquinone, which with Ac_2O and conc. H_2SO_4 affords the triacetate of hydroxy-*p*-xyloquinol, m. p. 109—110°; this is partly hydrolysed to the diacetate, m. p. 190—192°, from which 2 : 5-dimethyldihydroresorcinol is derived by reduction with Na-Hg. 2 : 5-Dimethyldihydroresorcinol is transformed by Br in CHCl_3 into dibromo- β -orcinol, m. p. 154—155°, dihalogenated by H_2 in presence of Pd-CaCO₃, EtOH, and piperidine to β -orcinol. The last-named is converted by AlCl_3 , HCN, and HCl in C_6H_6 and subsequent hydrolysis of the imine hydrochloride into the corresponding aldehyde, m. p. 166°. H. WREN.

Substituted di- β -phenylethylamines and benzyl- β -phenylethylamines. J. S. BUCK (J. Amer. Chem. Soc., 1931, 53, 2192—2200).—The following Schiff bases are prepared by interaction of their components at 100° under reduced pressure until no more H_2O is evolved: *veratrylidene*-, m. p. 69°, and *anisylidene-homoanisylamine*, m. p. 74°; *piperonylidene*-, m. p. 101°, *anisylidene*-, m. p. 63°, and *veratrylidene-homoveratrylamine*, m. p. 83°; *veratrylidene- β -phenylethylamine*, m. p. 60°; and *piperonylidene-homopiperonylamine*, m. p. 114°. By reduction with PtO and H_2 these are converted into *veratrylhomoanisylamine*, b. p. 197°/0.48 mm. (*hydrochloride*, m. p. 223°; *hydrobromide*, m. p. 233°); *anisylhomoanisylamine*, m. p. 44° (*hydrochloride*, m. p. 271°; *hydrobromide*, m. p. 254°); *piperonyl*-, m. p. 34°, b. p. 203°/0.44 mm. (slight decomp. ?) (*hydrochloride*, m. p. 219°; *hydrobromide*, m. p. 204°; *hydriodide*, m. p. 198°); *anisyl*-, m. p. 47° (*hydrochloride*, m. p. 234°; *perchlorate*, m. p. 198°), and *veratryl-homoveratrylamine*, m. p. 79° (*hydrobromide*, m. p. 187°; *hydrogen oxalate*, m. p. 230°); *veratryl- β -phenylethylamine*, b. p. 182°/0.35 mm. (*perchlorate*, m. p. 177°; *hydriodide*, m. p. 170°); and *piperonylhomo-piperonylamine* (A., 1927, 1199; *hydrochloride*, m. p. 243°; *hydrogen sulphate*, m. p. indef.); *benzylhomoveratrylamine*, b. p. 178°/0.75 mm. (*hydrochloride*, m. p. 200°; *picrate*, m. p. 160°), is prepared similarly. The following were prepared by interaction of the appropriate phenylethyl halide and primary amine: β -phenylethylhomoveratrylamine, b. p. 178°/0.48 mm. (*hydrochloride*, m. p. 183°; *hydrobromide*, m. p. 172°); *dihomoveratrylamine*, b. p. about 240°/1.0 mm., m. p. 51° [*hydrochloride*, m. p. 196°; *hydriodide*, m. p. 182° (softens 175°)]; and di- β -phenylethylamine [*hydrochloride*, m. p. 233° (lit. 260°, 265°); *hydrobromide*, m. p. 193°].

The following were prepared by demethylation with aq. HI (colourless; *d* 1.7), conversion into the hydrochlorides being effected by AgCl: benzyl-3 : 4-dihydroxy- [*hydrochloride*, m. p. 87° (resolidifies 120° and re-melts 180°); *dipicrate*, $\text{C}_{15}\text{H}_{17}\text{O}_2\text{N}_2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m. p. 131°], piperonyl-3 : 4-dihydroxy- (*hydriodide*, m. p. 237°; *hydrochloride*, m. p. 219°), 4-hydroxybenzyl-4'-hydroxy- (this base alone is stable), m. p. 118° (decomp.) (*hydriodide*, m. p. 192°; *hydrochloride*,

m. p. 234°), 4-hydroxybenzyl-3' : 4'-dihydroxy- [*hydrochloride*, m. p. 200—205°; *dipicrate*, m. p. 97° (solidifies and re-melts about 140°)], 3 : 4-dihydroxybenzyl-4'-hydroxy- (*hydriodide*, m. p. about 163°; *hydrochloride*, m. p. 180°), and 3 : 4-dihydroxybenzyl-3' : 4'-dihydroxy- β -phenylethylamine [*hydrochloride* (+1 H_2O), m. p. 182°, anhyd.; *dipicrate*, m. p. 173°]; 3 : 4 : 3' : 4'-tetrahydroxydi- β -phenylethylamine [*hydriodide*, m. p. 187°; *hydrochloride* (+2.5 H_2O), m. p. 230°].

3 : 4-Dimethoxy- β -phenylethyl alcohol, b. p. 166—168°/8 mm., d_{20}^{25} 1.1426 (*p-nitrobenzoate*, m. p. 81°; *phenylcarbamate*, m. p. 98—99°), was prepared by action of HNO_2 on homoveratrylamine, and converted into the *chloride* (not purified) by PCl_5 in CCl_4 .

H. A. PIGGOTT.

3 : 3' : 5 : 5'-Tetranitro-2 : 2'-dimethoxydi-phenyl. J. VAN ALPHEN (Ber., 1931, 64, [B], 1819—1820).—The compound exists in dimorphous forms, m. p. 179° and 191°, respectively. The variety of higher m. p. is obtained by inoculating the molten product at 185° or its boiling saturated solution in AcOH which is immediately diluted with H_2O . Inoculation with the variety, m. p. 191°, of solutions of the form, m. p. 179°, in boiling CO_2 , AcOH, or EtOH and subsequent slow cooling leads to separation of the form of lower m. p. H. WREN.

Stereoisomerism of disulphoxides and related substances. VII. Further pairs of isomeric dioxides. VIII. Isomeric tetrabromides of a disulphide. G. M. BENNETT and F. S. STATHAM (J.C.S., 1931, 1684—1689, 1690—1692).—VII. The same dioxide, m. p. 150° (decomp.) (cf. A., 1879, 37), is obtained by oxidation of diethyldithiolethane with either H_2O_2 or HNO_3 . Oxidation of ethylenedithiol-diacetic acid with H_2O_2 in AcOH gives the α -, m. p. 147° (decomp.), and β -dioxides, m. p. 133° (decomp.) (cf. A., 1914, i, 384). *pp'*-Dinitrodiphenyldithiolethane with HNO_3 (*d* 1.2) gives a mixture of α -, m. p. 195—197° (decomp.) (*monohydrochloride*), and β -disulphoxide, m. p. 174° (decomp.) (*diacetate*; *dihydrochloride*), and with an excess of CrO_3 in AcOH gives the *disulphone*, m. p. 303° (decomp.). From the corresponding *oo'*-dinitro-compound are obtained the α -, m. p. 174° (decomp.), and β -disulphoxide, m. p. 160.5° (decomp.), and a *disulphone*, m. p. 265° (lit. 164°). *p-Nitrodiphenyldithiolethane*, m. p. 79—80°, prepared by interaction of PhSK with *p*-nitrophenyl β -chloroethyl sulphide in EtOH, is oxidised by H_2O_2 in AcOH to α -, m. p. 173°, and β -, m. p. 155°, -disulphoxides, and by CrO_3 to the *disulphone*, m. p. 238°. 1 : 4-Diethyldithiolbenzene, m. p. 46.5°, the product of ethylation of dithioquinol with EtI and KOH in EtOH, similarly gives α -, m. p. 155°, and β -, m. p. 134°, -disulphoxides. Oxidation of 1 : 3-dithiolan with H_2O_2 in AcOH under varying conditions gives an amorphous, m. p. 128° (decomp.), and a *cryst. dioxide*, m. p. 157—158.5° (decomp.), and a *trioxide*, m. p. 128° (decomp.).

VIII. The "dimorphous" tetrabromides, m. p. 105—110° and 86—90°, of *p*-dimethyldithiolbenzene (A., 1909, i, 643) are shown by mixed-f. p. depressions in C_6H_6 to be stereoisomerides. They are converted by Ag_2O in H_2O into α - and a mixture of α - and β -di-

oxides, respectively; conversely, dry HBr in CHCl_3 converts the α -dioxide into a mixture of both tetrabromides, and the β -dioxide into the latter only: they are therefore regarded as the α - and β -forms, respectively. On crystallisation from CHCl_3 the latter is converted into the former. With Br in C_6H_6 *p*-diethylthiolbenzene and dibenzylthiolethane give single *tetrabromides*, m. p. 73–78° (decomp.) and 80–85° (decomp.), respectively. H. A. PIGGOTT.

Stereochemistry of diphenylbenzenes. *cis*- and *trans*-1:3:4:6-Tetrahydroxydi-3'-bromomesitylbenzenes and corresponding acylates. XV. P. R. SHILDNECK and R. ADAMS (J. Amer. Chem. Soc., 1931, 53, 2203–2214).— α -3:6-Dihydroxy-2:5-di-3'-bromomesityl-*p*-benzoquinone, decomp. 397–400° (block) [Na_2 salt; Ac_2 , m. p. 272–273° (corr.), and *dibutylryl*, m. p. 167°, derivatives], is prepared from the corresponding 3:6-dibromo-compound (α) and NaOH in aq. EtOH. It is reduced by SnCl_2 and HCl in EtOH to α -1:3:4:6-tetrahydroxy-2:5-di-3'-bromomesitylbenzene, m. p. 360–362° (decomp., block) [Ac_4 , m. p. 294–295° (corr.), and *tetrabutylryl*, m. p. 124° (corr.), derivatives], from which it is regenerated by oxidation with *p*-benzoquinone. Similar reduction of its Ac_2 derivative gives α -3:6-diacetoxy-2:5-di-3'-bromomesitylquinol, m. p. 251–252° (corr.), which is readily hydrolysed to the $(\text{OH})_4$ compound or acetylated to its Ac_4 derivative. All the above acyl derivatives are prepared by means of the anhydride and pyridine. An exactly similar series of reactions has been carried out in the β -series without any evidence of conversion into α -derivatives. The following are described: β -3:6-dihydroxy-2:5-di-3'-bromomesityl-*p*-benzoquinone, m. p. 387–390° (decomp., block) [Na_2 salt; Ac_2 , m. p. 272–273° (corr.), and *dibutylryl*, m. p. 147° (corr.), derivatives]; β -1:3:4:6-tetrahydroxy-2:5-di-3'-bromomesitylbenzene, m. p. 355–357° (block) [Ac_4 , m. p. 269–270° (corr.), *tetrabutylryl*, m. p. 103° (corr.), and 3:6-diacetyl, m. p. 240–241° (corr.), derivatives]. On account of their higher m. p. the α - are regarded as the *trans*-forms. Confirmation of this is afforded by conversion of the β -dihydroxyquinone and its Ac_2 and *dibutylryl* derivatives into the α -forms by heating with mesitylene or glacial AcOH, or, in the case of the last, alone above its m. p. The Br_2 , $(\text{OH})_4$, and tetraacyloxy-derivatives, however, appeared to be stable under these conditions. The isomerism, in accordance with theory, disappears when the mesityl nuclei become symmetrically substituted; bromination of both α - and β -forms of the $(\text{OAc})_4$ -compound gives a single 1:3:4:6-tetra-acetoxy-2:5-di-3':5'-dibromomesitylbenzene, m. p. 347–348° (corr.).

H. A. PIGGOTT.

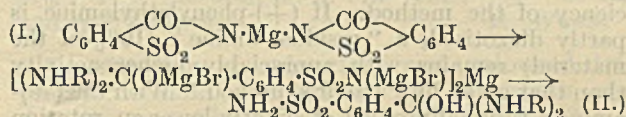
1-Trichloromethylcyclopentanol. C. E. GARLAND and W. A. WELCH (J. Amer. Chem. Soc., 1931, 53, 2414–2415).—*cyclopentanol*, CHCl_3 , and solid KOH are allowed to interact for 6 days at 0–10°, and the 1-trichloromethylcyclopentanol, b. p. 102–102.5°/10 mm., formed is separated from unsaturated by-products by bromination followed by fractional distillation. The corresponding product from *cyclohexanone* appeared to be formed in small amount, but could not be isolated.

H. A. PIGGOTT.

Oxidation of benzyl alcohol by chloronitrobenzenes. R. E. LYONS and G. H. STEMPEL, jun. (Proc. Indiana Acad. Sci., 1929, 38, 197–200).— $\text{CH}_2\text{Ph}\cdot\text{OH}$ with *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ gave BzOH and *pp'*-dichloroazoxybenzene, a little $(\text{ClC}_6\text{H}_4\text{N})_2$ also being formed when a xylene solution of $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ was employed instead of the solid. *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ and $\text{CH}_2\text{Ph}\cdot\text{OH}$ gave (*m*- $\text{C}_6\text{H}_4\text{Cl})_2\text{N}_2\text{O}$; the *o*-derivative gave unidentified products.

CHEMICAL ABSTRACTS.

Variations in sweetening power of saccharin and its derivatives. II. B. ODDO and Q. MINCOIA (Gazzetta, 1931, 61, 435–446; cf. A., 1927, 878).—Mg saccharinate (I) reacts as follows with *N*-magnesy derivatives, $\text{R}\cdot\text{NH}\cdot\text{MgBr}$:—



On boiling with Ac_2O and NaOAc the sulphonamide (II) gives instead of the Ac derivative the internal ester, $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{C}(\text{NHR})_2 \\ \text{SO}_2 \end{array} \right\rangle \text{O}$, analogous in structure to saccharin, but tasteless, which is hydrolysed by alkali (but much less easily than saccharin) to a carbinol-sulphonic acid, $\text{OH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})(\text{NHR})_2$. The following are described: *o*-sulphonamido- $\omega\omega$ -dianilino-benzyl alcohol, m. p. 195° (corresponding sulphonic acid, m. p. 285°; internal ester, m. p. 315°); *o*-sulphonamido- $\omega\omega$ -di-*o*-toluidinobenzyl alcohol, m. p. 183° (acid, m. p. 280°; ester, m. p. 278°); *o*-sulphonamido- $\omega\omega$ -diethylaminobenzyl alcohol, m. p. 159° (acid, m. p. 186–188°; ester, m. p. 276°). All these compounds are tasteless. Attempts to combine $\text{NH}_2\cdot\text{MgX}$ with Mg saccharinate were unsuccessful.

E. E. J. MARLER.

Optical activity and the Walden inversion. I. E. OTT [with E. ZINNIUS, R. WEGLER, D. BEISCHER, and K. PACKENDORFF] (Annalen, 1931, 488, 186–202).—Assuming that the differing action of bases in the replacement of Cl by OH in the Walden inversion is due to the differing rates of reaction, it is possible to reconcile the results with those obtained during the study of additive reactions and to explain both on common principles of energy. From this point of view observations have been made of the effect of varying the rate of reaction by alterations of temp. and concentration without change of reactants. Diazotisation of the NH_2 group consists in the reversible change $\text{R}\cdot\text{NH}_2 + \text{HNO}_2 \rightleftharpoons \text{R}\cdot\text{N}_2\cdot\text{OH}$ ($\text{R}\cdot\text{NH}\cdot\text{NO}$) + H_2O and the irreversible reaction $\text{R}\cdot\text{N}_2\cdot\text{OH} = \text{N}_2 + \text{R}\cdot\text{OH}$. In aq. solution the action of HNO_2 on α -phenylethylamine is accompanied by inversion, whereas in AcOH the alcohol has the same sign as the amine. Gradual addition of H_2O to the solution of the amine in AcOH causes the sign of rotation of the alcohol to pass from + through 0 to -. Addition of NaOAc, which functions as a retarding agent to solutions of const. H_2O , amine, AcOH, and NaNO_2 concentration, causes reversal of the sign of rotation which does not occur in absence of this addition.

The replacement of OH in phenylmethylcarbinol by Cl is effected by SOCl_2 , the disturbing effect of the HCl thereby formed being nullified by operating in

CCl_4 in which HCl is insol.; the action of the SOCl_2 is not greatly retarded and the effect can be compensated by increasing its amount. The rotatory power of the chloride increases with increasing rate of substitution; the latter is controlled by raising the temp. or varying the vol. of the solution. The presence of pyridine retards the reaction, since the additive product of the base and SOCl_2 is less active than SOCl_2 .

Further data are accumulated in favour of the view that racemic compounds exist in the liquid or dissolved condition without complete decomp. into the optical antipodes. α -Phenylethylamine is resolved by its H malate into the active forms, $[\alpha]_{\text{D}}^{16}$ yellow $\pm 42.63^\circ$, which appear to represent the limit of efficiency of the method. If (+)-phenylethylamine is partly diazotised, a "residual amine" (10% of the material) remains with appreciably higher activity than that given by Pasteur's method. With the (-)-amine a residual product of slightly lower sp. rotation remains. The b. p. and n of the residual (+)-amine agree with those of the initial active material. A (+)-amine, $[\alpha]_{\text{D}}^{16}$ yellow $+52^\circ$, is obtained from a prep. $[\alpha]_{\text{D}}^{16}$ yellow $+42.63^\circ$ by partial treatment with ClCO_2Et (Schotten-Baumann). The bulk of the amine gives the corresponding urethane, m. p. 35° , $[\alpha]_{\text{D}}^{16}$ yellow $+92.5^\circ$, from which the amine can be regenerated without undue racemisation by distillation with solid KOH . By similar means the (-)-amine gives a residual amine of the slightly enhanced activity, $[\alpha]_{\text{D}}^{20}$ yellow -44° . Fractional precipitation of the active amine by addition of alkali hydroxide to the acid solution yields a "residual amine," $[\alpha]_{\text{D}}^{20}$ yellow -44.3° or $[\alpha]_{\text{D}}^{18}$ yellow $+48.83^\circ$.

H. WREN.

Pharmacodynamic researches on derivatives of chloral-benzene condensation products.

FLORENCE (Bull. Soc. chim., 1931, [iv], 49, 925—929).—Condensation of CCl_3CHO with C_6H_6 in presence of AlCl_3 affords phenyltrichloromethylcarbinol, b. p. $160^\circ/23$ mm., oxidised to $\alpha\alpha\alpha$ -trichloroacetophenone, b. p. 128 — $132^\circ/14$ mm. Neither the carbinol, nor its *p*-nitrobenzoate, m. p. 109° , *p*-aminobenzoate, m. p. 131° (hydrochloride, m. p. 118°), *m*-nitrobenzoate, m. p. 90° , *m*-aminobenzoate (hydrochloride), *o*-nitrobenzoate, m. p. 119° , or *o*-aminobenzoate, m. p. 141° , possesses any pharmacodynamic action on rabbits and guinea-pigs, and in contrast to acetophenone and chloroacetophenone, the trichloroacetophenone has no hypnotic or lachrymatory properties.

R. BRIGHTMAN.

[New reaction of the aliphatic double linking.] Z. FÖLDI (Ber. 1931, 64, [B], 1911; cf. A., 1930, 1423).— α -Methylamino- β -hydroxy- α -phenylpropane has been described by Emde and Runne (A., 1911, i, 714).

H. WREN.

*iso*Phenylvinyl acetate, $\text{CHPh}\cdot\text{CH}\cdot\text{OAc}$, product of the oxidation of styryl methyl ketone by peracids. J. BÖESEKEN and A. KREMER (Rec. trav. chim., 1931, 50, 827—832).—Oxidation of $\text{CHPh}\cdot\text{CHAc}$ with perbenzoic acid in CHCl_3 or peracetic acid in AcOH gives a β -phenylvinyl acetate, b. p. 128 — $129^\circ/15$ mm., $63^\circ/0$ mm., which is hydrolysed by H_2O at 108° (to AcOH and $\text{CH}_2\text{Ph}\cdot\text{CHO}$) to about

the same extent as the isomeric acetate of Semmler (A., 1909, i, 239).

H. BURTON.

Action of formic acid on δ -phenyl- β -ethinylbutan- β -ol (the acetylene-carbinol from β -phenylethyl methyl ketone). H. RUPE and H. HIRSCHMANN (Helv. Chim. Acta, 1931, 14, 687—701).— δ -Phenyl- β -ethinylbutan- β -ol, b. p. 125 — $128^\circ/10$ mm., prepared from sodiobenzylacetone and C_2H_2 in Et_2O , is converted by boiling 86% HCO_2H into a mixture of carbonyl compounds, the main constituent of which, $\text{C}_{12}\text{H}_{14}\text{O}$, b. p. 140 — 141.5° (semicarbazone, m. p. 182°), does not combine with NaHSO_3 , is reduced to a dihydro-derivative, b. p. 123 — 124.5° (oxime, b. p. 158 — $162^\circ/9$ mm.; semicarbazone, m. p. 71 — 73.5°), and is oxidised to BzOH by alkaline KMnO_4 ; a hydrocarbon, $\text{C}_{12}\text{H}_{12}$, b. p. $98^\circ/10$ mm., and semicarbazones, m. p. 191 — 192° (carbonyl compound, b. p. 138 — $139^\circ/9$ mm.), 146 — 147° , and 148° , were also isolated.

The following were prepared for comparison with the substance, b. p. 140 — 141.5° , but all were different: γ -phenyl- α -methyl-*n*-propyl methyl ketone, b. p. 127 — $128^\circ/8$ mm. [semicarbazone, m. p. 180° (sinters 162°); oxime, b. p. 154 — $158^\circ/7$ mm., m. p. 95 — 96°], by interaction of ZnMe_2 and γ -phenyl- α -methylbutyryl chloride, b. p. 128 — $129^\circ/8$ mm.; β -phenylethyl *n*-propyl ketone, b. p. 133 — $135^\circ/8$ mm. [semicarbazone, m. p. 79° (sinters 71°); oxime, b. p. 162 — $165^\circ/8$ mm., m. p. 43° (sinters 30°)], by reduction with H_2 and Ni of the benzylidene derivative, b. p. 135 — $140^\circ/10$ mm., of COMePr^a ; β -phenylethyl isopropyl ketone, b. p. 126 — $127^\circ/8$ mm. (semicarbazone, m. p. 93 — 94° ; oxime, b. p. 156 — $158^\circ/8$ mm.), by a similar hydrogenation of the benzylidene derivative, b. p. 139 — $141^\circ/8$ mm., of COMePr^b ; and γ -phenylpropyl ethyl ketone, b. p. 137 — $140^\circ/10$ mm. (semicarbazone, m. p. 149°), by condensation of γ -phenylbutyryl chloride with ZnEt_2 .

H. A. PIGGOTT.

Condensations by sodium instead of by the Grignard reaction. I. Tertiary carbinols. A. A. MORTON and J. R. STEVENS (J. Amer. Chem. Soc., 1931, 53, 2244—2247).—Interaction of PhCl (2 mols.) with BzOEt (1 mol.) and Na (4 atoms) in Et_2O gives triphenylcarbinol in 98% yield. Other halogenobenzenes, with Me or Bz benzoates, Et_2CO_3 , or $\text{Et}_2\text{C}_2\text{O}_4$ as examples of carbonyl compounds, and hydrocarbon solvents may also be used. The method is extended to the prep. of phenyldiethylcarbinol from PhBr and COEt_2 , triethylcarbinol from EtBr and COEt_2 or $\text{Et}\cdot\text{CO}_2\text{Et}$, and di(?)phenylethylcarbinol from EtBr and PhCHO .

H. A. PIGGOTT.

Character of triarylcannabinol derivatives. I. S. KAWAI and K. TAMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 16, 17—19).—The tautomerism of *p*-hydroxydiphenyl- α -naphthylcarbinol (A., 1920, 735) is illustrated by the partial conversion of *p*-dimethylaminodiphenyl- α -naphthylcarbinol, m. p. 183° , into phenyl- α -naphthylquinomethane on heating with conc. HCl in AcOH , or by the action of AlCl_3 in C_6H_6 at room temp.

J. D. A. JOHNSON.

Derivatives of optically active triarylcannabinols and their halochromic salts. E. S. WALLIS (J. Amer. Chem. Soc., 1931, 53, 2253—2260).—*l*-Phenyldiphenyl- α -naphthylmethylthioglycolic acid (A.,

1930, 773) is slowly racemised in AcOH. It forms halochromic compounds with H_2SO_4 , $HClO_4$, $HgCl_2$, and $TiCl_4$, the first three of which give *dl*-phenyldiphenyl- α -naphthylmethylcarbinol, and the last regenerates the glycollic acid in an inactive form when decomposed with ice. The halochromic compounds with $FeCl_3$ and $ZnCl_2$, however, regenerate the original compound without any trace of racemisation. The regeneration of an optically active compound cannot be reconciled with the quinonoid theory of halochromism (cf. A., 1902, i, 89), but supports rather the "carbonium" theory (A., 1922, i, 24; 1925, i, 650) if the racemisation that occurs in some cases be explained by the inherent instability of this ion (cf. A., 1930, 1177). H. A. PIGGOTT.

Isomerisation of ergosterol and its derivatives.

A. WINDAUS, K. DITHMAR, H. MURKE, and F. SUCKFÜLL (Annalen, 1931, 488, 91—110).—The action of HCl on ergosteryl acetate in $CHCl_3$ yields *ergosteryl-B₁ acetate*, m. p. 142°, $[\alpha]_D^{25} -53.6^\circ$, hydrolysed by KOH in MeOH to *ergosterol-B₁*, m. p. 148°, $[\alpha]_D^{25} -40.3^\circ$ in $CHCl_3$. Treatment of the mother-liquors with maleic anhydride yields a sparingly sol. *ergosteryl-B₃ acetate-maleic anhydride*, m. p. 207° (*ergosteryl-B₃ acetate*, m. p. 132°, $[\alpha]_D^{25} -182.9^\circ$ in $CHCl_3$; *ergosterol-B₃*, m. p. 136°, $[\alpha]_D^{25} -190^\circ$ in $CHCl_3$), after removal of which *ergosteryl-B₂ acetate*, m. p. 100°, $[\alpha]_D^{25} -80.4^\circ$ in $CHCl_3$ (*ergosterol-B₂*, m. p. 126°, $[\alpha]_D -88.4^\circ$ in $CHCl_3$) is isolated. If treatment of ergosteryl acetate is effected at 0°, *ergosteryl-B₃ acetate* gradually accumulates in the product owing to the slow conversion of the *B₁* and *B₂* esters into the *B₃* product. In boiling $CHCl_3$ -HCl solution the *B₃ acetate* is extensively converted into the *B₁* and *B₂* substances. Contrary to Reindel, the $CHCl_3$ solution must not be warmed above 0° while HCl is present if ready isolation of the *B₃* ester is desired. Ergosterols *B₁*, *B₂*, and *B₃* have approximately the same absorption spectrum with max. at 248 μ . *B₁* and *B₂* do not react with maleic anhydride, with which *B₃* readily combines. The sterols are not hydrogenated by Na and EtOH. The literature is critically reviewed. Ergosteryl-*D* acetate behaves similarly to ergosteryl acetate towards HCl.

The action of NaOEt on sterols at about 200° causes (1) a more or less complete transformation at the *sec.* OH group leading to an equilibrium mixture of two alcohols differing only in arrangement of the H and OH groups and therefore yielding the same ketone. The new *epi*-derivatives, unlike the parent compounds, are not precipitated by digitonin. This property is shared by the irradiated products of ergosterol, which do not belong to the *epi*-series, since all the latter are transformed by NaOEt to a smaller or greater extent into the precipitable isomerides, whereas this is invariably not the case with irradiated products (dihydroergosterol I, ergosterol *B₁*, *B₂*, and *D*); (2) hydrogenation at the double linking combined with epimerisation (ergosterol, dehydroergosterol, and cholesterol); (3) steric transformation in the C skeleton combined with epimerisation and hydrogenation. The following transformations are recorded: ergosterol-*B₁* into *epi*ergosterol-*B₁*, m. p. 182—183° (*acetate*, m. p. 136°); ergosterol-*B₂* into *epi*ergosterol-*B₂*, m. p. 163° (*acetate*, m. p. 127°); ergosterol-*D* into *epi*ergosterol-*D*, m. p.

203—204°, $[\alpha]_D^{25} +36.2^\circ$ in $CHCl_3$ (*acetate*, m. p. 150°, $[\alpha]_D +40.6^\circ$ in $CHCl_3$); dihydroergosterol I into *epi*dihydroergosterol I, m. p. 156°, $[\alpha]_D +4.01^\circ$ in $CHCl_3$ (*acetate*, m. p. 215—216°, $[\alpha]_D -4.4^\circ$ in $CHCl_3$), dehydrogenated by $Hg(OAc)_2$ to *epi*ergosterol-*D* and a substance, m. p. 160—161°, $[\alpha]_D -34.4^\circ$ (*acetate*, m. p. 123—124°, and its additive product with maleic anhydride, m. p. 212°, $[\alpha]_D -56.7^\circ$); ergosterol to dihydroergosterol II, m. p. 163°, $[\alpha]_D^{25} -8.8^\circ$ in $CHCl_3$ (*acetate*, m. p. 164—165°, $[\alpha]_D^{25} -16.2^\circ$ in $CHCl_3$), and *epi*dihydroergosterol II, m. p. 216°, $[\alpha]_D^{25} -4.92^\circ$ in $CHCl_3$ (*acetate*, m. p. 155—156°, $[\alpha]_D^{25} +3.88^\circ$ in $CHCl_3$); dihydroergosterol II to *epi*dihydroergosterol II; dehydroergosterol to ergosterol *D*, m. p. 170°, $[\alpha]_D +17.8^\circ$ (*acetate*, m. p. 173—174°, $[\alpha]_D +20.7^\circ$), and *epi*ergosterol *D*. H. WREN.

Constitution of colourless and coloured triphenylmethane derivatives. A. HANTZSCH and A. BURAWOY (Ber., 1931, 64, [B], 1622—1635).—Aminated and non-aminated CPh_3 derivatives do not differ fundamentally. Colourless ψ -salts (homopolar compounds such as CPh_3Cl , triaminophenylacetoneitrile) exist as well as coloured, true salts (heteropolar compounds such as CPh_3ClO_4 , triaminophenylmethyl chloride) of quinonoid or quinolide structure. Their colour is not dependent on the quinonoid structure of a single C_6H_6 ring, but on a consequent conjugated system, e.g.,

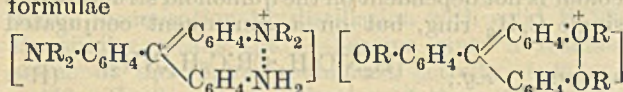


Colourless and coloured compounds are related to one another as "valency isomerides." They differ in that a certain linking in the colourless isomerides is esterlike (covalent), whereas in the coloured derivatives it is ionogenic (electrovalent). The solid compounds are either colourless ψ -salts or coloured true salts. A compound CAr_3X has not been isolated in the two forms. The occurrence of a compound as colourless ψ -salt or coloured true salt depends on the positive character of the triarylmethyl group or the negative nature of the acidic residue. The tendency towards the formation of coloured, true salts increases with increasingly positive character of the triarylmethyl residue caused mainly by the introduction of NH_2 and OR groups (CPh_3Cl is a colourless ψ -salt, whereas triaminotriphenylmethyl chloride is a coloured, true salt) and with increasingly negative nature of the acidic residue (CPh_3ClO_4 is coloured and triaminotriphenylacetoneitrile is colourless). The ability of inorg. ψ -salts, such as $SnCl_4$, $HgCl_2$, and of acid mols. to convert colourless triarylmethyl derivatives by addition into coloured salts is probably attributable to enhancement of the negative character of the acidic residue. In the absence of solvolysis, equilibrium usually exists between the true and ψ -salts in the solutions of the (solid) colourless and coloured triarylmethyl derivatives; the position of the equilibrium is displaced in the direction of the coloured salt with increasingly positive nature of the triarylmethyl

residue and increasingly negative character of the acidic radical. Rise in temp. and irradiation with ultra-violet light operate in the same sense. The position of the equilibrium is also influenced by the solvent. Colourless and coloured derivatives are solvatised in solution, but the nature and position of union with the solvent mols. remain undetermined.

H. WREN.

Absorption of light and constitution. III. Coloured triarylmethyl salts. A. BURAWOY (Ber., 1931, 64, [B], 1635—1646; cf. preceding abstract).—The constitution of triarylmethyl salts or their cations can be decided only by their optical behaviour and not on a chemical or an electrochemical basis. All are quinonoid or quinolide. Absorption of light is due to conjugated systems. Optical investigation of positively substituted triarylmethyl salts shows that the first positive groups are positively charged, since their bathochromic action increases in the sequence $\text{NR}_2 < \text{OR} < \text{SR}$; the atoms N^+ , O^+ , S^+ are negative auxochromic atoms. The atoms O, S, N of the second positive groups which have increasingly bathochromic action in the sequence $\text{OR} < \text{SR} < \text{NR}_2$ are positive auxochromic atoms. The third positive groups are in branchings of the chromophoric conjugated systems, since they exert a feeble hypsochromic effect. The formulae

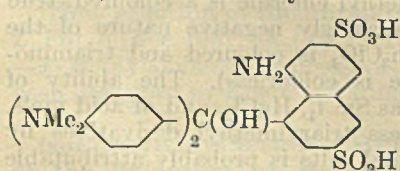


and $\left[\text{SR} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \swarrow \text{C}_6\text{H}_4 \cdot \text{SR} \\ \searrow \text{C}_6\text{H}_4 \cdot \text{SR} \end{array} \right]$ are advanced. Substi-

tution of the first and second C_6H_4 residue of the CPh_3 ion by the $\text{Ph} \cdot \text{C}_6\text{H}_4$ residue displaces the absorption bands appreciably towards the red end, whereas replacement of the third C_6H_6 groups does not appreciably alter the position of the max. of the bands. Phenylidibiphenylmethyl sulphate has two bands in the visible portion of the spectrum. The non-positively substituted triarylmethyl ions have the quinolide constitution, and the absorption of light depends on the presence of conjugated systems.

H. WREN.

Naphthalene-green-V. F. FRISCH (Helv. Chim. Acta, 1931, 14, 669—671).—Interaction of tetramethyldiaminobenzhydrol with α -naphthylamine-3 : 6-disulphonic acid in 15% H_2SO_4 at its b. p. for several days gives a leuco-compound in 3% yield, oxidised by PbO_2 to a pure blue dye (annexed formula) characterised by its fastness to alkalis. The



given structure is assigned on account of its conversion by elimination of the NH_2 -group into the Me_4 analogue of naphthalene-green-V in place of the desired analogue of the dye having the structure formerly assigned to the latter (cf. A., 1930, 1430).

H. A. PIGGOTT.

Alkamines in the tetrahydronaphthalene series. E. MOSETTIG and A. BURGER (J. Amer. Chem. Soc., 1931, 53, 2295—2300).—The action of diazomethane

on 2-ketotetrahydronaphthalene in $\text{Et}_2\text{O}-\text{MeOH}$ gives 2-methylenetetrahydronaphthalene oxide,

$\text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C} \begin{array}{l} \swarrow \text{O} \\ \searrow \text{CH}_2 \end{array}$ (I), b. p. 137—138°/1 mm., which on interaction with the appropriate *sec.*-amines gives 2-dimethylaminomethyl-, b. p. 116—118°/1 mm. [hydrochloride, m. p. 175—176°; perchlorate, m. p. 158—159°; chloroplatinate, m. p. 197—198° (decomp.)] [accompanied by a homologue (?) isolated as perchlorate, m. p. 184°; hydrochloride, m. p. 196—198°, chloroplatinate, m. p. 197—198°]; 2-diethylaminomethyl-, b. p. 135—137°/1 mm. [hydrochloride, m. p. 125—126° (+1H₂O, lost at 92°); perchlorate, m. p. 155—156°; chloroplatinate, m. p. 190° (decomp.)]; and 2-piperidinomethyl-2-hydroxytetrahydronaphthalene, b. p. 146—148°/1 mm. [hydrochloride, m. p. 200—200.5°; perchlorate, m. p. 147.5—148°; chloroplatinate, m. p. 214—216° (decomp., rapid heating)]. The oxide (I) is accompanied by a yellow oil of the same b. p., but inactive towards *sec.*-amines. Diazoethane reacts vigorously with 2-ketotetrahydronaphthalene, but no definite products were isolated on treatment with amines. The formation of an unstable additive compound of this ketone with piperidine is reported.

H. A. PIGGOTT.

Dissociable organic oxides. A fourth oxidation stage of rubrene: dihydroxydihydorubrene. C. DUFRAISSE and M. BADOCHÉ (Compt. rend., 1931, 193, 63—65).—Dihydroxydihydorubrene (I), m. p. 307—308° (Maquenne block), $\text{C}_{42}\text{H}_{28}(\text{OH})_2$, is one of the products formed by the action of Grignard reagents (or, in small yield, of MgI_2) on isorubrene oxide (A., 1930, 1173). On heating it yields rubrene monoxide, and on dehydration readily loses $2\text{H}_2\text{O}$ to yield a substance, $\text{C}_{42}\text{H}_{26}$, m. p. 455°, with a violet fluorescence, and apparently identical with the adulterant of rubrene previously reported (A., 1926, 945). (I) is not dissociable, but is reduced by Fe powder to rubrene. On the basis of these reactions (I) is assigned the formula $(\text{C}_6\text{H}_4 \langle \text{CPh} \rangle \text{C} \cdot \text{CPh}(\text{OH}))_2$. The capacity of rubrene to form dissociable, as well as non-dissociable but reducible, oxides by addition of O_2 indicates predisposition to attack by oxidising agents, and is shared by methæmoglobin. Methæmoglobin may, therefore, possibly form several oxides, one or other predominating according to the method of prep., which explains the discordant results in this field.

R. S. CAHN.

Syntheses of cyclic compounds. IX. Reduction of ethyl 3-methylcyclopentylidene-1-cyanoacetate with moist aluminium amalgam and its bearing on the configuration of the 3-methylcyclopentane ring. A. I. VOGEL (J.C.S., 1931, 1795—1801).—The condensation of 3-methylcyclopentanone with Et cyanoacetate in presence of piperidine gives α - (cf. this vol., 843) and β *Et*-3-methylcyclopentylidene-1-cyanoacetate, b. p. 155—156°/12 mm., both of which are oxidised by cold aq. KMnO_4 to 3-methylcyclopentanone, and reduced by Al-Hg in moist Et_2O to Et *r*-3-methylcyclopentyl-1-cyanoacetate (*loc. cit.*) and a mixture of bimol. esters, m. p. 69—70°, the last-named being produced in a yield of 16% from the α -form and 13% from the β -form, indicating that the

3-methylcyclopentane ring is strainless, a result in agreement with parachor measurements. Both α - and β -forms condense with Et cyanoacetate and NH_3 in EtOH to give the dicyanoimide (this vol., 727), and with KCN in EtOH to give a nitrile, converted by acid hydrolysis into 1-carboxy-3-methylcyclopentane-1-acetic acid, m. p. 117° (cf. this vol., 843; *anhydride*, b. p. 156—158°/11 mm.), and, in the case of the α -form, an isomeric (?) acid. H. A. PIGGOTT.

Equilibrium $\text{C}_6\text{H}_6 + \text{CO}_2 \rightleftharpoons \text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H}$. C. R. KINNEY and D. P. LANGLOIS (J. Amer. Chem. Soc., 1931, 53, 2189—2192).—The decarboxylation of BzOH is reversible in presence of Zn—Cu—Cr oxide catalysts (cf. B., 1930, 49). Decomp. of the acid begins at 240—250°, but equilibrium is not reached at the end of 5 days at 300°. At 300°/35 atm. 0.08% of BzOH, calc. on C_6H_6 , is obtained by the reverse reaction. H. A. PIGGOTT.

N-Acylsulphamic acids. P. BAUMGARTEN and I. MARGGRAFF (Ber., 1931, 64, [B], 1582—1588).—Acetamide and *N*-pyridiniumsulphonic acid at 100° yield *pyridinium acetamidodisulphonate*, m. p. 123—124°, converted by 1 mol. of KOH into the salt, $\text{NHAc} \cdot \text{SO}_3\text{K}$, also obtained by heating NH_2Ac with trimethylsulphamic acid at 150° and treatment of the product with K_2CO_3 , KHCO_3 , or KOH. It is rapidly decomposed by acids but converted by KOH into the K_2 salt, $\text{NKAc} \cdot \text{SO}_3\text{K} \cdot 2\text{H}_2\text{O}$, hydrolysed in boiling aq. solution to KOAc and $\text{NH}_2 \cdot \text{SO}_3\text{K}$. *K benzamidodisulphonate* (also + $1\text{H}_2\text{O}$) yields NH_2Bz in boiling PhCN; the last-named compound is obtained in 90% yield when NH_2Bz and *N*-pyridiniumsulphonic acid are heated at 220°. The K_2 salt is described. *K benzene-sulphonamidodisulphonate* is transformed by HClO_4 in H_2O into *K benzenesulphonamidodisulphonate*.

H. WREN.

Molecular rearrangements involving optically active radicals. II. Hofmann rearrangement of optically active acid amides. E. S. WALLIS and S. C. NAGEL (J. Amer. Chem. Soc., 1931, 53, 2787—2791).—*d*- α -Benzylpropionamide, m. p. 104.5°, from the corresponding chloride and NH_3 in Et_2O , is converted by the Hofmann method into *d*- α -benzylethylamine, having a sp. rotation identical with that of the compound obtained previously (A., 1926, 279) by rearrangement of *d*-benzylmethylacetamide. The results are discussed briefly with reference to the Walden inversion. H. BURTON.

Oxidation by permanganate of cinnamic acid. E. M. STODDART (J.C.S., 1931, 1874—1875).—Oxidation of boiling 1% aq. Na cinnamate with KMnO_4 gave, with absorption of 3.5 O_2 per mol. of acid, PhCHO (70% of theory) and phenylglyceric acid (about 10%), about 20% remaining unchanged. No oxalate was formed. H. A. PIGGOTT.

Hydroxy-complexes of iron. C. MORTON.—See this vol., 1022.

Electrolyses in liquid ammonia; reactive forms of free radicals. S. GOLDSCHMIDT and F. NAGEL (Ber., 1931, 64, [B], 1744—1755).—Electrolysis of a variety of org. compounds, mainly phenols and carboxylic acids, in liquid NH_3 shows that the effect of the current, if passing, consists essentially in

the transport from the cathode to the anode of the org. substance, which can be recovered almost quantitatively. H_2 and N_2 are liberated at the cathode and anode in the vol. ratio 3 : 1. The formation of N_2H_4 cannot be detected. The possibility of intermediate radical formation is examined with 9-chloro-10-hydroxyphenanthrene. The compound is dehydrogenated by $\text{K}_3\text{Fe}(\text{CN})_6$ in liquid NH_3 at -40° to the peroxide, which can be determined by titration with hydrazobenzene; evolution of N_2 and H_2 during electrolysis is not observed. If salicylic acid is substituted for the phenanthrol and electrolysis is effected in presence of NHPhMe or hydrazobenzene, *s*-diphenyldimethylhydrazine and azobenzene respectively are produced in modest amount. It is therefore concluded that the electrolysis of org. acids, largely independent of their constitution, leads to the production of discharged anions richer in energy than the radicals produced by chemical means and differing sharply from them in their reactions. They are incapable of forming stable, dimeric mols. with loss of energy. Their great chemical reactivity is shown by their reaction with NH_3 and other mols. and with the Pt electrodes, which are invariably corroded; in the case of salicylic acid an insol. loose deposit of a complex Pt salt is formed on the anode. If the new radicals lack opportunity to discharge their energy by chemical reaction, they decompose as, e.g., in the electrolysis of carboxylic acids in H_2O , either according to the Kolbe synthesis of hydrocarbons or to more complicated changes. H. WREN.

Mercury salicylate. P. BRENANS and B. RAPILLY (Compt. rend., 1931, 193, 55—58).—Hg salicylate, prepared by the older methods (A., 1902, i, 851; 1903, i, 246, 392), consists mainly of anhydro-5-hydroxy-mercurisalicylic acid, $\text{OH} \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{CO} \\ \text{Hg} \end{array} \right\rangle \text{O}$, since on treatment with I it gives 5-iodosalicylic acid (I) and 3 : 5-di-iodosalicylic acid (separated by its less sol. Ba salt), and on treatment with KCN followed by I in KI yields (I). The less sol. K cyanomercurisalicylate is the 5-cyanomercuri-derivative, since it yields (I) (contrast A., 1925, i, 1107). The salt obtained by treating salicylic acid or its Na salt with HgSO_4 (A., 1927, 685) contains a large amount of a dimeric compound, $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{Hg} (5-) \cdot \text{C}_6\text{H}_2(\text{OH}) \left\langle \begin{array}{c} (3-) \text{Hg} \\ \text{CO}_2 \end{array} \right\rangle$, since on treatment with hot aq. KCN it yields *K* 3 : 5-dicyanomercurisalicylate, which with I in KI gives 3 : 5-di-iodosalicylic acid. A volumetric and a gravimetric method of determining Hg in these compounds are given. R. S. CAHN.

Condensation of chloral with *m*-cresotic acid. N. M. SHAH and R. L. ALIMCHANDANI (J. Indian Chem. Soc., 1931, 8, 261—270; cf. J.C.S., 1921, 119, 201; A., 1925, i, 1272).—Condensation of chloral with *m*-cresotic acid by keeping in conc. or 90% H_2SO_4 for 1 or 3 days occurs in the *p*-position (cf. A., 1925, i, 111), as with the Me ether of the acid (A., 1929, 813), the products being α : 5-dihydroxy-2- $\beta\beta\beta$ -trichloroethyl-*p*-toluic acid (I), $\text{C}_6\text{H}_2\text{Me}(\text{OH})(\text{CO}_2\text{H}) \cdot \text{CH}(\text{OH}) \cdot \text{CCl}_3$, efflorescent, m. p. 218° (*Ac* derivative, m. p. 160°) (gives an intense violet colour with FeCl_3), the lactone of (I), m. p. 340° (decomp.), and 5-hydroxy-2-(α -

hydroxy-ββ-dichlorovinyl-*p*-toluic acid (II), $C_6H_2Me(OH)(CO_2H) \cdot C(OH) : CCl_2$, m. p. 165° (decomp.). Some sulpho-*m*-cresotic acid was also formed. The constitution of (I) is proved by the following reactions. Hydrolysis of (I) with aq. NaOH gave 4-*hydroxy-5-carboxy-2-methylmandelic acid* (III), m. p. 227° (decomp.) [Ba salt, +4H₂O, of which 2H₂O are lost at 115—120°; Ac derivative, +1H₂O, m. p. 168—170° (decomp.)], which on oxidation by KMnO₄ yielded α-cocinic acid, also obtained from (I) without isolation of (III). Reduction of (I) by Zn dust and AcOH afforded 4-*hydroxy-2-ββ-dichloroethyl-p*-toluic acid (IV), m. p. 206° [Ac derivative, m. p. 160°; Me ester of MeO-derivative (by Me₂SO₄ and NaOH below 45°) identical with that previously described], which yielded 4-*hydroxy-5-carboxy-o-tolylacetic acid*, m. p. 251° [Ba salt, +2H₂O, of which 1H₂O is lost at 115—120°; Me derivative identical with that previously obtained]. On methylation of (IV) above 45°, or on heating its Me derivative with NaOH, HCl was lost, and 5-*methoxy-2-β-chlorovinyl-p*-toluic acid, m. p. 163° (gives no colour with FeCl₃), obtained.

The structure of an internal β-lactone is assigned to the lactone of (I), because the substance does not give a colour with FeCl₃, dissolves slowly in hot NaOH, is obtained by heating (I) at 220—223°, forms an Ac derivative, m. p. 315° [with Zn dust and AcOH yields (IV)], and gives (III) on hydrolysis with NaOH and (IV) on treatment with Zn dust and AcOH.

The structure of (II) is assigned, since the substance gives a violet colour with FeCl₃, yields an Ac derivative, m. p. 216—217° (decomp.), but does not react with semicarbazide or phenylhydrazine, and is reduced by Zn dust and AcOH to 5-*hydroxy-2-ethyl-p*-toluic acid, m. p. 315° (decomp.). It thus reacts only in the enolic form (contrast A., 1927, 458).

When dry HCl is passed into *m*-cresotic acid and chloral hydrate in conc. H₂SO₄, 4-*hydroxy-2-αββ-tetrachloroethyl-p*-toluic acid, m. p. 227—228° (decomp.) (Ac derivative, m. p. 197°), is obtained. This yields (III) on hydrolysis by KOH, and (IV) on reduction by Zn dust and AcOH.

R. S. CARR.

Relation between chemical constitution and action on micro-organisms. X. Glycerol and dihalogenohydrin esters of benzoic and simple or substituted hydroxybenzoic acids. T. SABALITSCHKA and H. JEGLINSKI (Arch. Pharm., 1931, 269, 228—246; cf. A., 1930, 71; B., 1930, 530).—The phenol coefficients of the following esters (where sufficiently H₂O-sol.) are determined; glycerol α-monobenzoate, 0.5; α-salicylate, m. p. 76°, 0.3 (isopropylidene ether, m. p. 49.5°); α-*p*-hydroxybenzoate, m. p. 154° (isopropylidene ether, m. p. 124.5°); α-3-*hydroxy-p*-toluate, m. p. 98.5°, 1.6 (isopropylidene ether, m. p. 48.5°); α-4-*hydroxy-m*-toluate, m. p. 82°; α-5-*hydroxy-o*-toluate, m. p. 125°, 0.3; α-6-*chloro-3-hydroxy-p*-toluate, m. p. 91°, 60; α-3-*chloro-4-hydroxybenzoate*, m. p. 113°, 4.1; 5-*iodosalicylate*, m. p. 105°, 9.0; ββ'-*dichloroisopropyl benzoate*, b. p. 157—160°/12 mm.; *salicylate*, m. p. 49°; *p*-hydroxybenzoate, m. p. 101.5°, 61; 3-*hydroxy-p*-toluate, b. p. 192—194°/11 mm.; 4-*hydroxy-m*-toluate, m. p. 44°; 5-*hydroxy-o*-toluate, m. p. 104°; 6-*chloro-3-hydroxy-p*-toluate, m. p. 76°; β-*chloro-β'-iodoisopropyl salicylate*, m. p. 57°;

glyceryl tri-*p*-hydroxybenzoate, m. p. 190°, 48; tri-3-*hydroxy-p*-toluate, m. p. 115°. Staphylococci are killed in 15 min. by ββ'-*dichloroisopropyl p*-hydroxybenzoate alone at 0.07% concentration, or in admixture with glycerol α-salicylate in 5 min. at 0.10 concentration (mixture). C. HOLLINS.

Condensation of dichloroacetaldehyde with anisic acid and *p*-nitroanisole. F. D. CHATAWAY and L. H. FARINHOLT (J.C.S., 1931, 1828—1834).—Condensation of anisic acid with dichloroacetaldehyde alcoholate in presence of H₂SO₄ and HCl gives 2-*methoxy-5-carboxy-1-αββ-trichloroethylbenzene*, m. p. 189—190° (Et ester, m. p. 69°; chloride, m. p. 94°; amide, m. p. 156°), the orientation of which depends on its oxidation by alkaline KMnO₄ to 4-methoxyisophthalic acid and ββ'-*dichloro-αα-di*-(5-*carboxy-2-methoxyphenyl*)ethane, m. p. 315° (Me, m. p. 154°, and Et, m. p. 117°, esters; chloride, m. p. 134°; amide, m. p. 257°; anilide, m. p. 209°); the latter is the sole product in absence of HCl. The action of KOH in EtOH on the former gives αβ'-*dichloro-5-carboxy-2-methoxystyrene*, m. p. 227—228°. Similarly from *p*-nitroanisole are prepared 5-*nitro-2-methoxy-1-αββ-trichloroethylbenzene*, m. p. 140°, and ββ'-*dichloro-αα-di*-(5-*nitro-2-methoxyphenyl*)ethane, m. p. 237°. The former is converted by EtOH-KOH into αβ'-*dichloro-5-nitro-2-methoxystyrene*, m. p. 66° (dichloride, m. p. 165°, converted by EtOH-KOH into αββ'-*trichloro-5-nitro-2-methoxystyrene*), by oxidation with KMnO₄ in COMe₂ into 5-*nitro-2-methoxybenzoic acid*, and by further condensation with *p*-nitroanisole in conc. H₂SO₄ into the above ethane derivative, m. p. 237°.

H. A. PIGGOTT.

Preparation and properties of chloromandelic acids, methyl esters, and amides. S. S. JENKINS (J. Amer. Chem. Soc., 1931, 53, 2341—2343).—The prep. of *o*-chloromandelic acid (Me ester, b. p. 134—136°/6 mm.; amide, m. p. 87.5°), *m*-chloromandelic acid, m. p. 115—115.5° (Me ester, m. p. 84°; amide, m. p. 126.5°), and *p*-chloromandelic acid (Me ester, m. p. 55.6°) from the corresponding benzaldehyde through the cyanohydrin is described.

H. A. PIGGOTT.

Benzylidene- and furfurylidene-pyruvic acids. E. FRIEDMANN (Helv. Chim. Acta, 1931, 14, 783—793).—KOH is a better condensing agent than NaOH in the prep. of benzylidenepyruvic acid, the *K* salt being obtained in 81—91% yield. Furfurylidene-pyruvic acid, m. p. 112° (+1H₂O, lost below m. p.) [phenylhydrazone, m. p. 164—165°; Na salt (+2H₂O, lost at 100°)], is similarly prepared by condensation of the components in dil. aq. NaOH (cf. A., 1898, i, 300). It is oxidised by aq. H₂O₂ to β-furfurylacrylic acid.

H. A. PIGGOTT.

Resolution of spiroheptanedicarboxylic acid. H. J. BACKER and H. B. J. SCHURINK (Rec. trav. chim., 1931, 50, 921—930).—Improved methods of prep. of pentaerythritol, its tetra-bromide and -iodide, and spiroheptanedicarboxylic acid, m. p. 212° (cf. A., 1907, i, 906) [brucine (+6H₂O), m. p. (anhyd.) 133°, and strychnine, m. p. about 238° (decomp.)], salts; dianilide, m. p. 228], are recorded. The acid is resolved by brucine (cf. A., 1925, i, 339) into the *d*-form, [M]_D, +1.9° in Et₂O. spiroHeptane-

tetracarboxylic acid [*Ba* (+7H₂O) salt] has m. p. 219° (decomp.) (cf. J.C.S., 1912, 101, 476).

H. BURTON.

Strainless monocyclic rings. I. Isomerism of 1-carboxy-4-methylcyclohexane-1-acetic acid. Evidence of strainless cyclohexane ring. M. QUDRAT-I-KHUDA (J. Indian Chem. Soc., 1931, 8, 277—287).—1-Carboxy-4-methylcyclohexane-1-acetic acid (I; R=OH) (I) CHMe

has been isolated in four modifications, each giving different anhydrides and anilic acids (I; R=NHPh). These are considered to be the two pairs of *cis-trans* isomerides derivable from the boat- and chair-shaped cyclohexane rings, which are stabilised by the bulky substituents. Modified directions are given for the prep. of Et 4-methylcyclohexylideneacyanoacetate, b. p. 165°/12 mm., which on condensation with KCN (cf. A., 1928, 1243) yields Et 1-cyano-4-methylcyclohexane-1- α -cyanoacetate. This on hydrolysis by boiling conc. HCl gives a mixture of isomerides of (I) (R=OH), separable into acid *A*, m. p. 137° (anhydride, m. p. 77°; anilic acid, m. p. 195°; anil, m. p. 130°; imide, m. p. 119—120°; *p*-toluidinamic acid, m. p. 199°; *p*-toluidinimide, m. p. 210—215°; β -naphthylamic acid, m. p. 200°; β -naphthylimide, m. p. 162°), acid *B*, m. p. 129° (anhydride, m. p. 59°; anilic acid, m. p. 183°; anil, m. p. 142—143°; imide, m. p. 130°; *p*-toluidinamic acid, m. p. 174°; *p*-toluidinimide, m. p. 134°; β -naphthylamic acid, m. p. 192°; β -naphthylimide, m. p. 144°), acid *C*, m. p. 174° (anhydride, m. p. 104°; anilic acid, m. p. 185°; anil, m. p. 185°), acid *D*, m. p. 146° (anhydride, an oil; anilic acid, m. p. 184°), and a little oily residue.

R. S. CAHN.

Lichen substances. IX. Synthesis of divaricatic acid. H. SOHN (Ber., 1931, 64, [B], 1851—1852).—Et *n*-propylidihydroresorcinolcarboxylate, m. p. 87°, obtained from *n*- Δ^6 -hexene- α -carboxylic acid, is converted by Br in AcOH into Et dibromo-*n*-propylresorcinolcarboxylate, dehydrogenated by H₂ and Pd-CaCO₃ to Et divarate, m. p. 96—98°. Treatment of the ester with diazomethane in Et₂O affords Et divaricate [Et 2-hydroxy-4-methoxy-6-*n*-propylbenzoate], m. p. 44°, hydrolysed to divaricatic acid, decomp. 150—160°, identical with the products isolated from *Evernia divaricata* or *illyrica*.

H. WREN.

1:2-Diketohydrindene-3-acetic acid, a further carbon analogue of isatin. J. VON BRAUN and F. FISCHER (Ber., 1931, 64, [B], 1790—1793).—Et 1-ketohydrindene-3-acetate, b. p. 200—202°/18 mm., is converted by amyl nitrite and conc. HCl in EtOH into Et 1-keto-2-oximino-1-hydrindene-3-acetate, m. p. 132—133°, hydrolysed to 1-keto-2-oximinohydrindene-3-acetic acid, decomp. about 170° [*Bz* compound, m. p. 137° (decomp.)]; the corresponding dioxime and oximesemicarbazone, gradual decomp. above 190°, are described. The oximino-acid is transformed by conc. HCl and CH₂O into 1:2-diketohydrindene-3-acetic acid, m. p. 128—130°, the dark blue solutions of which in an excess of aq. KOH are slowly decolorised with formation of *o*- β -carboxyethylbenzoylformic acid, gradual decomp. above 230°. With thiophen and H₂SO₄ the diketone-acid gives the indopenin reaction with scarcely less intensity than does isatin. The phenyl-

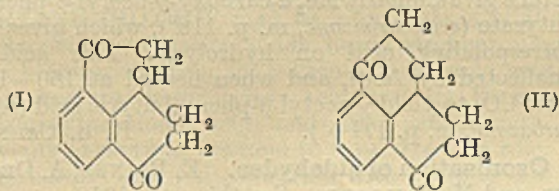
osazone, C₃₂H₂₀O₂N₄, m. p. 184°, and quinoxaline derivative, C₁₇H₁₂O₂N₂, m. p. 198—200° (decomp.), are described.

H. WREN.

Sulphonation of phthalic anhydride. H. WALDMANN and E. SCHWENK (Annalen, 1931, 487, 287—294).—Passage of SO₃ in an all-glass apparatus into phthalic anhydride at 190—210° for 66 hr. gives 4-sulphophthalic anhydride (K H₂ and Na H₂ salts of the corresponding acid lose H₂O at 220—230° in vac.), containing only 2.5% of H₂SO₄, and yielding with HCl and NaClO₃ 4-chlorophthalic acid. Addition of Hg₂SO₄ to the anhydride causes disulphonation to occur (contrast B., 1930, 941), 3:5-disulphophthalic anhydride (K₂ H₂ salt of the corresponding acid loses 2H₂O of crystallisation at 150°, and passes into the anhydride at 220—230° in vac.) being formed. This with SOCl₂ at 180° gives 3:5-dichlorophthalic anhydride, passing on boiling in H₂O into 3:5-dichlorophthalic acid.

R. S. CAHN.

Benzopolymethylene compounds. XVI. J. VON BRAUN and K. WEISSBACH (Ber., 1931, 64, [B], 1785—1790).— β -Phenylglutaric acid, m. p. 140°, is converted by PCl₅ but not by SOCl₂ into the corresponding chloride, b. p. 178—180°/18 mm., m. p. 46°, transformed by AlCl₃ in CS₂ into 3-ketohydrindyl-1-acetic acid in 80% yield; ill-defined compounds containing S and Cl are also produced. 4-Hydroxydiphenyl is partly hydrogenated in presence of Ni to 4-cyclohexylcyclohexanol and 4-phenylcyclohexanol, oxidised by CrO₃ in AcOH to 4-cyclohexylcyclohexanone and 4-phenylcyclohexanone, m. p. 78° [*NaHSO*₃ compound; semicarbazone, m. p. 229° (decomp.)]. Oxidation of the last-named ketone with alkaline KMnO₄ leads to β -phenyladipic acid, m. p. 148° (*Et* ester, b. p. 197—200°/10 mm.), converted into the chloride and thence by AlCl₃ in CS₂ into almost equal amounts of the diketone (I), m. p. 149° (*semi-*



carbazone, decomp. 395°), and (?)4-keto-1:2:3:4-tetrahydronaphthalene-1-acetic acid, m. p. 60—63° [*semicarbazone*, m. p. 228—230° (decomp.)] (cf. Manske, this vol., 620). γ -Phenylpentane- α -diol is converted into the corresponding dibromide and thence into α -dicyano- γ -phenylpentane, b. p. 184—186°/0.15 mm., m. p. 50—51°, transformed into γ -phenylpimelic acid, m. p. 85°. The corresponding chloride is converted by AlCl₃ in CS₂ mainly into the diketone (II), m. p. 182—185°/0.3 mm., with smaller quantities of β -4-keto-1:2:3:4-tetrahydronaphthalene-1-propionic acid. The diketone is converted by Reformatsky's reaction into the substance C₂₁H₂₄O₄, b. p. about 240°/0.1 mm.

H. WREN.

Positive ion catalysis in the Knoevenagel reaction. K. C. BLANCHARD, D. L. KLEIN, and J. MACDONALD.—See this vol., 1017.

Condensation of acetonedicarboxylic acid with phenols and phenolic ethers. I. Formation

of β -substituted glutaconic acids. D. B. LIMAYE and V. M. BHAVE (J. Indian Chem. Soc., 1931, 8, 137—141).—PhOMe condenses with acetonedicarboxylic acid to give β -*p*-anisylglutaconic acid, m. p. 176° (decomp.) [*Et* H ester, m. p. 126—127°; monoanilide, m. p. 190° (decomp.); anil, m. p. 204—205°], converted at 180° or by boiling Ac_2O into its anhydride, m. p. 160°, and decarboxylated to *p*-isopropenylanisole (A., 1901, i, 272). The anhydride reacts with semicarbazide to give a compound, m. p. 208.9° (decomp.), a similar compound, m. p. 193°, being obtained from β -phenylglutaconic anhydride.

J. W. BAKER.

Constitution of some δ -ketocarboxylic acids. M. QUDRAT-I-KHUDA (J. Indian Chem. Soc., 1931, 8, 215—221; cf. A., 1929, 1273).—In accordance with expectations from the modified strain theory, but contrary to the statements of Barat (A., 1930, 925), acids of the type $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHR}'\cdot\text{CH}(\text{CO}_2\text{H})_2$ and the corresponding monocarboxylic acids exist in the open-chain and not the lactol forms, as evidenced by the following reactions. α -Carboxy- γ -benzoyl- β -phenylbutyric acid (I), when heated alone, or with AcCl , yields only the monobasic acid, and not the dilactone; (I) on esterification gives the normal Me_2 ester, and not the OMe-ester of the lactol acid. The constitutions assigned to the anhydride of (I) (A., 1929, 443) and to γ -acetyl- β -phenylbutyric acid (II) (A., 1897, i, 285) are proved correct by reactions described in the literature. (II) and, contrary to the statements of Barat, (I) are sol. in NaHCO_3 , if finely divided. The Me_2 ester of (I) (*semicarbazone*, m. p. 143°) is conveniently prepared by condensation of $\text{CH}_2(\text{CO}_2\text{Me})_2$ with Ph styryl ketone in MeOH in the presence of NaOMe, and with KOH in aq. EtOH yields a little Ph styryl ketone and (I) [*semicarbazone*, m. p. 220°, not 215° (Barat)]. $\text{CH}_2(\text{CO}_2\text{Me})_2$ and styryl Me ketone give similarly Me_2 α -carboxy- γ -acetyl- β -phenylbutyrate (*semicarbazone*, m. p. 118°), which gives the corresponding acid on hydrolysis. This acid is unaffected by AcCl , and when heated at 160—165° loses CO_2 to yield γ -acetyl- β -phenylbutyric acid (*semicarbazone*, m. p. 171.5°).

R. S. CAHN.

Ozonisation of aldehydes. E. BRINER, A. DEMOLIS, and H. PAILLARD.—See this vol., 1016.

Aldehydes. IV. Catalytic reduction of simple and substituted cinnamaldehydes. M. T. BOGERT and G. POWELL (J. Amer. Chem. Soc., 1931, 53, 2747—2755).—Reduction of various substituted cinnamaldehydes with H_2 and colloidal Pd in aq. EtOH gives mixtures of the corresponding saturated aldehyde, saturated alcohol, and alkylbenzene. Unsaturated alcohols and alkenylbenzenes were not produced. Thus, 3 : 4-methylenedioxy-cinnamaldehyde gives dihydrosafrole and γ -3 : 4-methylenedioxyphenylpropyl alcohol, b. p. 149—150°/6 mm. (acetate, b. p. 145°/4 mm.); 3 : 4-methylenedioxy- α -methylcinnamaldehyde affords 3 : 4-methylenedioxyisobutylbenzene, b. p. 238—240°/760 mm., and β -3 : 4-methylenedioxybenzylpropyl alcohol, b. p. 147—148°/4 mm.; 3 : 4-methylenedioxy- α -ethylcinnamaldehyde yields α -3 : 4-methylenedioxybenzylbutaldehyde, b. p. 136°/3 mm., β -3 : 4-methylenedioxybenzylbutyl alcohol, b. p. 148—150°/2 mm., and 3 : 4-methylenedioxy-1- β -methylbutyl-

benzene, b. p. 255—260°/760 mm.; α -ethylcinnamaldehyde furnishes α -benzylbutaldehyde, b. p. 115—116°/12.5 mm., β -benzylbutyl alcohol, b. p. 105—107°/4 mm., and β -methylbutylbenzene; α -*n*-amylcinnamaldehyde gives β -benzylheptyl alcohol, b. p. 134—135°/3.5 mm. (acetate, b. p. 119—120°/2.5 mm.; 3 : 5-dinitrobenzoate), and β -methylheptylbenzene, b. p. 128—130°/16 mm.; *o*-methoxy- α -methylcinnamaldehyde affords α -*o*-methoxybenzylpropaldehyde, b. p. 113—114°/5.25 mm., β -*o*-methoxybenzylpropyl alcohol, b. p. 131.5—132.5° (corr.)/8.75 mm., and *o*-isobutylanisole, b. p. 111—112° (corr.)/31.25 mm.; *o*- and *p*-methoxy- α -ethylcinnamaldehydes yield α -*o*-, b. p. 144—145°/16 mm., and α -*p*-methoxybenzylbutaldehydes, b. p. 116—117°/3 mm., β -*o*-, b. p. 132—134° (corr.)/5.5 mm., and β -*p*-methoxybenzylbutyl alcohols, b. p. 129—130°/2.5 mm., and *o*-, b. p. 100.5—102.5° (corr.)/9 mm., and *p*- β -methylbutylanisoles, b. p. 135—136°/29 mm., respectively. The odours of the above compounds are recorded. H. BURTON.

Derivatives of veratrole and methylvanillin. III. 4 : 5-Dimethoxy-2-carboxybenzoylformic acid. B. L. VANZETTI and A. OLIVERIO (Gazzetta, 1931, 61, 479—483).—A new method of preparing this acid is given by oxidation of 5 : 6-dimethoxy-2-oximino-1-hydrindone with cold KMnO_4 . It forms a dihydrate, m. p. 84—85°, with loss of $2\text{H}_2\text{O}$ giving the acid, m. p. 151—152°. The aniline (m. p. 179—180°) and *p*-toluidine [m. p. 162—163° (decomp.)] derivatives indicate that it is identical with the acid of Fargher and Perkin (J.C.S., 1921, 119, 1724).

E. E. J. MARLER.

4 : 4'-Dihydroxydiphenyl-3 : 3'-dialdehyde and its derivatives. R. N. SEN and S. DUTT (J. Indian Chem. Soc., 1931, 8, 223—229).—Addition of $\text{EtOH}\cdot\text{CHCl}_3$ (4 : 1) to *pp'*-dihydroxydiphenyl in aq. NaOH at 40—50° and subsequent boiling for 12 hr. gives 4 : 4'-dihydroxydiphenyl-3 : 3'-dialdehyde (I) (sol. in NaOH and Na_2CO_3 to give a red solution), yellow, m. p. 185° (*diphenylhydrazone*, m. p. 215°; *disemicarbazone* and *dioxime*, m. p. above 300°; *Bz*₂ derivative, m. p. 100°). Condensation with CCl_4 gives 4 : 4'-dihydroxydiphenyl-3 : 3'-dicarboxylic acid. (I) undergoes the benzoin condensation to yield the substance $\text{HO}\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_3\cdot\text{OH}$ (II), m. p. above 303° (sol. in NaOH and Na_2CO_3 , and reduces Fehling's solution), and condenses with 2 mols. of COMe, in 40% NaOH solution to yield 4 : 4'-dihydroxy-3 : 3'-di(β -acetylvinyl)diphenyl, deep red, m. p. above 300°. On heating with Ac_2O , NaOAc, pyridine, and a little I, (I) yields 6 : 6'-dicoumaryl, yellowish-brown, decomp. above 200°, precipitated by CO_2 from its solution in NaOH. Azomethine dyes, prepared from (I) and the components stated below in hot EtOH, had the following m. p.: NH_2Ph (2 mols.) and NaOAc, reddish-brown, m. p. above 300°; *p*-toluidine (2 mols.) and NaOAc, red, softens at 175°; aminoazobenzene (2 mols.), red, m. p. 260°; benzidine (1 mol.), and *p*-phenylenediamine (1 mol.), reddish-brown, m. p. above 300°; the dye from *m*-phenylenediamine (2 mols.), m. p. above 300°, diazotises and, therefore, has free NH_2 groups. The following pyronine dyes, m. p. above 300° in all cases, were pre-

pared from (I) and the phenols stated below in conc. H_2SO_4 at the temp. given, the dye shades being for wool and silk: diethyl-*m*-aminophenol, 120—130°, violet, dyes violet; resorcinol, water-bath, red, dyes orange (K_4 salt; Br_2 -derivative, deep red, dyes brilliant red); pyrogallol, water-bath, greyish-black, dyes black with an Fe and green with a Cr mordant (K_3 salt). (I) with $NPhMe_2$ and HCl on the water-bath, and with *o*-cresotic acid and cold H_2SO_4 gives *leucobases*, oxidised by PbO_2 and nitrosyl sulphate, respectively, to triphenylmethane *dyes*. The former, m. p. above 300°, dyes wool and silk bluish-green; the latter, brown, decomp. 225°, dyes wool and silk yellowish-red with Fe, Al, or Cr mordants. R. S. CAHN.

Cyclic ketones. R. POGGI and V. GUASTALLA (*Gazzetta*, 1931, 61, 405—432).—Monobenzylidene-cyclohexanone (I) (A., 1908, i, 424) gives an oxime, m. p. 126·5°; a *hydroxylamino-oxime* (with excess of NH_2OH , $OH:N:(C_6H_9):CHPh:NH\cdot OH$ (1:2), m. p. 190° (decomp.), and a *semicarbazone*, m. p. 199° (decomp.). Bromination of (I) gives a *compound*, m. p. 135° (decomp.), which reacts with pyridine giving a *compound*, m. p. 105—107°. Bromination of the *oxime* of (I) gives a *dibromo-oxime*, $OH:N:(C_6H_8Br):CHBrPh$, m. p. 106° (decomp.). Treatment of (I) with $EtNO_3$ (cf. A., 1928, 641) gives an indefinite product. *cyclohexanone* condenses with *p*-anisaldehyde giving *mono-p-anisylidenecyclohexanone* (II), m. p. 72·5—74° (*oxime*, m. p. 135°). Condensation of (II) with $PhCHO$ or of (I) with *p*-anisaldehyde gives *2-benzylidene-6-p-anisylidenecyclohexanone*, m. p. 104·5°, disproving Wallach's conclusion that *o*-substituted *cycloketones* do not undergo further condensation. On oxidation with peracetic acid *cyclohexanone* gives a *peroxide*, m. p. 88—91°; (I) gives a mixture of $BzOH$ and adipic acid and dibenzylidene-cyclohexanone gives $BzOH$ and an *acid*, $C_{13}H_{14}O_4$, m. p. 174·5°, the results of further oxidation of which suggest that it is α -benzylideneadipic acid. Attempts to prepare the *oxime* and *semicarbazone* of dibenzylidene-cyclohexanone were unsuccessful. Exaltone, $(CH_2)_{14}CO$, does not react with $PhCHO$ or $EtNO_3$. E. E. J. MARLER.

4-Methyl-1-ethinylcyclohexanol and its rearrangement into 4-methylcyclohexenyl methyl ketone. H. RUPE and F. KUENZY (*Helv. Chim. Acta*, 1931, 14, 701—708).—The Na derivative of 4-methylcyclohexanone, prepared by action of $NaNH_2$ in dry Et_2O , combines with C_2H_2 with formation of 4-methyl-1-ethinylcyclohexanol (I), b. p. 73—75°/10 mm., m. p. 20° (*Ag* salt; *acetate*, b. p. 100—101°/13 mm.; *benzoate*, b. p. 175—176°/11 mm., m. p. 77°), and 1:1'-*dihydroxydicyclohexylacetylene*, m. p. 155°, b. p. 185—190°/11 mm. (*diacetate*, b. p. 186—187°/11 mm., m. p. 57°). The former isomerises in warm 71% HCO_2H into 4-methylcyclohexenyl Me ketone (II) (A., 1908, i, 402), reduced by Ni and H_2 in $EtOH$ to α -4-methylcyclohexylethyl alcohol (A., 1911, i, 472) (*acetate*, b. p. 90°/11 mm.). Ozonisation of (I) in CCl_4 and hydrolysis of the product gives β -methyladipic acid, and oxidation with $NaOBr$ gives Δ^1 -tetrahydro-*p*-toluic acid (A., 1894, i, 522); (II) with $NaOBr$ gives hexahydro-*p*-toluic acid. $MgEtBr$ adds to (I) in the 1:4-positions with formation of β -4-

methylcyclohexenylbutan- β -ol, b. p. 76—77°/11 mm. (*acetate*, b. p. 84—85°/11 mm.). H. A. PIGGOTT.

Palladium catalyst. II. Effect of hydrogen chloride in hydrogenation of oximinoketones. W. H. HARTUNG (*J. Amer. Chem. Soc.*, 1931, 53, 2248—2253).—The substance, m. p. 108—110°, obtained by hydrogenation of oximinopropiophenone in $EtOH$ in presence of Pd-charcoal (A., 1929, 1066) is identified by direct comparison as acetylphenylcarbinoloxime, m. p. 113° (corr.; cf. A., 1930, 935). In addition (in two experiments) phenylpropanolamine, two unidentified bases isolated as Bz , m. p. 164° (corr.), and benzenesulphonyl, m. p. 110°, derivatives, respectively, and a *tert*-amine (?), m. p. 88° (corr.; sinters, 82°), were formed. The oximes of propionylphenyl- and valerylphenyl-carbinols are similarly obtained from oximino-butyro- and -hexophenones. The effect of HCl on the catalytic hydrogenation of α -oximinoketones (cf. A., 1929, 1066; 1930, 1286) is discussed. H. A. PIGGOTT.

Isomerism of phenacylamine oximes. M. BUSCH [with K. KÜSPERT] (*Ber.*, 1931, 64, [B], 1816—1818; cf. A., 1930, 603).—If the evidence of the optical behaviour of phenacyl-*p*-toluidine-*n*-oxime is accepted as conclusive (cf. following abstract), its chemical reactions indicate that it can assume the ψ -oxime structure under certain conditions. Hydroxydiphenyl-*p*-tolylidihydroiminazole (*loc. cit.*) is reduced by Zn dust and $AcOH$ to *diphenyl-p-tolylidihydroiminazole*, m. p. 152—153°, dehydrogenated by $FeCl_3$ in $EtOH$ to *diphenyl-p-tolyliminazole*, m. p. 148°. H. WREN.

Structure and isomerism of oximes. K. VON AUWERS and H. WUNDERLING (*Ber.*, 1931, 64, [B], 1806—1816).—The probability suggested by Raikowa (A., 1929, 1276) that under certain conditions isomerisation of the type $R\cdot C:(NOH)\cdot CH_2R' \rightarrow R\cdot C(NH\cdot OH):CHR'$ may be impossible is fulfilled by the oximes of mesityl oxide, hexahydrobenzophenone, ω -bromoacetophenone, γ -keto- Δ^2 -pentenoic acid and its acetate, ketosuccinic acid and its Et ester, β -benzoylpropionic acid, and other compounds. The many exceptions are held to invalidate the rule. The formation of a red coloration with $FeCl_3$ is not valid evidence of the presence of the $\cdot NH\cdot OH$ group. Aldoximes generally give the reaction, but frequently only after some hrs. The oximes of $COMe_2$, $Ph Pr^{\beta}$ and *tert*-Bu ketones, and $PhCOMe$ are indifferent, as are those of dibenzyl ketone and hydrindone. $Ph Et$ ketoxime and $Me CH_2Ph$ ketoxime give immediate colorations. Styryl Me ketoxime gives an immediate red colour which is not observed with its α -chloro- and α -bromo-derivatives. Ph styryl ketoxime reacts with $FeCl_3$, whereas its α -halogeno-derivatives do not. It appears probable that the red coloration with $FeCl_3$ given by many oximes does not depend simply on the formation of a complex Fe compound, but that the chloride reacts chemically with the oximes. The (fully described) spectrochemical behaviour of the oximes of $MeCHO$, *isobutaldehyde*, $Me Et$ ketone, $Pr^{\alpha} Pr^{\alpha}$ ketone, $Pr^{\beta} Pr^{\beta}$ ketone, $PhCOMe$, $Ph Et$ ketone, $Ph Pr^{\alpha}$ ketone, $Ph Pr^{\beta}$ ketone, and Ph *tert*-Bu ketone does not distinguish sharply between the suggested structures, but observations with the oximes of

CH₂Ph Me ketone, CH₂Ph Pr^β ketone, dibenzyl ketone, *n*-cinnamaldehyde, styryl Me ketone, Ph styryl ketone, and its α-bromo-derivative are more decisive. The optical behaviour of certain simple oximes is not incompatible with Raikowa's hypothesis, which is definitely contradicted by that of other oximes. Since there is no chemical evidence for the assumption of the existence of groups of oximes of differing constitution, the customary uniform conception must be maintained.

The spectrochemical behaviour of the compounds obtained by the action of NH₂OH on phenacyl-*p*-toluidine contradicts the hypothesis that they are isomerides OH·N:CPh·CH₂·NH·C₆H₄Me and OH·NH·CPh:CH·NH·C₆H₄Me (cf. A., 1930, 603).

Benzyl isopropyl ketoxime has m. p. 60—61°.

H. WREN.

Condensations by sodium instead of by the Grignard reaction. II. Reaction with benzonitrile. Preparation of diphenylketazine. A. A. MORTON and J. R. STEVENS (J. Amer. Chem. Soc., 1931, 53, 2769—2772).—PhCN, PhCl, and Na in Et₂O and N₂ afford a red solution of sodiodiphenylmethyleneimine, converted by H₂O, O₂, and I into COPh₂, benzophenoneoxime, and diphenylketazine, respectively. PhCN and MgPhBr give the compound CPh₂:N·MgBr, converted by I into diphenylketazine.

H. BURTON.

Benzophenone diazide. S. GÖTZKY (Ber., 1931, 64, [B], 1555—1560).—*Benzophenonediazide*, C₁₃H₁₀N₆, m. p. 42°, prepared in 88% yield by the action of AgN₃ on benzophenone chloride in Et₂O, is stable at room temp. and little more sensitive than picric acid to shock. It passes in boiling amyl ether, or when distilled under diminished pressure, into N₂ and diphenyltetrazole, m. p. 146°. With MeOH it affords benzophenonedimethylacetal, m. p. 107°. With 70% H₂SO₄ it gives N₂, N₃H, and benzanilide. The last-named product is also obtained when H₂SO₄ or HNO₃ is added to the diazide in C₆H₆. The parachor indicates a cyclic structure of the N₃ group.

H. WREN.

Reduction of aromatic ketones and benzils by magnesium triphenylmethyl bromide. W. E. BACHMANN (J. Amer. Chem. Soc., 1931, 53, 2758—2763).—Xanthone, fluorenone, COPh₂, and 4-chloro-, 4-phenyl-, and 4:4'-diphenyl-benzophenones are reduced by MgCPh₃Br to the corresponding pinacols. The initial reaction COR₂+MgCPh₃Br→

CR₂·OMgBr+ĈPh₃, is followed by association of the free radicals. Benzil, 4:4'-dichloro-, and 4:4'-dimethyl-benzils are reduced by MgCPh₃Br to the corresponding benzoin; reaction occurs by way of the stilbenediol derivative (ĈPh·OMgBr)₂. MgPhI (2 mols.) in Et₂O added to PhCHO (1 mol.) in warm C₆H₆ gives a product containing CH₂Ph·OH (25%), CHPh₂·OH, and CPh₃·OH (16%) (cf. Marshall, A., 1925, 1, 1428).

H. BURTON.

Preparation of fluorenone from fluorene and from diphenic acid. E. H. HUNTRESS, E. B. HERSHBERG, and I. S. CLIFF (J. Amer. Chem. Soc., 1931, 53, 2720—2724).—Almost quant. yields of fluorenone are obtained when diphenic acid or anhydride or fluorenone-4-carboxylic acid is heated at

360°. An improved process for the prep. of fluorenone from fluorene is given.

H. BURTON.

Anthracene derivatives. V. E. DE B. BARNETT, J. A. LOW, and F. C. MARRISON. VI. E. DE B. BARNETT and C. L. HEWETT (Ber., 1931, 64, [B], 1568—1571, 1572—1581).—V. Me groups in the 2- and 3-position have a similar influence on the properties of 10-bromoanthrone, but the effect is more marked with the 2-compound. When the substituents are present in both positions, an enhanced action is observed. 2-Methylanthrone is converted by Br in CS₂ into 10-bromo-2-methylanthrone, decomp. 130°, transformed into 10-*p*-dimethylaminophenyl-2-methylanthrone, m. p. 170° (decomp.) after darkening, and 10-piperidino-2-methylanthrone, m. p. 108° (decomp.). 10-Bromo-3-methylanthrone, decomp. 118°, yields 10-*p*-dimethylaminophenyl-3-methylanthrone, m. p. 184° (decomp.) after softening, and 10-anilino-3-methylanthrone, decomp. about 180°, but is transformed by piperidine in CHCl₃ into 10-bromo-3:3'-dimethyldianthrone, decomp. about 175°. 2-Phenylanthrone is transformed by Ac₂O in pyridine into 2-phenylanthranyl acetate, m. p. 158°, and by Br in CS₂ into 10-bromo-2-phenylanthrone, decomp. 127°, which yields 2-phenyl-10-*p*-dimethylaminophenylanthrone, m. p. 183° (decomp.).

VI. The majority of the abnormalities found in the behaviour of 1:4-dimethylanthrone are not observed with the 1:3- or 2:4-Me₂ compounds. Investigation of the 2- and 3-Me and the 2:3-Me₂ derivatives indicates that this effect is not due to a hindering influence of the Me group in the β-position.

1:3-Dimethylanthrone, m. p. 119—120°, is obtained in 50% yield by condensation of phthalic anhydride with *m*-xylene followed by dehydration of the product with conc. H₂SO₄ at 100° and reduction with Al powder; 1:3-dimethylanthranyl acetate has m. p. 153°. *o*:2:4-Dimethylbenzoylbenzoic acid is reduced by activated Zn dust to *o*:2:4-dimethylbenzylbenzoic acid, converted by 80% H₂SO₄ into 2:4-dimethylanthrone, m. p. 157° (2:4-dimethylanthranyl acetate, m. p. 118°). 1:3-Dimethylanthrone and Mg benzyl chloride yield 9-benzyl-1:3-dimethylanthracene, m. p. 126°, converted into 10-bromo-9-benzylidene-1:3-dimethyl-9:10-dihydroanthracene, m. p. 139° (decomp.), which with CaCO₃ and MeOH yields 10-methoxy-9-benzylidene-1:3-dimethyl-9:10-dihydroanthracene. 2:4-Dimethylanthrone and MgMeI afford 2:4:9-trimethylanthracene, m. p. 100°. 9-Benzyl-2:4-dimethylanthracene, m. p. 149°, yields 10-bromo-9-benzylidene-2:4-dimethyl-9:10-dihydroanthracene (or 9-*α*-bromobenzyl-2:4-dimethylanthracene), m. p. 130°, transformed into 9-*α*-methoxybenzyl-2:4-dimethylanthracene, m. p. 153°, and the corresponding *α*-ethoxy-compound, m. p. 128°. 10-Bromo-1:3-dimethylanthrone, m. p. about 132° (decomp.), gives the corresponding 10-piperidino-, m. p. 122° (decomp.), 10-anilino-, m. p. 194° (decomp.) after softening, 10-*p*-dimethylaminophenyl-, m. p. 162° (decomp.), and 10-methoxy-, m. p. 79°, derivatives (10-methoxy-1:3-dimethylanthranyl acetate, m. p. 128°). Similarly, 10-bromo-2:4-dimethylanthrone, m. p. 151° (decomp.), gives the corresponding 10-piperidino-, m. p. 123°, 10-anilino-, m. p. 196° (decomp.), 10-*p*-dimethylaminophenyl-, m. p. 186° (decomp.), and 10-methoxy-, m. p.

86°, compounds (2 : 4-dimethoxyanthranyl acetate, m. p. 93°). 10-Phenyl-1 : 3-dimethylanthrone, m. p. 161°, from the 10-bromo-compound, AlCl_3 and C_6H_6 (10-phenyl-1 : 3-dimethylanthranyl acetate, m. p. 149°), is converted by MgMeI into 10-phenyl-1 : 3 : 9-trimethylanthrone, m. p. 165°. 10-Phenyl-2 : 4-dimethylanthrone, m. p. 154° (10-phenyl-2 : 4-dimethylanthranyl acetate, m. p. 203°), gives 10-phenyl-2 : 4 : 9-trimethylanthrone, m. p. 121°. 10-Phenyl-9-benzyl-2 : 4-dimethylanthrone has m. p. 137°. Reduction of 1 : 3- or 2 : 4-dimethylanthrone with activated Zn , NH_3 , and NaOH yields dihydroanthranols converted by HCl in MeOH into 1 : 3-dimethylanthrone, m. p. 82°.

H. WREN.

Mixed benzoin. V. Reversibility of benzoin condensation and preparation of mixed from simple benzoin. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1931, 53, 2350—2353).—The reversibility of the reaction of benzoin formation is proved by the formation of mixed benzoin from a simple benzoin (e.g., benzoin, piperoin, or furfuroin) and a suitable aldehyde in aq.-alcoholic KCN . *p*-Dimethylaminobenzpiperoin, m. p. 132° (turbid, clear at 136°), is obtained either from the appropriate aldehydes in the usual way, or from piperoin and *p*-dimethylaminobenzaldehyde as described above.

H. A. PIGGOTT.

Mixed benzoin. VI. Further examples of reversibility. Formation of additive compounds. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1931, 53, 2784—2787).—*o*-Chloroanisoin and *p*- $\text{NMe}_2\text{C}_6\text{H}_4\text{CHO}$ in aq.-alcoholic KCN give *o*-chloro-*p*'-dimethylaminobenzoin; benzanisoin or benzpiperoin with the same aldehyde give *p*-dimethylaminobenzoin. Similarly, benzpiperoin and *o*- $\text{ClC}_6\text{H}_4\text{CHO}$ afford *o*-chlorobenzpiperoin, whilst benzoin with piperoin and furin yields benzpiperoin and benzfuroin, respectively.

Cryst. additive compounds of 1 mol. of benzoin and 1 mol. of benzpiperoin, anisoin, or piperoin, and of 1 mol. of piperoin with 1 mol. of anisoin or *p*- $\text{NMe}_2\text{C}_6\text{H}_4\text{CHO}$, are readily obtained; they do not persist in solution.

H. BURTON.

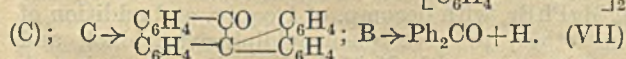
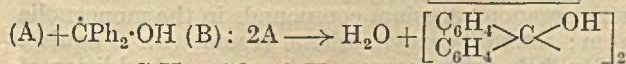
Pinacol-pinacolin [transformation]. E. BERGMANN and W. SCHUCHARDT (Annalen, 1931, 487, 225—263).—The synthesis of pinacols from a ketone, Mg , and I (A., 1929, 1067) is considered to proceed by way of $(\text{R}_2\text{C}\cdot\text{O})_2\text{Mg}$ and $\begin{matrix} \text{CR}_2\cdot\text{O} \\ \text{CR}_2\cdot\text{O} \end{matrix} > \text{Mg}$ rather than by formation of " MgI ," partly from known facts, and partly because, using $\text{Ph}\alpha$ -naphthyl ketone, gradual addition of dioxan causes a ppt. with a varying $\text{Mg} : \text{I}$ ratio. The I functions by activating the Mg . The Tiffeneau-Meerwein theory of the pinacol-pinacolin transformation is considered too narrow, partly from known facts, and partly for the following reasons.

(a) 9- α -Hydroxybenzhydrylfluoreneol (I), which with conc. H_2SO_4 or POCl_3 gives 9 : 9-diphenylphenanthrone (II) (A., 1913, i, 485), with AcCl or SOCl_2 gives 9-benzoyl-9-phenylfluorene (III) [accompanied by (II) in one experiment with SOCl_2]. (III) with cold conc. H_2SO_4 gives (II), and is, therefore, the primary product of the transformation, contrary to the above theory. Different results, however, were obtained

with the corresponding *p*-anisyl- and *p*-tolyl-pinacols. Me fluoreneol-9-carboxylate, Mg , and *p*-bromoanisole gave 9-(hydroxydi-*p*-anisylmethyl)fluoreneol (IV), m. p. 134—137° (variable), which with AcCl or SOCl_2 gave 9 : 9-di-*p*-anisylphenanthrone (V), m. p. 150°, but tars with POCl_3 or conc. H_2SO_4 . (V) was synthesized from 9 : 9-dichlorophenanthrone, PhOMe , and AlCl_3 in CS_2 . 9-Hydroxy-9-*p*-anisylfluorene, an oil (from fluoreneone and Mg *p*-anisyl bromide), AcCl , and HCl in C_6H_6 gave 9-chloro-9-*p*-anisylfluorene, m. p. 147°; transformed by hot MeOH into 9-methoxy-9-*p*-anisylfluorene (VI), m. p. 173—174°, which with Na in Et_2O and *p*-anisoyl chloride gave 9-*p*-anisoyl-9-*p*-anisylfluorene, m. p. 137°. This was unchanged by hot AcCl . (VI) with Na in Et_2O , followed by EtOH , yielded 9-*p*-anisylfluorene, m. p. 121°. 9-(Hydroxydi-*p*-tolylmethyl)fluoreneol (VII), m. p. variable (163° to 174—175°) (similarly prepared), with AcCl , SOCl_2 , or conc. H_2SO_4 gave 9 : 9-di-*p*-tolylphenanthrone, m. p. 158°, which with KOH in MeOH gave an acid, probably 2-di-*p*-methylbenzhydryldiphenyl-2'-carboxylic acid. The fact that this acid was not *p*-toluic acid proves the constitution of the phenanthrone.

(b) The diastereomeric forms of phenyl-naphthyl- and phenyl-*p*-chlorophenyl-pinacols behave differently on rearrangement. Reduction of $\text{Ph}\alpha$ -naphthyl ketone by Zn and AcOH gave the pinacol (A), m. p. 159°, or, if air was excluded, a substance, $\text{C}_{68}\text{H}_{50}\text{O}_5$, m. p. 234°, which liberates I from KI in AcOH , and yields BzOH on oxidation with CrO_3 . A form, m. p. 220°, could not be obtained (cf. A., 1929, 316). Prep. of the pinacol by Gomberg's method gave, under certain conditions, a substance, m. p. 215°. The isomeride, m. p. 199° (A., 1929, 1175) (best prepared from $\text{Et}\alpha$ -naphthoate and MgPhBr), gave with AcCl , SOCl_2 , or AcOH and I an amorphous substance, which liberated I from KI in AcOH , whereas isomeride A with SOCl_2 gave α -naphthyl diphenyl- α -naphthylmethyl ketone (cf. *loc. cit.*), which was synthesised by treatment of diphenyl- α -naphthylmethyl chloride (from the carb-inol, AcCl , and HCl in C_6H_6) with Na in Et_2O , followed by α -naphthoyl chloride. No substance, m. p. 180—183°, could be isolated on reduction of *o*-chlorobenzophenone (contrast *loc. cit.*). The pinacol, m. p. 164°, from *o*-chlorobenzophenone was unchanged by SOCl_2 , but with AcCl , or AcOH and 70% H_2SO_4 gave *p*-chlorophenyl diphenyl-*p*-chlorophenylmethyl ketone, m. p. 139°, the constitution of which is proved by hydrolysis with KOH in MeOH to *o*-chlorotriphenylmethane and *o*-chlorobenzoic acid. The isomeric pinacol, m. p. 186°, was unchanged by AcCl , but with AcOH and 70% H_2SO_4 , AcOH and I , or SOCl_2 gave the above ketone, m. p. 139°.

(c) PhNCO and (I) at 120—130°, or at 90° yield diphenylcarbamide, 9-diphenylphenanthrone, and benzophenone. The following mechanism, involving free radicals, is assumed: $(\text{I}) \rightarrow \text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{C}_6\text{H}_4$



similarly gives diphenylcarbamide, 9-diphenylphenanthrone, and di-*p*-tolyl ketone, but (IV) gives the normal product of pinacolin transformation (V).

Similar rupture of the ethane C·C linking was observed with xanthonepinacol. This pinacol (H₂O must be excluded during its prep.) with AcCl gives xanthone, dixanthylene, and (probably) *dixanthyl peroxide*, $\left[\text{O} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \right\rangle \text{CH} \cdot \text{O} \right]_2$, decomp. 237° (liberates I from KI in AcOH). This is interpreted as dehydration to

$\text{O} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \right\rangle \text{C} \cdot \text{C} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \right\rangle \text{O}$, which dissociates to xanthone and $\text{O} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \right\rangle \text{C} \cdot$, two free radicals then combining to yield dixanthylene. Simultaneously some of the pinacol dissociates to $2\text{O} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \right\rangle \dot{\text{C}}(\text{OH})$,

which isomerise to $2\text{O} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \right\rangle \text{CH} \cdot \text{O}$, and these unite to form the peroxide. Xanthonepinacol and PhNCO yield xanthone and a little dixanthylene. A possible mechanism, involving free radicals, for this reaction is discussed. The velocity of the disproportionation of tetra-arylpinacols, on heating in indifferent solvents, into ketones and secondary alcohols was studied ebullioscopically (1 mol. \rightarrow 2 mols.) with xanthopinacol in PhMe, the pinacols of *o*-chlorobenzophenone (m. p. 186° form) and Ph α -naphthyl ketone in *m*-xylene, and benzpinacol in *m*-xylene and PhCl. The reactions are unimol. The heat of activation of benzpinacol and the relative values of the velocity coeff. are in harmony with the assumption that disproportionation is a very rapid reaction, preceded by dissociation into free radicals. This view is supported by the change of the low-melting pinacol of *o*-chlorobenzophenone into the high-melting isomeride on heating in indifferent solvents. The ebullioscopic consts. (determined by fluorene) for PhMe, PhCl, and *m*-xylene are 3.16, 4.42, and 4.09, respectively.

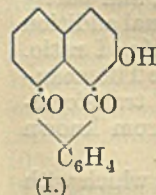
Anthrapinacol with AcCl gave α -anthrapinacolin, m. p. 215°, and in one experiment also a little 9 : 9'-dianthryl, m. p. 300—302°, which was always formed with AcOH and H₂SO₄ (whereas methods of prep. hitherto described often fail). Dianthryl, m. p. 360° (J.C.S., 1923, 123, 380), could not be obtained. The compound, m. p. 298—300° (A., 1926, 295), described as dihydroanthryl is the above dianthryl, the constitution being proved because, on treatment with Na in Et₂O, followed by CH₂PhCl and H₂O, the ratio of ionic Cl to recovered dianthryl was 3 : 1, showing that 4 Na atoms had reacted. The pinacolin has the α -structure because, like α -benzpinacolin, it does not react with MgPhBr, which, contrary to statements in the literature, reacts with β -benzpinacolin in the cold to give pentaphenylethyl alcohol. R. S. CAHN.

Cleavage of β -diketones. I. Cleavage by organic magnesium compounds. E. P. KOHLER and J. L. E. ERICKSON (J. Amer. Chem. Soc., 1931, 53, 2301—2309).—Highly-enolised β -diketones react with organomagnesium compounds in the monoenolic form; thus dibenzoylmethane reacts with 2 equivs. of MgPhBr, with decomp. of 1 equiv. and addition of the other, to give phenacyldiphenylcarbinol, and acetylacetone with MgMeI gives diacetone alcohol. In the case of mono- and di-substituted derivatives of these ketones, which do not normally exhibit enolic

properties, 2 equivs. of Grignard reagent are added, and fission of the primary Mg derivative occurs; e.g., dibenzoylmethane gives deoxybenzoin and triphenylcarbinol on account of fission of the primary additive product: $\text{COPh} \cdot \text{CHPh} \cdot \text{CPh}_2 \cdot \text{OMgBr} \rightarrow \text{CPh}(\text{OMgBr}) \cdot \text{CHPh} + \text{COPh}_2$. A slight tendency to fission of this character occurs in the case of the mono-Mg derivative from CH₂Bz₂; consequently PhCOMe and COPh₂ are usually found among the reaction products. It is also characteristic of the Mg-enolate of phenacyldiphenylcarbinol, which with MgPhBr gives triphenylcarbinol and $\alpha\gamma\gamma$ -tetraphenylpropane- $\alpha\gamma$ -diol. In some cases it can be avoided; e.g., addition of MgPhBr to dibenzoylmethane at -10° followed immediately by acidification gives tetraphenylpropanone in 67% yield. The interaction of diphenylpropanetrione with MgPhBr gives triphenylcarbinol and benzoin on account of primary attack of the central CO group and subsequent behaviour of the reaction product as a typical β -diketone. The inverse reaction with 1 equiv. only of MgPhBr gives, not the expected carbinol, but its isomeride, *benzoin benzoate*, m. p. 123—124°. Further examples are afforded by the reaction with MgPhBr of $\alpha\alpha$ -dibenzoyl ethane, which gives propiophenone and triphenylcarbinol, $\beta\beta$ -dibenzoylpropane, which gives PhCOPr ^{β} and triphenylcarbinol, and dimethylacetylacetone, which gives MeCOPr ^{β} and $\alpha\alpha$ -diphenylethyl alcohol; dimethylacetylacetone also reacts with Mg mesityl bromide (or iodide?) to give MeCOPr ^{β} and acetomesitylene (*m*-nitrobenzylidene derivative, m. p. 82°). Mono- and di-bromodibenzoylmethanes interact in an essentially different manner and yield CH₂Bz₂ and β -bromo- $\alpha\gamma\gamma$ -triphenylpropan- α -ol- γ -one (cf. A., 1905, i, 215) respectively. H. A. PIGGOTT.

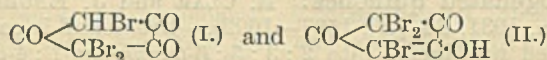
Supposed chalkone from phloracetophenone and piperonal. A. SOHN and H. FISCHER (Ber., 1931, 64, [B], 1909—1910).—Contrary to Shriner and Kleiderer (A., 1929, 701), the compound C₁₆H₁₂O₆ is formed only in very small amount by the condensation of phloracetophenone or pyrogallol with piperonal in alkaline solution. The product appears to be formed when the solution is acidified. It is suggested that it is due to the loss of 1H₂O from 2 mols. of phloroglucinol and 1 mol. of piperonal and further loss of 1H₂O during desiccation. H. WREN.

Phthalyl- β -naphthol, an instance of peri-condensation of phthalic anhydride. A. RIECHE and E. FRÜHWALD (Ber., 1931, 64, [B], 1603—1606).— β -Naphthol and phthalic anhydride in conc. H₂SO₄ containing H₃BO₃ at 160—165° yield 1 : 8-*phthalyl- β -naphthol* (I), m. p. 196°, identical with the "hydroxynaphthanthraquinone" of G.P. 298345. It is not reduced by Zn and NaOH and does not react with Br or NHPh·NH₂ in AcOH. The corresponding *Ac*, m. p. 216°, and *Bz*, m. p. 213°, derivatives are described. It is converted by NaOH at 240—280° into 7-hydroxynaphthoic acid, m. p. 252—253° (*Ac* derivative, m. p. 222—223°). H. WREN.



Isomerism of the compounds C₅HO₃Br₃, the so-called tribromotriketopentamethylene and xanthogallic acid. A. HANTZSCH and E. STRASSER

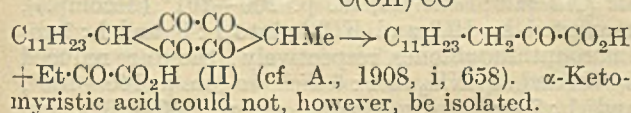
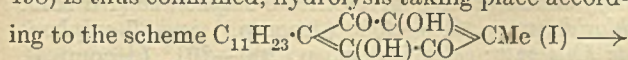
(Annalen, 1931, 488, 203—210).—Xanthogallic acid (cf. A., 1888, 1084; 1917, i, 460) and the "tribromotriketopentamethylene" of Hantzsch (A., 1888, 1190; cf. Henle, A., 1907, i, 222) are represented as



respectively. (I) reacts very slowly with Et diazoacetate, whereas (II) reacts violently. (I) and CH_2N_2 in Et_2O give a *Me ether*, m. p. 109—111°, also formed from the Ag salt of (I) and MeI; an isomeric *Me ether*, m. p. 88°, is obtained from (II) and CH_2N_2 . (I) and Br in AcOH afford 1 : 1 : 3 : 3-tetrabromo-2 : 4 : 5-triketocyclopentane, m. p. 149° (decomp.), whilst (I) and (II) are converted by aq. HBr into penta- and hexabromoacetone, respectively. Xanthogallol (*loc. cit.*) and PCl_5 at 260—290° give octachlorocyclopentene. The non-identity of the above Me ethers suggests that (I) and (II) are stable isomerides; the unusual stability is due to the negative groups in the mol.

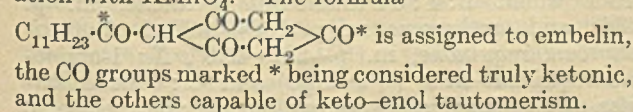
H. BURTON.

Constitution of embelin. K. S. NARGUND and B. W. BHIDE (J. Indian Chem. Soc., 1931, 8, 237—240).—Oxidation of embelin (I) with KMnO_4 in CO_2 or aq. NaOH gives *n*-lauric acid (cf. A., 1900, i, 498; 1929, 1306). Hydrolysis of (I) with aq. KOH yields α -ketomyristic acid, m. p. 63.8° (*Na salt*; *oxime*, m. p. 94—95°; *semicarbazone*, decomp. above 170°), the constitution of which is proved by oxidation with boiling HNO_3 or alkaline KMnO_4 to tridecoic acid. The constitution (I) assigned to embelin (A., 1900, i, 498) is thus confirmed, hydrolysis taking place according to the scheme



R. S. CAHN.

Constitution of the active principle of *Embelia ribes*. II. R. KAUL, A. C. RAY, and S. DUTT (J. Indian Chem. Soc., 1931, 8, 231—235; cf. A., 1929, 1306).—Embelin contains two reactive CH_2 groups, since it condenses with one or two mols. of aldehydes or NO-compounds. It also reacts with HCO_2Et , but the product could not be purified. With HNO_2 it yields a yellow cryst. compound, unstable above 0°. Boiling with dil. HNO_3 oxidises embelin to *n*-lauric acid, and a small quantity of an acid, m. p. 34—35°, which may be impure *n*-lauric acid, or *isolauric acid*. *n*-Lauric, and not *isolauric acid* (*loc. cit.*), together with $(\text{CO}_2\text{H})_2$ and $\text{CH}_2(\text{CO}_2\text{H})_2$ are obtained on oxidation with KMnO_4 . The formula



The following embelin derivatives were prepared by the method indicated by the letter in parentheses, viz., condensation in (A) H_2SO_4 in EtOH under reflux, (B) dry HCl in abs. EtOH at room temp., or (C) EtOH-AcOH (1 : 1) on the water-bath. *Benzylidene-*, + H_2O , (A) (isol. in NaOH; gives a red colour with conc. H_2SO_4 and chars), m. p. 112°; *dibenzylidene-*, + H_2O , (B), m. p. 142° (insol. in NaOH, and

with conc. H_2SO_4 gives a reddish-violet colour); *disalicylidene-*, + H_2O , (A), m. p. 152°; *dianisylidene-*, + H_2O , (A), m. p. 167°; *divanillylidene-*, + H_2O , (A), m. p. 230°; *di-p-toluylidene-*, + H_2O , (B), m. p. 244°; *diethylidene-*, + H_2O , (B), m. p. 123° (from paraldehyde); *dibutylidene-*, + H_2O , (B), m. p. 120°; *bisphenylimino-*, (C), m. p. 195° (decomp.); *bis-p-hydroxyphenylimino-*, (C), m. p. 207°; *bis-p-dimethylaminophenylimino-*, (C), m. p. above 290°; *p-dimethylaminophenylimino-*, (B), m. p. above 290°; *bis-2:4-dihydroxyphenylimino-*, (C), m. p. 230°; *bis-2-hydroxynaphthylimino-embelin*, (C), m. p. above 290°. The compounds with aldehydes lose the H_2O of crystallisation with partial decomp. at 120°, or without decomp. at 70° in vac., are yellow to orange-red, form dibromides, and with dil. KMnO_4 regenerate the ketone with destruction of the embelin mol. The imino-compounds, which are buff to dark brown, are readily reduced, e.g., by Zn dust and AcOH, to embelin and the aromatic amine; with stronger reducing agents, dihydroembelin is formed. R. S. CAHN.

Alteration of the additive capacity of quinones by the introduction of substituents. K. BRASS and E. TENGLER (Ber., 1931, 64, [B], 1654—1664).—Introduction of halogen, NH_2 , or OH into quinones generally diminishes their power of forming additive compounds with metallic salts. Particularly in the SbCl_5 series, this generalisation is not in harmony with the view that the metallic atom is united with the carbonyl O in the molecular compounds of quinones with metallic salts. It is more probable that the total amount of free valency of the substituted quinone is responsible for the saturation of the metallic atom. The compounds of SnCl_4 with dihalogenated anthraquinones appear exceptional. The compounds are prepared from the components in CHCl_3 , C_6H_6 , PhMe, $\text{C}_6\text{H}_4\text{Me}_2$, or PhNO_2 at room temp. or (max.) 100°. *Adducts* from the following are described: $2\text{C}_{14}\text{H}_8\text{O}_2$, SnCl_4 ; di-1-chloroanthraquinone, SbCl_5 ; 2-iodoanthraquinone, SbCl_5 ; 2-aminoanthraquinone, SbCl_5 ; 1-aminoanthraquinone, SbCl_5 ; 1 : 2-dibromoanthraquinone, SbCl_5 (also + CHCl_3); 1 : 2-dibromoanthraquinone, SnCl_4 ; 2 : 3-dibromoanthraquinone, SbCl_5 , CHCl_3 ; 2 : 3-dibromoanthraquinone, SnCl_4 ; di-2 : 3-dibromoanthraquinone, AlCl_3 ; di-2 : 3-dibromoanthraquinone, FeCl_3 ; di-2 : 3-dibromoquinizarin, SbCl_5 ; di-2 : 3-dibromoquinizarin, SnCl_4 ; di-2 : 3-dibromoalizarin, SnCl_4 , and the complex salt, $\text{C}_{20}\text{H}_8\text{O}_6(\text{OH})_2\text{Br}_4$, SnCl_4 ; α -naphthaquinone, SnCl_4 ; 2 : 3-dibromo- α -naphthaquinone, SbCl_5 ; 2 : 3-dibromo- α -naphthaquinone, SnCl_4 ; di- β -naphthaquinone, SbCl_5 ; dichloro- β -naphthaquinone, SnCl_4 ; bisdichloro- β -naphthaquinone, SbCl_5 ; 2-bromophenanthraquinone, SbCl_5 ; di-2-bromophenanthraquinone, SnCl_4 . H. WREN.

Direct formation of quinones from 2 : 6-disubstituted derivatives of 4-nitrophenol. E. C. S. JONES and J. KENNER (J.C.S., 1931, 1842—1857).—4-Nitro-2 : 6-diphenylphenol decomposes spontaneously in AcOH solution into 2 : 6-diphenyl-1 : 4-benzoquinone, NO, H_2O , and a substance, $\text{C}_{108}\text{H}_{72}\text{O}_8$, which is readily oxidised to the quinone by aq. $\text{H}_2\text{Cr}_2\text{O}_7$. The reaction, which is also brought about by heat in absence of a solvent, appears to depend on the pre-

sence of *op*-directing groups in the 2 : 6-positions, and is not undergone by 2-nitro-*s*-xylenol, nor apparently by the 2-Ph or 2-Et derivatives of *p*-nitrophenol. Except in the cases of 4-nitro-2 : 6-diphenyl- and -2 : 6-di-*m*-tolyl-phenols, the evolution of NO is far from quant., and the decomp. is not undergone at all by the 2 : 6-di-*o*-tolyl derivative. The nature of the second org. product also seems to vary with the substituents. In every case, however (with the exception of the 2 : 6-dihalogeno-derivatives, which on thermal decomp. evolve nitrosyl halides in addition to NO), smooth oxidation to quinone is brought about by Pb(OAc)₄. The reaction, the mechanism of which is discussed at length, is similar to the thermal decomp. of the quinotrols (A., 1899, i, 30); 3 : 5-dichloro-4-methylquinotrol, when heated with AcOH, gives NO, NOCl, and a little N₂.

s-Di-*o*-, m. p. 50—52°, b. p. 201°/16 mm. (*semicarbazone*, m. p. 142—143°), and *s*-di-*m*-tolylacetone, b. p. 204°/16 mm. (*semicarbazone*, m. p. 92—93°), are obtained by distillation of the Ca tolylacetates. Di-*p*-tolylacetonesemicarbazone has m. p. 84—85°. The following are obtained by interaction of the appropriately substituted COMe₂ with Na nitromalonaldehyde: 4-nitro-2 : 6-diphenylphenol; 4-nitro-2 : 6-di-*o*-tolyl-, m. p. 192—193°, -2 : 6-di-*m*-tolyl-, m. p. 145°, -2 : 6-di-*p*-tolyl-, m. p. 137°, -2 : 6-diethyl-, m. p. 130—131°, -2 : 6-dicarbethoxy-, m. p. 61°, -2-methyl-6-ethyl-, m. p. 135—136°, and -2-ethyl-phenol, m. p. 79—80°; 5-nitro-*m*-2-xylenol, also prepared, together with 2 : 6-xyloquinone, by nitration of *m*-2-xylenol. The following quinones are formed by heating the corresponding nitrophenols with Pb(OAc)₂ in glacial AcOH: 2 : 6-diphenyl-1 : 4-benzoquinone; 2 : 6-xyloquinone; 3 : 5-dibromo-2 : 6-xyloquinone; 2 : 6-di-*o*-tolyl-, m. p. 124°, 2 : 6-di-*p*-tolyl-, m. p. 161° (*quinol*, m. p. 105°), 2-methyl-6-ethyl-, m. p. 40—41° (*quinol*, m. p. 99—100°), 2 : 6-diethyl- (*quinol*, m. p. 102—103°), and 2 : 6-di-*m*-tolyl-1 : 4-benzoquinone, m. p. 103—104°.

4-Amino-2 : 6-di-*o*-tolylphenol, m. p. 215°, obtained by reduction of the corresponding nitrophenol with SnCl₂-HCl in AcOH, is converted into 2 : 6-di-*o*-tolyl-1 : 4-benzoquinone by oxidation with Na₂Cr₂O₇ and H₂SO₄ in the usual way. H. A. PIGGOTT.

Synthesis of polyporic acid and atromentin dimethyl ether. P. R. SHILDNECK and R. ADAMS (J. Amer. Chem. Soc., 1931, 53, 2373—2379; cf. A., 1926, 407).—The prep. of 2 : 5-diphenylquinol (cf. A., 1922, i, 1164) in 65% yield is described. Its 3 : 6-Br₂-derivative, m. p. 237°, is oxidised by benzoquinone in 95% EtOH to 3 : 6-dibromo-2 : 5-diphenylbenzoquinone, m. p. 224° (uncorr.), which is hydrolysed by NaOH in aq. MeOH to 3 : 6-dihydroxy-2 : 5-diphenylbenzoquinone (polyporic acid : Ac₂ derivative, m. p. 215°), yields of 90% or more being obtained at every stage. Reduction of diacetylpolyporic acid with SnCl₂ in COMe₂ gives 3 : 6-diacetoxy-2 : 5-diphenylquinol, m. p. 246° (Ac₂ derivative, m. p. 267—268°).

2 : 5-Dianisylquinol (A., 1922, i, 1164) is converted by bromination in AcOH into 3 : 6-dibromo-2 : 5-dianisylbenzoquinone, m. p. 282—283°, which is hydrolysed as above to 3 : 6-dihydroxy-2 : 5-dianisylbenzoquinone, m. p. 297—298° (atromentin Me₂ ether). Interaction of benzoquinone and PhOBu^a with AlCl₃

in CS₂ gives 2 : 5-di-(*p*-*n*-butoxyphenyl)benzoquinone, m. p. 173°. H. A. PIGGOTT.

Action of organomagnesium compounds on halogenated quinones. E. CLAR and J. ENGLER (Ber., 1931, 64, [B], 1597—1602).—Bromoanil is converted by MgMeI into 2 : 3 : 5 : 6-tetrabromo-1 : 4-dihydroxy-1 : 4-dimethyl-1 : 4-dihydrobenzene, m. p. 229—230° (decomp.), from which the Br atoms are not removed by KOH in EtOH. 2 : 3-Dichloro-1 : 4-naphthaquinone affords 3-chloro-1 : 4-dihydroxy-1 : 2 : 4-trimethyl-1 : 4-dihydronaphthalene, m. p. 115—117°. Chloranil and MgPhBr afford a mixture of 6-chloro-1 : 4-dihydroxy-1 : 2 : 3 : 4 : 5-pentaphenyl-1 : 4-dihydrobenzene, m. p. 264—266°, and 3 : 6-dichloro-1 : 4-dihydroxy-1 : 2 : 4 : 5-tetraphenyl-1 : 4-dihydrobenzene, m. p. 242° (decomp.). Bromoanil gives 6-bromo-1 : 4-dihydroxy-1 : 2 : 3 : 4 : 5-pentaphenyl-1 : 4-dihydrobenzene, m. p. 206° (decomp.), converted by KOH in boiling EtOH into 1 : 4 : 6-trihydroxy-1 : 2 : 3 : 4 : 5-pentaphenyl-1 : 4-dihydrobenzene, m. p. 208—210°. 2 : 4-Dichloro-1 : 4-naphthaquinone is converted by MgPhBr into 1 : 4-dihydroxy-1 : 2 : 3 : 4-tetraphenyl-1 : 4-dihydronaphthalene, m. p. 241·5°, and by MgC₁₀H₇Br into 2 : 3-dichloro-1 : 4-dihydroxy-1 : 4-di- α -naphthyl-1 : 4-dihydronaphthalene, m. p. 261° (decomp.) after darkening at 249°. H. WREN.

Synthesis and orientation of trichloroanthraquinones and amino-disulphonates of anthraquinone. I. A. A. GOLDBERG (J.C.S., 1931, 1771—1794).—Sulphonation of 1-chloroanthraquinone with 20% oleum at 160° gives the -6-sulphonate [Na salt; chloride, m. p. 207—208° (decomp.)] and -7-sulphonate [Na salt; chloride, m. p. 200—201° (decomp.)], converted by HCl and KClO₃ into 1 : 6, and 1 : 7-dichloroanthraquinones, respectively; these are reduced by Zn and aq. NH₃ to 1 : 6-dichloro-, m. p. 149—150°, and 1 : 7-dichloro-anthracene, m. p. 160—161°. In presence of HgSO₄ the sulphonation gives 1-chloro-anthraquinone-5-sulphonic acid [Na salt; chloride, m. p. 243—244° (decomp.)] and -4 : 5-disulphonic acid (Na salt), converted by chlorination as above into 1 : 5-dichloro- and 1 : 4 : 5-trichloro-anthraquinone, m. p. 254°. By the action of NH₃ on the corresponding chloro-derivative, 1-aminoanthraquinone-6-sulphonic acid [Na salt (+0·5H₂O)] is obtained; Na 1-diethylaminoanthraquinone-6- (+0·5H₂O) and -7-sulphonates, Na 1-aminoanthraquinone-7-sulphonate, and 1-piperidinoanthraquinone-6-sulphonic acid were similarly prepared. Sulphonation of Na 1-chloro-anthraquinone-6-sulphonate gives the -4 : 6- (Na₂ and Na H salts) and -2 : 6-disulphonic acids (Na₂ salt), from which 1 : 4 : 6-trichloro-anthraquinone, m. p. 236°, and -anthracene, m. p. 158—159°, 1 : 2 : 6-trichloroanthraquinone, m. p. 222—223°, Na 1-aminoanthraquinone-4 : 6- (+2·5H₂O) and -2 : 6-disulphonates, and 1-diethylaminoanthraquinone-4 : 6-disulphonic acid are prepared. Na 1-chloroanthraquinone-5-sulphonic acid gives on further sulphonation the -2 : 5-disulphonic acid (Na₂ salt), converted by chlorination into 1 : 2 : 5-trichloroanthraquinone, m. p. 228—230°. 1 : 2-Dichloroanthraquinone is conveniently prepared from 1-chloro-2-aminoanthraquinone by Sandmeyer's reaction, and is converted by sulphonation into its -6- (Na salt) and -7-sulphonic acids (Na salt), from which

1:2:6- (above) and 1:2:7-*trichloroanthraquinone*, m. p. 225—226°, are obtained by Ullmann's method. The last-named is similarly prepared from 1-*chloroanthraquinone-2:7-disulphonic acid* (*Na* salt; *Na* 1-*aminoanthraquinone-2:7-disulphonate*), obtained from the -7-sulphonic acid, and is converted by reduction into 1:2:7-*trichloroanthracene*, m. p. 208—209°. 1:3-Dichloro- and 1:2:3-*trichloroanthraquinone*, m. p. 194—195°, are obtained by diazo-reactions from 1:3-dichloro-2-*aminoanthraquinone*. The former gives on sulphonation 1:3-*dichloro-6-* (*Na* salt) and -7-*sulphonic acids* (*Na* salt), converted as usual into 1:3:6-*trichloro-*, m. p. 212—213°, and 1:3:7-*trichloroanthraquinone*, m. p. 216—217°. Similarly, from 1:4-dichloroanthraquinone the -6-*sulphonic acid* (*Na* salt) and 1:4:6-*trichloroanthraquinone*, from 1:8-dichloroanthraquinone the -4-*sulphonic acid* (*Na* salt), 1:4:5-*trichloro-* and (by use of a large excess of HCl and KClO₃) 1:4:5:8-*tetrachloroanthraquinone*, m. p. 341—342° (block), and from 1:5-dichloroanthraquinone the -2- (*Na* salt); 1:2:5-*trichloroanthraquinone*, m. p. 235—236° and -4-*sulphonic acids* (*Na* salt; 1:4:5-*trichloroanthraquinone*), the -2:8-*disulphonic acid* (crude Na₂ salt), and, in presence of Hg, the -4-*sulphonic acid* and -4:8-*disulphonic acid* (isolated as *Na* salts, and identified by conversion into the corresponding chloroanthraquinones) are obtained.

The action of gaseous Cl₂ on *Na* anthraquinone-1:5-disulphonate in conc. H₂SO₄ with I as catalyst at 160° gives 1:5-dichloroanthraquinone only. Attempts at nitration of the 1:5-, 1:8-, 2:6-, and 2:7-disulphonic acids in conc. H₂SO₄ or oleum at 100° failed. The slow addition of aq. NaClO₃ to anthraquinone-1:5-disulphonic acid and HCl at 100° gives a small amount of 1-chloroanthraquinone-5-sulphonic acid. The interaction of phthalic anhydride, *o*-chlorophenol, and AlCl₃ in tetrachloroethane gives 3'-*chloro-4'-hydroxybenzoylbenzoic acid*, m. p. 224—225°, cyclised by H₂SO₄ to 2-*chloro-3-hydroxyanthraquinone*, identified by its conversion by PCl₅ in xylene into 2:3-dichloroanthraquinone (cf. A., 1930, 1183). H. A. PIGGOTT.

Stereochemistry of diphenyls. Preparation and properties of 1:1'-*dianthraquinonyl-4:4'-dicarboxylic acid*. XVII. W. M. STANLEY and R. ADAMS (J. Amer. Chem. Soc., 1931, 53, 2364—2368).—1-*Chloro-4-cyanoanthraquinone*, m. p. 271—272°, is prepared from the corresponding aminoanthraquinone, and hydrolysed by 86% H₂SO₄ at its b. p. to 1-chloroanthraquinone-4-carboxylic acid; the *Me* ester, m. p. 187.5—188.5°, of this is heated with Cu powder at 265—300° (exothermic reaction), and the product hydrolysed by EtOH-KOH to give 1:1'-*dianthraquinonyl-4:4'-dicarboxylic acid*, m. p. 448° (block, corr.). According to X-ray data this should be resolvable, but attempts at this by fractionation of its *di-1-menthyl* ester, m. p. 298—299°, or of its quinine salts failed. H. A. PIGGOTT.

Constitution of alkannin. H. RAUDNITZ, L. REDLICH, and F. FIEDLER (Ber., 1931, 64, [B], 1835—1841).—The spectroscopic behaviour of alkannin in KOH and H₃BO₃-AcOH solutions differs

so widely from that of quinizarin, 5:6:7:8-tetrahydroquinizarin, and naphthazarin that Liebermann and Römer's conception of it as an anthraquinone derivative cannot be maintained. 1:4-*Dihydroxy-5:6:7:8-tetrahydroanthraquinone*, m. p. 155°, is obtained from 1:4-dihydroxy-5:6:7:8-tetrahydro-naphthalene and maleic anhydride in presence of NaCl and AlCl₃ at 180°. Technical alkannin is purified by dissolution in aq. KOH and precipitation with acid, followed by protracted distillation with steam; repeated dissolution in C₆H₆ and precipitation with ligroin are necessary to remove a previously undetected nitrogenous impurity. When purified through *leucoalkannin acetate*, C₂₁H₂₄O₈, in which the presence of two ethylenic linkings is shown by catalytic hydrogenation, it has the composition C₁₅H₁₄O₄. When sublimed in vac. at 300° it yields quinizarin in small amount. Oxidation with dil. HNO₃ affords oxalic acid. The close relationship to naphthazarin and the formation of anthracene and 2-methylanthracene on distillation with Zn dust indicate that the substance is 5:8-dihydroxy-2-β-methyl-Δ^{9,7}-pentadienyl-1:4-naphthaquinone. Short action of SOCl₂ on alkannin leads to the formation of the substance C₁₆H₁₃O₃Cl, converted by aq. alkali into alkannin, whereas prolonged action affords the compound C₁₆H₁₂O₃Cl₂. H. WREN.

Benanthraquinones. H. WALDMANN (J. pr. Chem., 1931, [ii], 131, 71—81).—The interaction of naphthalene-1:2-dicarboxylic anhydride with C₆H₆ and AlCl₃ (cf. A., 1930, 1292) gives, in addition to 1-benzoyl-2-naphthoic acid (*Me* ester, m. p. 113—114°), 2-benzoyl-1-naphthoic acid (*Me* ester, m. p. 153—154°). The anhydride also condenses with quinol in presence of AlCl₃-NaCl to give 5:8-*dihydroxy-1:2-benanthraquinone*, m. p. 222° (*Ac* derivative, m. p. 212—214°; *Me*₂ ether, m. p. 185—186°), reduced by Sn and HCl to 5:8-*dihydroxy-1:2-benzoxanthrone*, m. p. 206°, and converted by *p*-toluidine and H₃BO₃ into 5:8-*di-p-toluidino-1:2-benanthraquinone*, m. p. 310°. By similar condensations of naphthalene-1:2-dicarboxylic anhydride with appropriate substances the following are obtained: 6(or 7)-*methyl-5:8-dihydroxy-*, m. p. 245—246°; 6(or 7)-*chloro-5:8-dihydroxy-*, m. p. 233—235°; 5:6(or 7):8-*trihydroxy-*, m. p. 250—251°; 5(or 8)-*chloro-8(or 5)-hydroxy-*, m. p. 204—205° (accompanied by the intermediate ketonic acid, m. p. 261—262°); and 8(or 5)-*hydroxy-5(or 8)-methyl-1:2-benanthraquinone*, m. p. 173—175°; 5:8-*dihydroxy-*, m. p. 246°, and 5(or 8)-*hydroxy-1:2:6:7-dibenanthraquinone*, m. p. 261—263°. The condensation of 4:5-dichlorophthalic anhydride and C₁₀H₈ by the Friedel-Crafts method gives 4:5-*dichloro-2-naphthoylbenzoic acid*, m. p. 207.5° (*Me* ester, m. p. 151°), dehydrated by conc. H₂SO₄ to 6:7-*dichloro-1:2-benanthraquinone*, m. p. 227°. Phthalic anhydride and 1:4-dichloro-naphthalene yield a mixture of acids, cyclised as before to a mixture of three *dichlorobenanthraquinones*, *ang.*, m. p. 248°, and *lin.*, m. p. 296° and 310°, neither of the two last being identical with the known *lin.*-dichlorobenanthraquinone; consequently a change in position of a Cl atom is believed to occur during condensation. H. A. PIGGOTT.

Reduction products of naphthacenequinone.

L. F. FIESER (J. Amer. Chem. Soc., 1931, 53, 2329—2341).—Improvements in the prep. of *o*-tetrahydro- β -naphthoylbenzoic acid and derived tetrahydro-naphthanthraquinones (cf. A., 1921, i, 861) are described. Naphthacenequinone is obtained in 81% yield by action of Br in AcOH on 2:3-tetrahydro-naphthanthraquinone. It is reduced by Sn and glacial AcOH, or by strongly alkaline $\text{Na}_2\text{S}_2\text{O}_4$, to 2:3-benz-9-anthrone, m. p. about 196°, from which it is regenerated by air-oxidation in EtOH-NaOH. Reductive acetylation with Sn, Ac_2O , and NaOAc gives naphthacenequinol diacetate, m. p. 269°; Zn gives poor results owing to over-reduction. The quinone is reduced by $\text{Na}_2\text{S}_2\text{O}_4$ in a weakly alkaline EtOH suspension to 10-hydroxy-2:3-benz-9-anthrone, m. p. 230°, which enolises readily in boiling pyridine, the solution rapidly acquiring the characteristic deep red colour of naphthacenequinol, which disappears on account of oxidation to quinone on shaking with air; enolisation also occurs with Ac_2O and pyridine, naphthacenequinol diacetate being formed. 9:10-Dihydro-2:3-benz-9-anthranol is the first product of reduction of the -9-anthrone with Zn and alcoholic alkali, but is best prepared, together with a little dihydronaphthacene, by reduction of naphthacenequinone with Zn and aq. EtOH-NaOH for 1 hr. (more dihydronaphthacene is formed on prolonged reduction); it is dehydrated by gentle heating alone or in EtOH, very rapidly in presence of a trace of HCl, to naphthacene. Naphthacene is also obtained by distillation of 2:3-tetrahydronaphthanthraquinone with Zn dust. 10:10'-Di-(2:3-benz-9-anthronyl) ether, m. p. 295°, is obtained in small amount during reduction of the quinone with alkaline $\text{Na}_2\text{S}_2\text{O}_4$, and in good yield by action of S in EtOH in presence of a little alkali on 2:3-benz-9-anthrone; it contains no active H (Zerevitinov), but rapidly adds more than 1 mol. of Grignard reagent. It is oxidised by CrO_3 , reduced to the anthrone by Sn and AcOH, and converted into the hydroxyanthrone by a drop of H_2SO_4 in Ac_2O . Naphthacenequinol is produced by hydrolysis of its diacetate in an atm. of N_2 , a series of colour changes leading finally to a bright red solution which in the course of a few days at the b. p. becomes purple. Acidification at the purple stage results immediately, and at the red stage after about 15 min., in a pale yellow solution containing naphthacenequinone and the anthrone, the products of disproportionation of the quinol. The quinol is also produced, but very slowly, by enolisation of the hydroxyanthrone by alcoholic alkali. The marked



tendency of completely aromatic derivatives of naphthacene to pass into dihydro-compounds, and their strong colours, are regarded as evidence in favour of an *o*-quinonoid structure for the hydrocarbon (annexed formula).

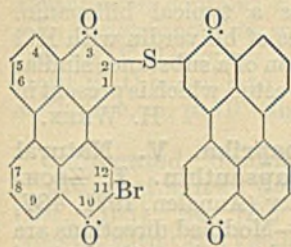
H. A. PIGGOTT.

lin-Benzanthraquinone series. H. WALDMANN and H. MATHIOWETZ (Ber., 1931, 64, [B], 1713—1724).—2-Amino-3-naphthoic acid is diazotised and converted into 2-cyano-3-naphthoic acid hydrolysed by H_2SO_4 in AcOH to naphthalene-2:3-dicarboxylic anhydride, m. p. 246°. This condenses with AlCl_3

in C_6H_6 to 2-benzoyl-3-naphthoic acid, m. p. 209-5° (*Me* ester, m. p. 119—120°), converted by AlCl_3 and NaCl at 130—140° into 2:3-benzanthraquinone, m. p. 294°. With PhMe the anhydride affords 2-*p*-toluoyl-3-naphthoic acid, m. p. 214°, transformed by the successive action of SOCl_2 and AlCl_3 in CS_2 into 2-methyl-6:7-benzanthraquinone, m. p. 240—242°. PhCl yields successively 2-*p*-chlorobenzoyl-3-naphthoic acid, m. p. 232° (*Me* ester, m. p. 113°), and 2-chloro-6:7-benzanthraquinone, m. p. 245°, converted by conc. NH_3 solution and CuCl_2 at 230° into 2-amino-6:7-benzanthraquinone, not molten below 310°. *p*-Chlorophenol smoothly affords 1-chloro-4-hydroxy-6:7-benzanthraquinone, m. p. 289°, converted by PCl_5 at 160° into 1:4-dichloro-6:7-benzanthraquinone, which with NH_2Ph or *p*-toluidine in presence of KOAc and Cu powder at 185° gives 1:4-dianilino-, m. p. above 310°, and 1:4-di-*p*-toluidino-6:7-benzanthraquinone, not molten below 310°, respectively. 1:4-Di-*p*-toluenesulphonamido-6:7-benzanthraquinone, m. p. 290—291°, from the dichloro-compound, *p*-toluenesulphonamide, KOAc, and $\text{Cu}(\text{OAc})_2$ in PhNO_2 at 200—210°, is transformed by conc. H_2SO_4 at 100° into 1:4-diamino-6:7-benzanthraquinone, not molten below 310°. 1-*p*-Sulphonamido-4-hydroxy-6:7-benzanthraquinone, m. p. 281°, from the 1-chloro-compound, yields 1-amino-4-hydroxy-6:7-benzanthraquinone, m. p. 295°. Naphthalene-2:3-dicarboxylic anhydride with the requisite quinol or substituted quinol in presence of AlCl_3 and NaCl affords the following compounds: 1:4-dihydroxy-6:7-benzanthraquinone, m. p. 304°, converted by *Me p*-toluenesulphonate and K_2CO_3 in trichlorobenzene at 170—180° into 1:4-dimethoxy-6:7-benzanthraquinone, m. p. above 310°, and reduced by Sn and conc. HCl to 1:4-dihydroxy-6:7-benzoxanthrone, m. p. 229°; 2-chloro-1:4-dihydroxy-6:7-benzanthraquinone, m. p. 295—296°; 1:4-dihydroxy-2-methyl-6:7-benzanthraquinone, m. p. 274—275°; 1:2:4-trihydroxy-6:7-benzanthraquinone, not molten below 310°. 1:4-Dihydroxy-2:3:6:7-dibenzanthraquinone, m. p. above 310°, is derived from 1:4-dihydroxynaphthalene and 4-hydroxy-1-methyl-6:7-benzanthraquinone, m. p. 270°, from *p*-cresol. Since phthalic anhydride and α -naphthol yield α -hydroxynaphthacenequinone, the analogous product from naphthalene-2:3-dicarboxylic anhydride is regarded as 1-hydroxy-2:3:6:7-dibenzanthraquinone, not molten below 310°. C_{10}H_8 in presence of AlCl_3 and CS_2 gives a mixture of 2:1'- and 2:2'-naphthoynaphthalene-3-carboxylic acid converted by ring closure into 2:3:6:7-dibenzanthraquinone, m. p. 371—372°, and 1:2:6:7-dibenzanthraquinone, m. p. 229°, separable from one another by crystallisation from C_6H_6 . 2-*p*-Chlorobenzoyl-3-naphthoic acid is converted by Na_2CO_3 , Na_2SO_3 , and CuSO_4 in H_2O at 180° into *Na* 2-*p*-sulphobenzoylnaphthalene-3-naphthoate, transformed by 5% oleum at 150° into 2:3-benzanthraquinone-2:2-disulphonic acid. H. WREN.

Action of sodium sulphide on dibromo-3:10-perylenequinone. K. BRASS and E. TENGLER (Ber., 1931, 64, [B], 1646—1649).—Perylene (improved prep. given) is transformed successively into 3:10-perylenequinone, decomp. 350°, and dibromo-3:10-perylenequinone, decomp. above 400°, which when

reduced and benzoylated



(I)

but not molten below 300°.

affords the Bz_2 derivative of *dibromoperylene-3:10-quinol*, m. p. 238°. *Dibromoperylenequinone* is converted by Na_2S at 210–250° into *bromodi-3:10-perylenequinonyl sulphide* (I), reduced and benzoylated to the Bz_1 derivative of *bromodi-3:10-perylenequinonyl sulphide*, darkening at 240°

H. WREN.

Crystalline solvates of rotenone. H. A. JONES (J. Amer. Chem. Soc., 1931, 53, 2738–2741).—Cryst. solvates of 1 mol. of rotenone and 1 mol. of C_6H_6 , CCl_4 , and $CHCl_3$, and of 2 mols. of rotenone and 1 mol. of $AcOH$ are prepared. These compounds, when heated, lose the solvents of crystallisation and then melt at 171–179°. Solvates were not formed with $COMe_2$, $PhCl$, $AcOEt$, $EtOH$, and ethylene dichloride.

H. BURTON.

"Yellow compounds" from decomposition of rotenone in solution. H. A. JONES and H. L. HALLER (J. Amer. Chem. Soc., 1931, 53, 2320–2324).—On exposure to air a pyridine solution of rotenone deposits a mixture of dehydrorotenone and rotenone; the same changes are undergone more slowly in other solvents, e.g., $COMe_2$, $CHCl_3$, diacetone alcohol, and amylene dichloride. Similar changes are observed with dihydro- and *iso*-rotenones in pyridine.

H. A. PIGGOTT.

Rotenone. XII. Derivatives of rotenol. H. L. HALLER and F. B. LAForge (J. Amer. Chem. Soc., 1931, 53, 2271–2275).—*Dehydrotetrahydrorotenol*, m. p. 171°, is produced from dihydrorotenol by action of alkaline $K_3Fe(CN)_6$, and is reconverted into it by Zn and KOH ; it does not give an oxime, and is unaffected by boiling Ac_2O and $NaOAc$. *Dehydrotetrahydrorotenol*, m. p. 124°, is similarly prepared from and reconverted into rotenol, but with H_2 and PtO_2 gives dehydrotetrahydrorotenol and *dehydrotetrahydrorotenonic acid*, m. p. 206° [*Ac* derivative (mixed anhydride), m. p. 136°]; the last-named is also the product of reduction of dihydrorotenonic acid with Zn and aq. KOH . Rotenol is converted into *isorotenol* by H_2SO_4 - $AcOH$ at 100°, and this is reduced (Clemmensen) to *deoxyisorotenol*, m. p. 149°, and consequently rotenol and *isorotenol* are regarded as having ketonic structures; the optical inactivity of *isorotenol* is also at variance with the alternative alcoholic structure.

H. A. PIGGOTT.

Deguelin. II. Relationships between deguelin and rotenone. E. P. CLARK (J. Amer. Chem. Soc., 1931, 53, 2369–2373).—The oxidation of deguelic acid with alkaline H_2O_2 gives derric acid, and with alkaline $KMnO_4$, ristic acid; these are therefore obtained from deguelin by methods similar to those by which they are derived from rotenone (cf. A., 1930, 967; this vol., 491). Dihydrodeguelic acid, obtained by reduction with H_2 and Pt, is identical with "dehydrodihydroxy- β -dihydrorotenonic acid" (this vol., 491), and is oxidised by alkaline H_2O_2 to derric acid. Catalytic reduction (Pt and H_2 in $AcOH$) of dehydro-

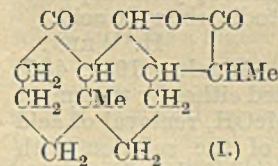
deguelin gives a dihydro-derivative identical with dehydro- β -dihydrorotenone (this vol., 491), and converted by oxidation with $Na_2Cr_2O_7$ in aq. $AcOH$ into *oxydehydrodeguelin*, $C_{23}H_{20}O_8$, m. p. 303°, and by Zn and aq. $EtOH$ - KOH into dihydrodeguelic acid. A non-phenolic mono-*Ac* derivative of deguelic acid, m. p. 128–129°, is obtained by action of a large excess of Ac_2O in pyridine.

H. A. PIGGOTT.

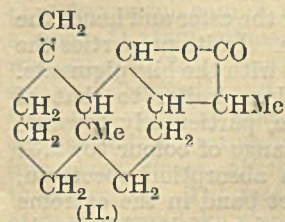
Toxicarol. II. Acetyl derivatives. E. P. CLARK (J. Amer. Chem. Soc., 1931, 53, 2264–2271; cf. A., 1930, 1223).—With Ac_2O and anhyd. $NaOAc$ toxicarol gives a Ac_2 derivative, m. p. 233–236°, reduced by H_2 and Pt in $AcOH$ to *diacetyldihydro-*, m. p. 238–240°, and *monoacetyldihydrodeoxy-toxicarol*, m. p. 156°; the last-named gives *dihydrodeoxytoxicarol*, m. p. 188°, with $NaOMe$ - $MeOH$. Toxicarol itself is reduced catalytically to *dihydro-*, m. p. 206–209° [*Ac*, m. p. 207° (sinters 200°) and Ac_2 derivatives], and oxidised by alkaline $K_3Fe(CN)_6$ to *dehydro-toxicarol*, m. p. 223° (*Ac* derivative, m. p. 231–232°). Dehydrotoxicarol and its *Ac* derivative on hydrogenation give dihydro- and acetyldihydro-toxicarol. The action of I in $EtOH$ - $KOAc$ converts toxicarol into an *iododehydro-* derivative, (highest) m. p. 225°, reduced by Zn and $AcOH$ to dehydrotoxicarol. Oxidation of dihydrotoxicarol with alkaline $K_3Fe(CN)_6$ gives *dehydrodihydrotoxicarol*, m. p. 260°. The interrelations of the above products are regarded as indicating the presence of only one true OH group in toxicarol.

H. A. PIGGOTT.

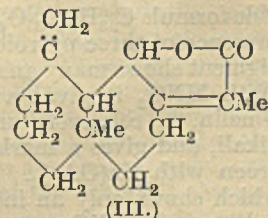
Bitter substances. III. Constitution of *iso*-alantolactone. K. F. W. HANSEN (Ber., 1931, 64, [B], 1904–1908).—The proportion of alanto- to *iso*alanto-lactone is determined by treating the mixture with a small excess of diazomethane in Et_2O , removing the precipitated adduct of diazomethane and the *isolactone*, and isolation of the adduct of diazomethane and alantolactone from the filtrate. Dihydro-*iso*alantolactone is ozonised in $CHCl_3$ and the ozonide is decomposed with H_2O , thus yielding CH_2O , HCO_2H , and the keto-lactone (I), m. p. 204–205° [*semicarbazone*, m. p. 232–233° (decomp.)],



reduced by Zn-Hg and conc. HCl and subsequently dehydrogenated by Se to 2-ethylnaphthalene (picrate, m. p. 69–70°). Dihydro-*iso*alantolactone is therefore (II). The expected displaceability of the double linking in the substance is achieved by the action of HCl in Et_2O , whereby a difficultly separable mixture of two *monohydrochlorides*, m. p. about 145° and about 135°,



(II)

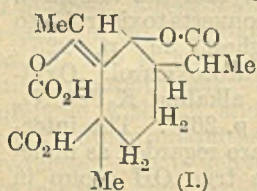


(III)

respectively, is obtained. When heated above their m. p. the hydrochlorides lose HCl quantitatively; that of m. p. 145° regenerates the original bitter

substance, whereas that of lower m. p. affords an isomeric compound, m. p. 90—91°. Treatment of the ozonide from isoalantolactone with boiling H₂O is accompanied by complete resinification; CH₂O and HCO₂H are identified in the aq. distillate. Addition of K₂Cr₂O₇ and H₂SO₄ and subsequent distillation gives AcOH derived from pyruvic acid. isoAlantolactone is therefore (III).
H. WREN.

Santonin series. XVI. Constitution and oxidative degradation of santonin. E. WEDEKIND and K. TETTWEILER (Ber., 1931, 64, [B], 1796—1802; cf. this vol., 490).—Santonin chlorohydrin does not react with Br in CHCl₃ and α-santonin oxide is stable towards perbenzoic acid. The last-named substance transforms santonin in CHCl₃ into α-santonin oxide, m. p. 214° (formerly designated santonin oxide), and β-santonin oxide, m. p. 157°. Hydrogenation of the β-compound in presence of Pt-black and MeOH leads to α-dihydro-β-santonin oxide, m. p. 146°, and β-dihydro-β-santonin oxide, m. p. 117°. O₃ in CHCl₃ affects the oxide ring of α-santonin oxide, giving an ozonide, C₁₅H₁₈O₆, m. p. 189°, converted by boiling H₂O into H₂O₃ and santoniniketodicarboxylic acid (I) (formerly santononic acid), m. p. 207—208°, which titrates as a monobasic or tribasic acid in cold and hot solution respectively; the



oxime, decomp., 228°, and quinoxaline derivative, C₂H₂₂O₅N₂, m. p. 289° (decomp.), are described. Hydrogenation in presence of Pt-black affords dihydrosantoniniketodicarboxylic acid, m. p. 174°, whereas oxidation with alkaline KMnO₄ gives heptane-ββζ-tetracarboxylic acid, m. p. 165—166° (decomp.). α-Dihydro-α-santonin oxide is converted by O₃ in CHCl₃ into dihydrosantoniniketodicarboxylic acid. Santonin and alkaline KMnO₄ yield heptane-tetracarboxylic and santoniniketodicarboxylic acid.

H. WREN.

Oocyan. I. R. LEMBERG (Annalen, 1931, 488, 74—90).—The pigment is isolated either by treatment of the egg-shells with HCl in MeOH, removal of acid and porphyrin by agitation of the solution with anhyd. Na₂CO₃, and transference of the pigment to Et₂O or by adsorbing the pigment on the albumin coagulate from aq. HCl, esterifying the MeOH extract, and, after transference to Et₂O, removing porphyrin ester and other impurities by Willstätter's method. Oocyan Me ester, m. p. 233—234°, is hydrolysed by Na₂CO₃ in MeOH to oocyan. Analytical data combined with determinations of OMe indicate the probable formula C₂₈H₃₁₋₃₃O₆N₃ for the ester and hence the presence of three pyrrole rings. In its properties the pigment shows many analogies with the bile pigments. With HNO₃ it gives a reaction similar to that of Gmelin, is relatively unstable, particularly towards alkali, and gives a marked change of colour towards green with Zn(OAc)₂. In its absorption spectrum, which shows only an indistinct band in the extreme red, oocyan differs entirely from the bilicyanin class, and the Zn salt does not exhibit the typical fluorescence or the absorption in the red. If the solution of the Zn salt is rendered feebly alkaline

with NH₃ and preserved, fluorescence bands are developed and HCl liberates a typical bilicyanin. Treatment of different samples of biliverdin with HCl and MeOH leads to the isolation of a substance similar to or identical with oocyan Me ester, which is present in very small proportion.
H. WREN.

Colouring matter of paprika. V. Natural and synthetic esters of capsanthin. L. ZECHMEISTER and L. VON CHOLNOKY (Annalen, 1931, 487, 197—213; cf. A., 1930, 479).—Modified directions are given for isolating the coloured wax from the fruit of *Capsicum annum*. On hydrolysis with KOH in MeOH, this yields capsanthin, m. p. 177—178°. C₃₅H₅₀O₃ (or C₃₆H₅₀O₃) (not C₃₄H₄₈O₃, as hitherto), a yellow cryst. dye, and oleic, myristic, palmitic, carnaubic, and some stearic and unidentified unsaturated acids. Carotene was also isolated. Capsanthin, therefore, occurs as mixed esters. The same acids are obtained from the colourless waxes. Esterification of capsanthin by acyl chlorides in pyridine solution (diacetate, m. p. 145—146°; dipropionate, m. p. 140°; dihexoate, m. p. 102°; dimyristate, m. p. 88°; dipalmitate, m. p. 85°; distearate, m. p. 84°; dioleate, m. p. below room temp.; dibenzoate, m. p. 121—122°) shows the presence of 2 OH groups, the third O atom forming part of a ring or CO group. The synthetic esters, like the natural products, crystallise in several forms, and mixtures resemble the natural wax in having varying properties, and in being difficult to separate. The diacetate, dihexoate, dipalmitate, and distearate were perhydrogenated, and then yielded perhydrocapsanthin on hydrolysis. Capsanthin is possibly a mixture. All m. p. were taken on a Berl block.
R. S. CAHN.

Vegetable dyes. XXXI. Constitution of second form of carotene (α-carotene). P. KARRER and R. MORF. XXXII. Composition of physalien. P. KARRER and B. PREPER. XXXIII. Constitution of the xanthophylls. R. NILSSON and P. KARRER. XXXIV. Dihydrolycopene. P. KARRER and R. MORF (Helv. Chim. Acta, 1931, 14, 833—838, 838, 843—845, 845—846).—XXXI. Dihydro-α-carotene on complete hydrogenation absorbs 10 H₂ in accordance with its constitution; oxidation with alkaline KMnO₄ gives αα-dimethylglutaric acid, pointing to CH₂<CH₂·CMe₂>C:[CH·CH:CMe·CH]₂:CH·CH:[CH·CMe·CH·CH]₂:C<CMe₂·CH₂>CH₂ as the formula for α-carotene. Hydrolysis of its ozonide gives geronic acid.

XXXII. A small amount of zelaic acid is obtained by ozonisation of cryst. physalien, but not of zeaxanthin, and therefore the dye is not homogeneous, but contains the zeaxanthin ester of an acid, CHR:CH·[CH₂]₇·CO₂H, probably oleic acid.

XXXIII. The xanthophyll, m. p. 188°, from nettles on catalytic hydrogenation followed by 30% HBr·AcOH at 150° gives an unstable dibromo-derivative, which at 100° passes into a mixture of mono(?)bromo-derivatives; this mixture, when reduced with the Zn-Cu couple and AcOH-H₂O-Et₂O, gives a hydrocarbon, C₄₀H₇₈, b. p. 244—250°/0.16 mm., [α]_D +0.51° in Et₂O (of the same order as perhydrocarotene).

From the value of $[\alpha]_D$ it is considered that the xanthophyll contains a considerable amount of the α -form, corresponding with α -carotene.

XXXIV. Lycopene when reduced with Al-Hg in moist Et_2O passes into a cherry-red, unstable *dihydro*-derivative, m. p. 70° (sinters above 60°).

H. A. PIGGOTT.

Conjugated double linkings. XVIII. Constitution of safran dye. R. KUHN and F. L'ORSA (Ber., 1931, 64, [B], 1732—1736).—Oxidation of crocetin with CrO_3 yields AcOH in amount indicating the presence of 4 Me groups. This result is not in harmony with the crocetin formula $\text{C}_{19}\text{H}_{22}\text{O}_4$, but agrees with $\text{C}_{20}\text{H}_{24}\text{O}_4$. This view is confirmed by fresh elementary analyses, determination of the equiv. of tetradecahydrocrocetin and of the sap. val. of its Me_2 ester, and by the röntgenographic determination of the mol. wt. of crocetin Me_2 ester. Crocin is therefore $\text{C}_{14}\text{H}_{16}\text{O}_6$, whilst crocetin is probably $\text{CO}_2\text{H}\cdot[\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}]_3\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$. Crocetin Me_2 ester, m. p. $222\text{--}5^\circ$ (corr.), *perhydrocrocetin* Me_2 ester, $\text{C}_{22}\text{H}_{42}\text{O}_3$, m. p. 27° , and *perhydrocrocetin* are incidentally described.

H. WREN.

Polyterpenoids. IV. Elemic acid. L. RÜZICKA, J. R. HOSKING, and A. WICK (Helv. Chim. Acta, 1931, 14, 811—820).—The method of isolation of elemic acid has been improved, and the previous analyses have been confirmed (cf. A., 1924, i, 1132). It gives with Se at 340° 1 : 2 : 7-trimethylnaphthalene and a hydrocarbon, C_nH_n , m. p. $136\text{--}137^\circ$, b. p. about 350° , and on dry-distillation a dehydration product, $\text{C}_{27}\text{H}_{40}\text{O}_2$, m. p. 200° (not quite pure); it forms additive compounds, m. p. $222\text{--}223^\circ$ and 158° , respectively, with $\text{H}\cdot\text{CO}_2\text{H}$ and Ac_2O ; these give the acid on long heating with EtOH . Its *Me*, m. p. about 80° , b. p. $250\text{--}253^\circ/0\cdot2$ mm., and *Et*, m. p. $115\text{--}117^\circ$, b. p. $268\text{--}270^\circ/0\cdot4$ mm., esters show an optical exaltation corresponding with two double linkings; hydrogenation of the acid in presence of PtO_2 gives a mixture from which a *dihydro*-derivative, m. p. $246\text{--}247^\circ$ (*Et* ester, m. p. 90°), is isolated. Reduction of the *Me* ester with Na and amyl alcohol gives a substance, $\text{C}_{27}\text{H}_{44}\text{O}_2$, b. p. $255^\circ/0\cdot5$ mm. Elemic acid (*loc. cit.*) contains 2 active H atoms (Zerevitinov), and its *Me* ester, m. p. $146\cdot5\text{--}147^\circ$, unlike the acid itself, forms an *oxime*, m. p. 184° . On treatment with O_3 in CCl_4 elemic acid absorbs 6 O, but no definite products were isolated.

H. A. PIGGOTT.

Isoprene and caoutchouc. XXXIV. Molecules or micelles in a caoutchouc solution. XXXV. Soluble and insoluble caoutchouc and fractionation of caoutchouc. H. STAUDINGER and H. F. BONDY [with, in part, J. JOSEPH and E. O. LEUPOLD] (Annalen, 1931, 488, 127—153, 153—175).—XXXIV. A distinction is drawn between depolymerisation, the rupture of larger to smaller mols. of the same polymeric homologous series and ultimately to the monomeres, and disaggregation, the rupture of complexes to ready-formed colloidal particles. The viscosity of caoutchouc solutions exhibits greater alterations in the ϕ values than does that of polystyrene solutions, but it is considered improbable that two complex, colloidal hydrocarbons should have a completely different structure, and the difference is attributed to

the greater sensitiveness of caoutchouc in consequence of the presence of double linkings. In dil. solution in tetrahydronaphthalene, caoutchouc exhibits only slight deviations from the Hagen-Poiseuille law; in gel solutions the deviations are more pronounced and increase with increasing concentration. For the determination of the mol. wt. of the most complex caoutchouc fractions by measurements of viscosity, it is necessary to use very dil. solutions; with products of mean mol. wt. 40,000 or less, the deviations from the Hagen-Poiseuille law are so slight that they may be neglected. Decrease in the viscosity of caoutchouc solutions in tetrahydronaphthalene by agitation is not observed in the absence of O_2 . Caoutchouc of all degrees of complexity suffers marked degradation when heated at 60° in tetrahydronaphthalene. The presence of traces of O_2 causes caoutchouc to dissolve much more rapidly in tetrahydronaphthalene and to yield sols of much lower viscosity than in the presence of N_2 . The stability of solutions of crude caoutchouc in contrast to those of purified or synthetic caoutchouc is due to the presence of anti-catalysts which inhibit oxidation. Precipitation of aged and fresh *Hevea* latex and examination of the viscosity of solutions of the ppts. shows that these are much more mobile than solutions of caoutchouc in C_6H_6 , probably because of the nearly spherical form of the latex droplets.

XXXV. Fractionation of caoutchouc in the complete absence of light and O_2 leads to the conclusion that two types must be distinguished. "Sol. caoutchouc," built of thread mols., has the same structure as polystyrene and constitutes a mixture of polymeric homologues ($n=500\text{--}3000$) separable by solvents into fractions. The simplest members have mean mol. wt. < about 100,000 and are sol. in Et_2O , whereas the higher members swell in Et_2O but dissolve in C_6H_6 . The most complex products have mol. wt. about 225,000 and the mols. are about $1\cdot5\ \mu$ long and about $3\cdot0\ \text{\AA}$. in diameter. Pummerer's "gel caoutchouc," sol. in C_6H_6 , is a higher fraction of this sol. caoutchouc and consists of thread mols. The second variety, "insol. caoutchouc," swells strongly in C_6H_6 or CHCl_3 and is regarded as a three-dimensional macromol. Pummerer's "total caoutchouc" obtained by purifying latex with NaOH consists of varying mixtures of sol. and insol. caoutchouc. Fresh latex contains little insol. caoutchouc, which constitutes aged latex almost exclusively. The transition from the sol. to the insol. variety occurs very readily on contact with air and most rapidly with the fractions of high mol. wt. The change takes place by conversion of the thread mols. into three-dimensional macromols. by O atoms which cannot be detected analytically, since a single O atom suffices for the union of 2 chains of mol. wt. 150,000. The insol. variety can be rendered sol. by chloroacetic and other acids or air; the product is of low viscosity and the action is not therefore a reversal but a rupture of the three-dimensional mols. into short pieces, which again are thread mols., and therefore sol. The majority of the chemical changes of caoutchouc take place with marked degradation of the chains; the products are in the main derivatives of hemicolloidal material. As a consequence of the profound degradation, the same products are derived

from sol. and insol. caoutchouc. The few points of union at which the long chains of sol. caoutchouc are joined in the three-dimensional macromols. of insol. caoutchouc cannot be detected analytically. The union of long thread to three-dimensional mols. influences the physical properties, particularly the solubility, in a very marked degree, but not the chemical properties, since the majority of the isoprene residues remain intact after union. Polystyrene (n = about 3000) with the same length of chain as a non-degraded, sol. caoutchouc (n = 1500), behaves similarly with regard to swelling and viscosity, but differs in not exhibiting ageing phenomena. This is explained, since by reason of the saturated C chains it is not autoxidisable and formation of three-dimensional mols. cannot occur.

H. WREN.

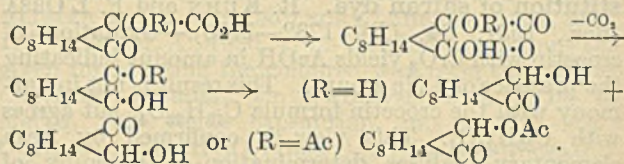
Rearrangement of acetylenecarbinols from fenchone and tetrahydrocarvone to aldehydes. H. RUPE and F. KUENZY (Helv. Chim. Acta, 1931, 14, 708—718; cf. A., 1926, 821).—The action of Na and C_2H_2 on fenchone gives in small yield *ethinyl-fenchyl alcohol*, b. p. 89°/12 mm. (*Ag* salt), which when heated with 86% HCO_2H undergoes rearrangement into *fenchylideneacetaldehyde*, b. p. 121—123°/30 mm. [*semicarbazone*, m. p. 214° (decomp.); *oxime*, resinous].

Interaction of tetrahydrocarvone with C_2H_2 and $NaNH_2$ in C_6H_6 similarly gives 2-methyl-5-isopropyl-1-ethinylcyclohexanol, b. p. 104°/9 mm. (*Ac* derivative, b. p. 112—113°/9 mm.), converted by 70% HCO_2H into 2-methyl-5-isopropylcyclohexylidene-1-acetaldehyde (I) [*semicarbazone*, m. p. 139—140° (decomp.); *oxime*, b. p. 150—153°/10 mm.]. Hydrolysis of the *oxime* with aq. oxalic acid gives tetrahydrocarvone, but the *semicarbazone*, in contrast, regenerates the aldehyde. With $MgEtBr$ (2 equivs.) (I) gives γ -hydroxy- δ -2-methyl-5-isopropylcyclohexylidenebutane, b. p. 112°/12 mm. with partial decomp. into H_2O and a hydrocarbon, $C_{14}H_{24}$, b. p. 108—109°/12 mm. Hydrogenation of (I) in presence of Ni gives 2-methyl-5-isopropylcyclohexyl-1-acetaldehyde, b. p. 103—104°/9 mm. [*semicarbazone*, m. p. 178—179°; *oxime*, m. p. 87° (decomp.)]. Oxidation of (I) with alkaline $KMnO_4$ gives isopropylsuccinic and (probably) β -isopropyladipic acids.

H. A. PIGGOTT.

Hydroxycamphor. IV. 3-Hydroxycamphor and 2-hydroxyepicamphor, and 3-hydroxycamphor-3-carboxylic acid and 2-hydroxy-2:3-oxidocamphane-3-carboxylic acid. J. BREDT [with M. FISCHER] (J. pr. Chem., 1931, [ii], 131, 49—67).—2-Hydroxyepicamphor is converted into an equilibrium mixture with 3-hydroxycamphor by heating with conc. aq. KOH, but not by heating alone at 200—210°, or with pyridine or quinoline. The formation from camphorquinone by the cyanohydrin reaction of two apparently stereoisomeric hydroxycamphorecarboxylic acids, m. p. 184° and 206—207° (cf. J.C.S., 1901, 79, 377), is confirmed. Both give the same *acetate*, m. p. 90—91°, but in the case of the acid of m. p. 184° it is accompanied by an oil that slowly solidifies on keeping and is then identical with the *acetate* of m. p. 90—91°. This *acetate* gives on hydrolysis the higher-melting acid, and is slowly decarboxylated at 115—120° to 3-acetoxycamphor, un-

accompanied by any epicamphor derivative. This behaviour, and the formation of both 3-hydroxycamphor and 2-hydroxyepicamphor from either of the hydroxycarboxylic acids by decarboxylation (*loc. cit.*) is explained by lactonisation followed by decomp. to the dienolic form, which can rearrange in two ways in the case of the hydroxy-acids, but not in that of the acetoxy-acid:



The acid, m. p. 208—209°, obtained by oxidation of bornylene-3-carboxylic acid with $KMnO_4$ (A., 1909, ii, 499), is not identical, but isomeric, with 3-hydroxycamphor-3-carboxylic acid, differing in cryst. form, and in the m. p. (110—112°) of its *monoacetate* (+2 H_2O), m. p. 81—82°. It is regarded as 2-hydroxy-2:3-oxidocamphane-3-carboxylic acid.

H. A. PIGGOTT.

Transformations of camphorquinone. II. Camphorquinone diethylacetal and its rearrangement into 2-hydroxyepicamphor. M. BREDT-SAVELSBERG and E. BUND (J. pr. Chem., 1931, [ii], 131, 29—48).—Camphorquinone diethylacetal does not react with the usual ketone reagents, but with $MgMeI$ gives β -hydroxyhomocamphor diethylacetal, b. p. 130—135°/11 mm., which possesses a single active H atom (Zerevitinov), and on keeping gradually passes into β -hydroxyhomocamphor, m. p. 199°. The presence of a CO group in the original substance is also proved by its reduction by Na and EtOH to β -hydroxycamphor diethylacetal, b. p. 126—130°/12 mm., which is oxidised by $KMnO_4$ to camphoric acid, and hydrolysed by aq. H_2SO_4 to β -hydroxycamphor, and by $MeOH-HCl$ to its bimol. Me ether and a small amount of a substance, $C_{22}H_{45}O_4Cl_2$, m. p. 255—257°; with 65% H_2SO_4 as hydrolysing agent the by-products are epiborneol (*dinitrobenzoate*, m. p. 103°) and an isomeride (*dinitrobenzoate*, m. p. 152°). The following *dinitrobenzoates* are also described: α -hydroxycamphor, m. p. 129° (additive compound with α -naphthylamine, m. p. 184°); β -hydroxycamphor, m. p. 151—152° (+ α -naphthylamine, m. p. 154°); borneol, m. p. 154°, [α]_D²⁰ +13.38° in toluene (+ α -naphthylamine, m. p. 140.5°); isoborneol, m. p. 133°, [α]_D²⁰ +7.19° (+ α -naphthylamine, m. p. 148°); epiborneol (+ α -naphthylamine, m. p. 164°). An improved method of prep. of epicamphor is described in which bornylenecarbonyl chloride is heated with NaN_3 at 90° until the calc. vol. of N_2 is evolved, and the resulting product hydrolysed with conc. HCl until the calc. vol. of CO_2 is evolved.

H. A. PIGGOTT.

Cedrenene, $C_{15}H_{22}$, and its transformation into cedrene. A. BLUMANN and L. SCHULZ (Ber., 1931, 64, [B], 1540—1545; cf. A., 1929, 1076).—Cedrenol, m. p. 103—104°, obtained by autoxidation of cedarwood oil, is converted by $NaOAc$ and Ac_2O at 130° into cedrenene, d_{4}^{25} 0.944, α_D +148° 20'. When in contact with Ac_2O or when distilled under ordinary pressure, the hydrocarbon is partly converted into a

solid *polymeride*, from which it is smoothly regenerated when heated. *Cedrene dibromide* has m. p. 93—95° (decomp.), $[\alpha]_D -375.4^\circ$ in C_6H_6 . The hydrocarbon is also obtained by reduction of cedrene by Ponndorf's method or by treatment of cedrol with 100% HCO_2H and oxidation of the *l*-cedrene thus produced with O_2 in presence of a Co drier. It is reduced by EtOH and Na to cedrene, identified as cedrenonesemicarbazone. The purest *l*-cedrene, $d^{15} 0.9340$, $\alpha_D -85.00'$, is obtained by treatment of cedrol, $C_{15}H_{26}O$, with HCO_2H . Conversion of cedrene into cedrene and treatment of the ketonesemicarbazone according to Wolff-Kishner yields a less highly optically active product.
H. WREN.

Synthesis of furyl ketones with sodamide. N. MAXIM (Bull. Soc. chim., 1931, [iv], 49, 891—897).—When treated with $NaNH_2$ in C_6H_6 , 2-furyl ketones, $C_4H_3O \cdot CHR \cdot CH_2 \cdot COPh$, yield Na derivatives which on alkylation give the ketones, $C_4H_3O \cdot CHR \cdot CHR' \cdot COPh$. The latter with $NaNH_2$ in PhMe are similarly converted, although with greater difficulty, into ketones, $C_4H_3O \cdot CHR \cdot CR'R'' \cdot COPh$, the yields being very small when R is an aromatic radical. Cryst. oximes, semicarbazones, and phenylhydrazones were not obtained. Thus β -2-furyl- β -ethylpropiofenone affords β -2-furyl- α -methyl- β -ethyl-, b. p. 178°/19 mm.; β -2-furyl- α -dimethyl- β -ethyl-, b. p. 182°/23 mm.; β -2-furyl- α -diethyl-, b. p. 182°/18 mm., and β -2-furyl- α -triethyl-propiofenone, b. p. 176°/12 mm. β -2-Furyl- β -propylpropiofenone, b. p. 190°/18 mm. (*semicarbazone*, m. p. 94°), from $MgPrBr$ and *furfurylideneacetophenone* in Et_2O (yield 70%), similarly gives β -2-furyl- α -methyl-, b. p. 198°/28 mm., and β -2-furyl- α -dimethyl- β -propylpropiofenone, b. p. 205°/50 mm., and β -2-furyl- β -phenylpropiofenone affords β -2-furyl- β -phenyl- α -methyl-, b. p. 222°/22 mm., β -2-furyl- β -phenyl- α -dimethyl-, b. p. 226°/22 mm., and β -2-furyl- β -phenyl- α -ethyl-propiofenone, b. p. 275°/78 mm. (yield 60%, together with an indefinite fraction of higher b. p.).
R. BRIGHTMAN.

Action of mixed magnesium organo-compounds on furylideneacetone. N. MAXIM (Bull. Soc. chim., 1931, [iv], 49, 887—891).— $MgMeI$, $MgBu^tI$, Mg isoamyl bromide, and $MgPhBr$ with *furylideneacetone* yield almost exclusively resinous products. $MgEtBr$ in Et_2O gives γ -2-furylhexan- ϵ -one, b. p. 120°/20 mm. (*semicarbazone*, m. p. 112°) (yield, 50%). γ -2-Furyl- β -methylhexan- ϵ -one (61%), b. p. 135°/55 mm. (*semicarbazone*, m. p. 148°), δ -2-furylheptan- β -one (50%), b. p. 115°/18 mm. (*semicarbazone*, m. p. 90°), and δ -2-furylmethylheptan- β -one, b. p. 116°/18 mm. (*semicarbazone*, m. p. 100°), are similarly obtained from $MgPr^{\beta}Br$, $MgPr^{\alpha}Br$, and $MgBu^{\beta}Br$, respectively.
R. BRIGHTMAN.

Derivatives of 4-phenylchroman. P. C. MITTER and P. K. PAUL (J. Indian Chem. Soc., 1931, 8, 271—276).—2 : 4-Dimethoxybenzophenone, Et bromoacetate, and Zn in C_6H_6 give Et β -hydroxy-2 : 4-dimethoxy- β - β -diphenylpropionate, m. p. 79—80°, which could not be dehydrated by Ac_2O and $NaOAc$, or by $AcCl$, but passed on distillation in vac. into Et 2 : 4-dimethoxy- β - β -diphenylacrylate (I), b. p. 228—232°/11 mm. This is hydrolysed to the corresponding acid, m. p. 169—170°, which with $AcCl$ and $AcOH$ gives

7-methoxy-4-phenylcoumarin, m. p. 114—115° (also obtained by methylation of the condensation product of Et benzoylacetate with resorcinol). This with Na and dry EtOH yields 2-hydroxy-4-methoxy- β - β -diphenylpropyl alcohol, b. p. 253—254°/10 mm., which is converted by dry HCl in EtOH into 7-methoxy-4-phenylchroman, b. p. 203—204°/10 mm. Reduction of (I) by Na-Hg gave 2 : 4-dimethoxy- β - β -diphenylpropionic acid, m. p. 129—130° (Et ester, m. p. 54°). Resorcinol Me_2 ether, veratroyl chloride, and $AlCl_3$ give 2 : 4 : 3' : 4'-tetramethoxybenzophenone, m. p. 126°, which with Et bromoacetate and Zn in C_6H_6 , followed by hydrolysis with alcoholic alkali, yields 2 : 4 : 3' : 4'-tetramethoxy- β - β -diphenylacrylic acid, m. p. 157°, reduced by Na-Hg to 2 : 4 : 3' : 4'-tetramethoxy- β - β -diphenylpropionic acid, m. p. 121°, and converted by $AcCl$ and $AcOH$ into 7-methoxy-4-(3' : 4'-dimethoxy)-phenylcoumarin, m. p. 163°. The same coumarin derivative is obtained in better yield when veratroyl chloride is condensed with Et sodioacetoacetate in Et_2O , the product hydrolysed with 10% aq. NH_3 at 40—50°, and the resulting veratroylactic ester (which decomposes on distillation in vac.) treated with resorcinol Me_2 ether and conc. H_2SO_4 at 0°. It is also formed by methylating 7-hydroxy-4-(3' : 4'-dimethoxy)-phenylcoumarin, m. p. 236°, prepared from Et veratroylacetate, resorcinol, and H_2SO_4 . On reduction with Na and EtOH it yields 7-methoxy-4-(3' : 4'-dimethoxy)phenylchroman, b. p. 263—266°/4 mm., uncrystallisable.
R. S. CAHN.

Conversion of 7-hydroxy-3 : 4-dimethylcoumarin into 2 : 4-dimethoxy- α - β -dimethylcinnamic acid. F. W. CANTER and A. ROBERTSON (J.C.S., 1931, 1875—1876).—The product of interaction of resorcinol and Me α -methylacetoacetate in presence of P_2O_5 is 7-hydroxy-3 : 4-dimethylcoumarin (of. this vol., 963), because on methylation and subsequent hydrolysis it yields 2 : 4-dimethoxy- α - β -dimethylcinnamic acid, m. p. 133°, oxidised by $KMnO_4$ to 2 : 4-dimethoxyacetophenone.
R. S. CAHN.

Reactivity of the methylene group in coumarin-4-acetic acids. III. Condensation of 7-methylcoumarin-4-acetic acid with *m*- and *p*-hydroxybenzaldehydes. B. B. DEY and T. R. SESHADRI (J. Indian Chem. Soc., 1931, 8, 247—249; cf. A., 1925, i, 953).—The theory previously advanced to explain the colour changes of 7-methyl-4-(4'-hydroxy-3'-methoxystyryl)coumarin (I) in NaOH is supported by the absence of similar changes with the 3' : 4'-dimethoxy-, 4'-acetoxy-3'-methoxy-, and 3'-hydroxy-compounds, and by their presence with the 4'-hydroxy-compound. (I) with Me_2SO_4 and NaOH gives the 3' : 4'-(OMe) $_2$ -derivative, m. p. 188° [sol. in dil. aq. KOH on boiling (by rupture of the pyrone ring) to a faintly yellow solution, from which it is precipitated unchanged by acids], and with Ac_2O and a drop of pyridine the 4'-acetoxy-3'-methoxy-derivative, m. p. 172°, which is slowly deacetylated by dil. NaOH. Condensation of *p*-hydroxybenzaldehyde and 7-methylcoumarin-4-acetic acid by Knoevenagel's method afforded 7-methyl-4-(4'-hydroxystyryl)coumarin, m. p. 218°, giving colours with aq. NaOH and conc. H_2SO_4 similar to those given by (I). The 4'- OMe -derivative, m. p. 180°, dissolves slowly in boiling aq. KOH to a

nearly colourless solution; the 4'-Ac derivative, m. p. 209°, dissolves slowly in cold KOH. Both derivatives are precipitated unchanged on acidification of the KOH solutions. *m*-Hydroxybenzaldehyde gave similarly 7-methyl-4-(3'-hydroxystyryl)coumarin, m. p. 207°, sol. in cold dil. NaOH with a pale yellow colour, which fades slowly on keeping and quickly on warming; the yellow solution rapidly, and the colourless solution slowly deposited the substance on acidification. The 3'-OMe- and 3'-OAc-derivatives, m. p. 146° and 159°, respectively, slowly dissolved in aq. alkalis. R. S. CAHN.

Coumarin series. II. Conversion of substituted coumarins into benzopyrylium salts.

I. M. HEILBRON, D. W. HILL, and H. N. WALLS (J.C.S., 1931, 1701—1704; cf. A., 1927, 1082).—MgPhBr converts 3-substituted coumarins into 2-phenylbenzopyrylium salts, but with 4-substituted coumarins the yield is poor, or nil. Chromens result from the use of conc. solutions, or elevated temp. in the latter series. 3-Methoxycoumarin, m. p. 162° (from OMe·CH₂·CO₂Na, salicylaldehyde, and Ac₂O at 160°), and MgPhBr in cold Et₂O-C₆H₆ gave 3-methoxy-2-phenylbenzopyrylium chloride (*ferrichloride*, yellow), but under reflux a mixture of 3-methoxy-2:4-diphenylchromen, m. p. 172°. 2-Phenyl-3-methylbenzopyrylium chloride (*ferrichloride*, m. p. 132°) and 2:3-diphenylbenzopyrylium chloride, unstable in air (*ferrichloride*), were similarly prepared. 4-Methylcoumarin gave a poor yield of 2-phenyl-4-methylbenzopyrylium chloride (*ferrichloride*); the yield was the same in conc. solution, but 2:2-diphenyl-4-methyl-Δ³-chromen was the main product. β-*o*-Anisyleinnamic acid and AcCl gave, in the first experiment only, a modification of 4-phenylcoumarin, m. p. 92°, passing on melting into the normal form, m. p. 104—105°. This with cold MgPhBr gave a poor yield of 2:4-diphenylbenzopyrylium chloride (*ferrichloride*), but in boiling Et₂O gave 2:2:4-triphenyl-Δ³-chromen, m. p. 130°, which was unchanged by boiling AcOH, and on refluxing with aq. or amylalcoholic KOH gave a stereoisomeride, m. p. 162—163°. 4-Methoxy- and 4:7-dimethoxy-coumarin gave no benzopyrylium salt. R. S. CAHN.

Pyryleninium compounds. XVIII. Oxidation products of pyryleninium salts.

W. DILTHEY and F. QUINT (J. pr. Chem., 1931, [ii], 131, 1—28).—Pyryleninium salts are readily oxidised by H₂O₂ in AcOH, fission of the ring occurring at the 2:3-position with formation of *o*-hydroxybenzoin derivatives, thus indicating a 4-carbonium rather than an oxonium structure; an exception is afforded by the weakly-basic or non-basic NO₂-derivatives, however, which oxidise to coumarins. The condensation of dibenzyl ketone with salicylaldehyde in presence of piperidine gives a mixture of the colourless *ψ*-base, m. p. 166—167° (*Na* salt, red), and the corresponding anhydro-base, 3-phenyl-2-benzylidenbenzopyran (I), m. p. 112° (*perchlorate*, m. p. 182°). Use of salicylaldehyde Me ether in place of the aldehyde gives a compound, m. p. 140—142°, of *o*-methoxybenzylidenedibenzyl ketone, m. p. 138—139°, with piperidine, readily decomposed into its constituents by warming with AcOH, the former of which is demethylated by

AlBr₃ in boiling C₆H₆ to (I). Oxidation of (I) with H₂O₂ in AcOH gives *o*-hydroxydeoxybenzoin phenylacetate, m. p. 103—104°, and an unidentified substance, m. p. 195—196°; the oxidation is accelerated by acid, and occurs only very slowly in MeOH or EtOH. Hydrolysis of the former with MeOH-KOH gives 2-phenylcoumarone and phenylacetic acid; NH₂OH, HCl and KOH give *o*-hydroxydeoxybenzoin oxime, m. p. 138—139°, hydrolysed by alcoholic HCl to 2-phenylcoumarone. 6-Nitro-3-phenyl-2-benzylidenbenzopyran, m. p. 195—196°, exists in yellow and orange forms, the latter being unstable in solvents and above 165°; it is prepared by use of 5-nitrosalicylaldehyde in the above condensation, and does not form a stable perchlorate. It is oxidised by H₂O₂ in presence or absence of HClO₄ to BzOH and 6-nitro-3-phenylcoumarin, m. p. 252—253°, synthesised for comparison from phenylacetic acid, 4-nitrosalicylaldehyde, and piperidine. 8-Nitro-3-phenyl-2-benzylidenbenzopyran, m. p. 145.5°, similarly prepared, does not form a perchlorate, and is oxidised to 3-nitro-3-phenylcoumarin, m. p. 238.5—240°. Oxidation of 2:3-diphenylbenzopyryleninium perchlorate, m. p. 245° (decomp.) (cf. A., 1909, i, 116), gives *o*-hydroxydeoxybenzoin benzoate, m. p. 106—107°, converted as before into 2-phenylcoumarin.

Condensation of deoxybenzoin with *p*-nitrosalicylaldehyde in alcoholic HCl, and addition of HClO₄ gives 6-nitro-2:3-diphenylbenzopyryleninium perchlorate, m. p. 245° (decomp.), readily hydrolysed by addition of H₂O to its solution in glacial AcOH to the *ψ*-base, m. p. 162° (*Na* salt), and converted by EtOH and MeOH into the corresponding *Et*, m. p. 126.5—127.5°, and *Me* ethers, m. p. 136—137°. The perchlorate is oxidised by H₂O₂ in AcOH to 3-nitro-6-hydroxydeoxybenzoin benzoate, m. p. 111—112°, which is hydrolysed to 3-nitro-6-hydroxydeoxybenzoin, m. p. 182—183°, by dil. NaOH, and regenerated from it by BzCl and pyridine. The same product is obtained from the ethers in EtOH in presence of AcOH, but in its absence they are completely unattacked. Both the benzoin and its Bz derivative are dehydrated by AcOH containing a little H₂SO₄ to 5-nitro-2-phenylcoumarone, m. p. 159—160°; the same product is obtained with P₂O₅ in C₆H₆ in the case of the former. The oxidation product of 2:3-dimethylnaphthopyryleninium perchlorate (A., 1926, 1254) is 2-acetoxy-1-naphthylacetone, and is converted by hot 10% NaOH into 2-methylnaphthocoumarone, m. p. 57—58°, and by NH₂OH, HCl and KOH in EtOH into 2-hydroxy-1-naphthylacetoneoxime, m. p. 186°, which gives the coumarone with 70% H₂SO₄. The product from 2-methyl-3-naphthopyryleninium perchlorate (*loc. cit.*) is similarly 2-acetoxy-1-phenacylnaphthalene, and is likewise converted into 2-phenylnaphthocoumarone, m. p. 143—144°. The oxidation of 3-phenyl-2-benzylidenenaphthopyran (A., 1928, 767; also obtained with piperidine as condensing agent) gives 1-phenacyl-β-naphthyl phenylacetate, m. p. 126—127°, converted as before into the coumarone. 2:4:6-Triphenylpyryleninium perchlorate gives the *O*-Bz derivative of CH₂Bz₂. H. A. PIGGOTT.

Indicators. III. Iodoeosin. I. V. KULIKOV and A. G. PUKIREV (Trans. Inst. Pure Chem. Reag.,

1931, 10, 46—52).—A diminution of the I content of iodo eosin does not influence its indicator properties. The I content of iodo eosin can be determined by fusion with Na_2CO_3 and NaNO_3 , followed by reduction with SO_2 . E. S. HEDGERS.

Oxidative fission of thioindigo-red. E. RIESZ (Ber., 1931, 64, [B], 1893—1894).—*o*-Sulphobenzoic acid is obtained by the oxidation of thioindigo-red with fuming and conc. HNO_3 at 80° . H. WREN.

Supposed isomeride of 1 : 3 : 5-trithian. F. D. CHATTAWAY and E. G. KELLETT (J. Amer. Chem. Soc., 1931, 53, 2187—2188).—The supposed isomeride, m. p. 247° (decomp.), of 1 : 3 : 5-trithian (Hinsberg, A., 1912, i, 546) is obtained by interaction of H_2S , CH_2O , and aq. HCl; on crystallisation or dissolution, or on exposure to air, by heating at 100° , or by shaking with cold dil. aq. H_2O_2 , it is converted into pure 1 : 3 : 5-trithian, m. p. 216° . In the last case reduction of the H_2O_2 is observed. The conversion of 1 : 3 : 5-trithian into this substance is brought about, not only by aq. HI (Hinsberg), but also by other reducing agents, e.g., SnCl_2 , which do not normally cause inversion in the trithioacetaldehydes. The existence of a stereoisomeride is irreconcilable with the accepted formula of 1 : 3 : 5-trithian, and it is concluded that the supposed isomeride is an unstable reduction product. H. A. PIGGOTT.

Oxidation of dithioparachoral. F. D. CHATTAWAY and E. G. KELLETT (J. Amer. Chem. Soc., 1931, 53, 2182—2187).—2 : 6-Bistrichloromethyl-4-dichloromethylene-1 : 3 : 5-oxadithian is oxidised by an excess of H_2O_2 in cold AcOH to the dioxide, m. p. 166 — 167° , which is unaffected by Cl_2 or Br in the cold or by Sn in boiling HCl-AcOH. Dithioparachoral (α - or β -) is oxidised only with difficulty, and then with elimination of HCl from two $\cdot\text{CH}\cdot\text{CCl}_2$ groups and complete loss of one of them; thus by CrO_3 in AcOH it is converted into 2 : 6-bisdichloromethylene-1 : 3 : 5-oxadithian 3 : 3 : 5-tetroxide, m. p. 185° (4 : 4-dichloro-derivative, m. p. 143°), a little of the above dioxide, and decomp. products. With warm 10% aq. NaOH, or KOAc in EtOH, or Cl_2 in warm AcOH the dioxide gives 6-trichloromethyl-2 : 4-bisdichloromethylene-1 : 3 : 5-oxadithian 3 : 3-dioxide, m. p. 148° , but with aq.-EtOH-NaOH Et 2 : 6-bisdichloromethyl-1 : 3 : 5-oxadithian 3 : 3-dioxide-4-carboxylate, m. p. $112\cdot5^\circ$, is formed; the corresponding Me ester, m. p. 126° , is similarly prepared. These esters could not be hydrolysed to acids. By Cl_2 in AcOH the Et ester is converted successively into Et 6-chloro-, m. p. 151 — 152° , and 4 : 6-dichloro-6-trichloromethyl-2-dichloromethylene-1 : 3 : 5-oxadithian 3 : 3-dioxide-4-carboxylate, m. p. $161\cdot5^\circ$. H. A. PIGGOTT.

Compounds of tungsten and molybdenum sulphides with sulphides of organic [bases]. L. DEBUCQUET and L. YELLUZ (Compt. rend., 1931, 193, 58—60).—Prolonged passage of H_2S into solutions of MoO_3 or WO_3 (freshly precipitated from Na_2WO_4 , and dialysed) in piperidine or piperazine hydrate gives double salts, of which the following are described: $(\text{WS}_3\cdot\text{C}_4\text{H}_{10}\text{N}_2)_2\cdot\text{H}_2\text{S}$, lemon-yellow, decomp. on heating, passing on crystallisation from piperazine hydrate into $\text{WS}_3\cdot(\text{C}_4\text{H}_{10}\text{N}_2)_2\cdot\text{H}_2\text{S}$, ochre-yellow;

$\text{MoS}_3\cdot(\text{C}_5\text{H}_{11}\text{N})_2\cdot\text{H}_2\text{S}$, ruby-red; $\text{MoS}_3\cdot\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{S}$, brick-red, unchanged by crystallisation from piperazine hydrate. The formulæ are confirmed by hydrolysis by dil. HCl to metallic sulphide, hydrochloride of the base, and H_2S . R. S. CAHN.

Piperidine derivatives. XI. Ethyl 4-piperidone-3-carboxylate and 4-piperidone hydrochloride. G. M. KUETTEL and S. M. McELVAIN (J. Amer. Chem. Soc., 1931, 53, 2692—2696).— $\beta\beta'$ -Dicarbethoxydiethylamine (hydrochloride, m. p. $79\cdot5$ — $80\cdot5^\circ$) (improved method of prep. given) and Na in xylene at 85° give 11% of Et 4-piperidone-3-carboxylate [hydrochloride, m. p. 168 — 169° (decomp.)], hydrolysed by 20% HCl to 4-piperidone [hydrochloride (+1.5EtOH), m. p. 139 — 141° (decomp.), (+ H_2O), m. p. 92 — 94°]. H. BURTON.

Pyridine derivatives. XII. Mercaptans and sulphonic acids of pyridine. C. RATH. XIII. 2-Pyridine-3-arsinic acid. A. BINZ and H. MAIER-BODE. XIV. Derivatives of 3-cyanopyridine. C. RATH and F. SCHIFFMANN (Annalen, 1931, 487, 105—119, 119—126, 127—134).—XII. The following are prepared by interaction of the corresponding chloro-derivatives with KSH in MeOH: 5-nitro-2-thiopyridine, m. p. 168° (decomp.) (disulphide, m. p. 150 — 151°); 5-chloro-, m. p. 198° (disulphide, m. p. 80°), 5-bromo-, m. p. 203 — 204° (disulphide, m. p. 102°), 5-iodo-, m. p. 210 — 211° (in poor yield: disulphide, m. p. 155°), 3-chloro-5-nitro-, m. p. 193 — 194° (disulphide, m. p. 203 — 204°), 3-bromo-5-nitro-, m. p. 189° (decomp.), and 3-iodo-5-nitro-2-thiopyridine, m. p. 195° (decomp.); 2-thiopyridine-5-carboxylic acid, m. p. 272° (decomp.) (Au salt, m. p. 253°), and 3-chloro-2-thiopyridine-5-carboxylic acid, m. p. 235° . The above disulphides are prepared by means of aq. H_2O_2 or I in MeOH. Interaction of 2-chloro-5-iodopyridine with KSH (1 equiv.) in MeOH at 130° gives 2-thiopyridine and the disulphide; the former is also produced from 5-iodo-2-hydroxypyridine and P_2S_5 . 5-Amino-2-thiopyridine, m. p. 170 — 171° , is prepared by reduction of the 5-nitro-derivative with SnCl_2 and HCl.

Chlorocyanopyridines are converted by NaSH in MeOH into thioamides of the corresponding thiolpyridinecarboxylic acids from which the acids themselves are produced by hydrolysis with conc. HCl at 120° . 2-Thiopyridine-3-thiocarboxylamide, m. p. 252° (decomp.), 3-chloro-, m. p. 193° (decomp.), 3-bromo-, m. p. 195° (decomp.) (carboxylic acid, m. p. 230°), and 3-iodo-2-thiopyridine-5-thiocarboxylamide, m. p. 194° (decomp.) [carboxylic acid, m. p. 232° (decomp.)], are described.

3-Nitro-, decomp. 260° , and 3-bromo-2-amino-pyridine-5-sulphonic acid, m. p. above 300° , are produced by nitration and bromination, respectively, of the aminosulphonic acid. The chloride, m. p. 51° , of 2-chloropyridine-5-sulphonic acid, m. p. 265° (amide, m. p. 159°), is prepared by heating 2-hydroxypyridine-5-sulphonic acid with PCl_5 and a drop of POCl_3 to 130 — 140° . The chloride, m. p. 72° , of 2-chloro-3-bromopyridine-5-sulphonic acid, m. p. above 280° (amide, m. p. 150°), is similarly prepared from the crude residue obtained by evaporating a diazotised solution of 3-bromo-2-aminopyridine-5-sulphonic acid.

XIII. 2-Pyridone-3-arsinic acid, m. p. 219—220° (*NaH* and *Na*₂ salts; *N-Me* derivative, m. p. 255—257°), is prepared in the usual way from 3-amino-2-hydroxypyridine, and is more stable to hydrolysis than is the corresponding -5-arsinic acid. It is converted into 2-pyridone-3-arsenious oxide, m. p. 244—247°, and 3:3'-arseno-2:2'-pyridone by reduction with H₂S and a little HI, and HPO₂, respectively: the former interacts with PhSH at 130° with formation of 2-pyridone-3-diphenylthiolarsine, m. p. 132°, the *N-Me* derivative, m. p. 122°, of which is similarly obtained from 1-methyl-2-pyridone-3-arsinic acid, decomp. 255—257°, itself obtained by methylation. The product of fusion of 2-pyridone with arsenic acid (A., 1930, 486) is separated by fractional precipitation with MeOH of the aq. *NaH* salts into 2-pyridone-3- and -5-arsinic acids. 1-Methyl-2-pyridone under similar conditions gives the -3-arsinic acid only.

XIV. The presence of substituents, reactive or otherwise, in the 2-position, does not inhibit the formation of nitrile through the diazo-compound from 3- or 5-aminopyridines. The following are described: 5-cyano-2-methylpyridine, m. p. 84—85°, b. p. 216—217°/750 mm. (hydrochloride, m. p. 210°), hydrolysed by 50% H₂SO₄ to the -5-carboxylic acid; 5-cyano-2-hydroxypyridine, m. p. 252—253° (also prepared by diazotising 5-cyano-2-aminopyridine); 2-chloro-5-cyanopyridine, m. p. 115°, hydrolysed by aq. HCl at 150° to 2-hydroxy- [*Et* ester, m. p. 150° (*N-Me* derivative, m. p. 74°, b. p. 190—200°/15 mm.)], and by HCl and Et₂O (A., 1898, i, 196) to 2-chloropyridine-5-carboxylic acid and amide, m. p. 205°; 2:3-dichloro-5-cyanopyridine, m. p. 150°, hydrolysed by HCl and Et₂O to the -5-carboxylic acid, m. p. 168°; 2-chloro-3-bromo-5-cyano-, m. p. 160°; 2-chloro-3-iodo-5-cyano-, m. p. 148°; 5-iodo-3-cyano-2-hydroxy-, and 2:5-dichloro-3-cyano-pyridine, m. p. 118—119°. 2-Amino-pyridine-5-carboxylic acid, decomp. 310—312°, is obtained by heating the nitrile with conc. HCl to 150—170°. Interaction of 2-chloro-5-cyanopyridine with MgMeI gives 2-chloro-5-pyridyl methyl ketone, m. p. 104° (phenylhydrazone, m. p. 164°), and the -5-carboxylamide. H. A. PIGGOTT.

Benzyl derivatives of pyridine. J. VON BRAUN and W. PINKERNELLE (Ber., 1931, 64, [B], 1871—1874).—Pyridine is readily converted by CH₂PhCl and Cu into a mixture of mono- and di-benzylpyridine, roughly separable by fractional distillation; from the fraction of lower b. p. 2-benzylpyridine, b. p. 275°, is readily isolated as the picrate, m. p. 139°. It is reduced, preferably by Na and EtOH, to 2-benzylpiperidine, b. p. 268° (picrate, m. p. 157°; *Ac* derivative, b. p. 197—200°/16 mm.; nitroso-compound). It is converted by Et bromoacetate into *Et* 2-benzylpiperidine-1-acetate, b. p. 192—196°/15 mm., hydrolysed to a non-cryst. hydrochloride. With methylal and conc. HCl, α -benzylpiperidine yields small amounts of 2:3-tetramethylene-1:2:3:4-tetrahydroisoquinoline, b. p. about 160°/15 mm. (picrate, m. p. 177°). The fractions of higher b. p. from CH₂PhCl and pyridine contain a mixture of dibenzylpyridines from which the 2:4-derivative, b. p. 220—222°/12 mm., is isolated through the picrate, m. p. 161°; the hygroscopic hydrochloride, m. p. 156°, and methiodide, m. p.

149°, are described. The constitution of the base follows from its formation from CH₂PhCl, 4-benzylpyridine, and Cu powder. 2:6-Dibenzylpyridine, m. p. 73—75°, gives a picrate, m. p. 177°, hygroscopic hydrochloride, m. p. 162°, and methiodide, m. p. 142°.

H. WREN.

Substituted aromatic aldehydes in Hantzsch's pyridine condensation. II. Methyl- and nitrobenzaldehydes. L. E. HINKEL, E. E. AYLING, and W. H. MORGAN (J.C.S., 1931, 1835—1841; cf. A., 1929, 704).—Hantzsch's pyridine synthesis, applied under standard conditions (which give usually concordant results) to benzaldehydes substituted by the Me, NO₂, Cl, OMe, and OH groups, gives yields in accordance with anticipations from current electronic theories, with the possible exception of the OH group. The following are the mean yields, the radicals named being the substituents R in the Et 4-R-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylates obtained. Tolylyl-, *o*-, m. p. 114°, 8.6%; *m*-, m. p. 138°, 56.5%; *p*-, m. p. 140°, 36.8%. Nitrophenyl-, *o*- (I), m. p. 125°, not 119—120° (A., 1887, 845), phototropic, 61.7% (a small amount of a compound, m. p. 171°, was also formed); *m*-, m. p. 164°, not 161° (*loc. cit.*), 87.7%; *p*-, m. p. 136°, not 118—122° (*loc. cit.*), 63.6% (a small amount of a compound, m. p. 140°, was also formed). Chlorophenyl-, *o*-, 61.6%; *m*-, 75.6%; *p*-, 72.6%. Anisyl-, *o*-, 57.3%; *m*-, 75.2%; *p*-, 63.8%. Hydroxyphenyl-, *m*-, 66.7%; *p*-, 67.5%; *o*-hydroxybenzaldehyde gave a small quantity of mixed products. Phenyl-, 74.2%. Xylyl-, *o*-4-, m. p. 114°, 34.6%; *m*-4-, m. p. 157°, 33.1%; *p*-3-, m. p. 140°, 43.6%. 3':5'-Dinitro-*p*-tolyl-, m. p. 166°, 67.9%. 2':4':6-Trimethylphenyl-, and 3':5'-dinitro-2':4':6'-trimethylphenyl-, nil; instead of the latter, <1% of a compound, m. p. 273°, was obtained. *Et* 4-*o*-nitrophenyl-2:6-dimethylpyridine-3:5-dicarboxylate, obtained by oxidation of (I) with boiling *N-HNO*₃, has m. p. 75°.

R. S. CAHN.

Indolenines. IV. Indolenines from *as*-dibenzyl- and tribenzyl-acetone. H. LEUCHS and H. S. OVERBERG (Ber., 1931, 64, [B], 1896—1904).—*as*-Dibenzylacetone is reduced by Zn-Hg and 5*N*-HCl to α -phenyl- β -benzyl-*n*-butane, b. p. 166°/12 mm. The ketone condenses with PhCHO in presence of NaOH in aq. EtOH forming β -phenyl- α -benzylethyl styryl ketone, m. p. 64—65° (dibromide, m. p. 124°), transformed by phenylhydrazine in AcOH into 1:5-diphenyl-3-dibenzylmethylpyrazoline, m. p. 88° (monobromo-derivative, m. p. 114—115°). The unsaturated ketone is reduced by Na-Hg and EtOH to α -diphenyl- β -benzylpentan- γ -one, m. p. 61—62°. The corresponding phenylhydrazone, m. p. 87—88°, is converted by ZnCl₂ in EtOH at 110—120° into a compound, C₃₀H₂₇N, m. p. 123—124°, which does not give a picrate or perchlorate, is unaffected by Ac₂O, and is not smoothly hydrogenated. 2-Methyl-3:3-dibenzylindolenine is transformed by PhCHO in H₂ at 140—150° into 3:3-dibenzyl-2-styrylindolenine, m. p. 88—89°, readily oxidised by KMnO₄ (hydrochloride, m. p. 145°; perchlorate), and the compound, C₃₂H₁₆N₂, m. p. 245—246° (vac.). Hydrogenation of the base in presence of PtO₂ and AcOH affords 3:3-dibenzyl-2- β -phenylethylindolenine, isolated as the

hydrochloride, m. p. 251—253° (vac.), and perchlorate, decomp. above 255—260° after blackening. 3 : 3-Dibenzyl-2-methylindolenine and *m*-nitrobenzaldehyde at 120° yield 3 : 3-dibenzyl-2-*m*-nitrostyrylindolenine, m. p. 187—188° [tetrahydrochloride, m. p. 174—176° (decomp.)], and β -*m*-nitrophenyl- α -di-3 : 3-dibenzyl-2-indolenylpropane, m. p. 182—185° (decomp.) after softening. The nitrostyryl compound is oxidised by KMnO_4 in COMe_2 to *m*-nitrobenzoic acid and 3 : 3-dibenzylindolenine-2-carboxylic acid, m. p. 147—149°. 3 : 3-Dibenzyl-2-methylindolenine is converted by NaNO_2 in AcOH into 3 : 3-dibenzylindolenine-2-formoxime, m. p. 225—227° (decomp.) [also + $\frac{1}{2}$ EtOH; Bz derivative, m. p. 160°], transformed by boiling Ac_2O into 3 : 3-dibenzylindolenine-2-nitrile, m. p. 122—123°, which is hydrolysed by KOH in EtOH to 3 : 3-dibenzylindolin-2-one, m. p. 197—199° (bromo-derivative, m. p. 235—237°), and 3 : 3-dibenzylindolenine-2-carboxylic acid, m. p. 147—149° (decomp.) (see above). 3 : 3-Dibenzyl-2-methylindolenine methiodide, m. p. 152—153° (slight decomp.), is transformed by NH_3 and Et_2O into 3 : 3-dibenzyl-1-methyl-2-methyleneindoline, m. p. 118—119°. 3 : 3-Dibenzyl-2-methylindolenine is reduced by Zn-Hg and 12N-HCl to 3 : 3-dibenzyl-2-methylindoline, which regenerates the indolenine when attempts are made to isolate it as the picrate. The indoline is identified with certainty by reduction of the indolenine in presence of PbO_2 and immediate conversion of the product into the Ac derivative, m. p. 102—103° and 119°, respectively. The dimorphous acetate is obtained less smoothly by hydrogenation of 1-acetyl-3 : 3-dibenzyl-2-methyleneindoline.

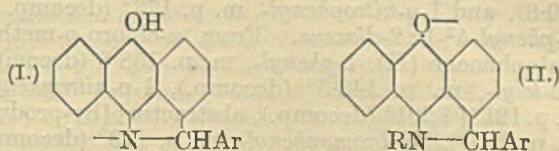
H. WREN.

Quinoline derivatives. XXV. Synthesis of 4'-hydroxy-2'-methyl-5'-isopropyl-2-phenylquinolines. H. JOHN and E. ANDRASCHKO (J. pr. Chem., 1931, [ii], 131, 90—96).—Condensation of isatin with 4-hydroxy-2-methyl-5-isopropylacetophenone in presence of 33% KOH gives 2-(4-hydroxy-2-methyl-5-isopropylphenyl)quinoline-4-carboxylic acid, m. p. 282° (Et ester, m. p. 131°), converted by distillation into 2-(4-hydroxy-2-methyl-5-isopropylphenyl)quinoline, m. p. 121°. Similarly from 5-iodoisatin 6-iodo-2-(4-hydroxy-2-methyl-5-isopropylphenyl)quinoline-4-carboxylic acid, m. p. 142°, is prepared. Interaction of *o*-aminoacetophenone and 4-hydroxy-2-methyl-5-isopropylacetophenone in presence of 10% NaOH gives 2-(4-hydroxy-2-methyl-5-isopropylphenyl)-4-methylquinoline, m. p. 121°. Various salts of these compounds are described.

H. A. PIGGOTT.

Free organic radicals. X. "Arylperipyrrolinoanthranolazyls" as novel, nitrogenous, homogeneously-crystallised, free radicals, with univalent oxygen and as components of molecular compounds with methane hydrocarbons. R. SCHOLL and O. BÖTTGER [with O. BENNDORF] (Ber., 1931, 64, [B], 1878—1893).—*m*-Xylyl 1-anthraquinonyl ketone, m. p. 196—197° (improved method of prep. substituting FeCl_3 for AlCl_3 given), is converted by NH_2Me in EtOH in presence of ZnCl_2 at 120—125° into two radicals, one of which is identical with the compound regarded previously as the azyl (I) ($\text{Ar}=\text{m-C}_6\text{H}_4\text{Me}_2$), whereas the other (isolated through its additive compound with *n*-heptane) is identical

with the product considered to be its *O*-Me ether. The new synthesis, combined with the observation



that the Me is attached to N, has caused a revision of the formulation of the complete group, since the absorption curves of the parent substance and its Me derivatives are nearly identical. The parent substance is therefore regarded as py-*m*-xylylperipyrrolinoanthroxyl ($\text{R}=\text{H}$) and the Me compound is formulated according to II ($\text{R}=\text{Me}$). This harmonises with its production from 1-*m*-xyloylantraquinoneoxime, with the stability of the radical in solution, and its indifference towards NO. With the aryloxyperihydrofurananthroxyls they comprise the only known homogeneous radicals with univalent O. These can be readily purified, e.g., by crystallisation from aq. EtOH. They have no tendency towards dimerisation. They form dark violet-blue crystals giving blue or violet to red solutions respectively in more and less highly solvating media; the last-named solutions generally exhibit vivid fluorescence. The solutions are rapidly decolorised by strong sunlight; in the dark they are very resistant to O_2 and not sensitive to NO. The radicals have feebly basic properties accompanied by weakly acidic nature if an alkyl or acyl group is not attached to the N atom; the radical nature does not disappear in the salts. Readily in dil. aq. NH_3 , more difficultly in dil. NaOH, they dissolve to blue solutions of salts which probably conform to the anthroxyl type. Similar salts are derived from the radicals and Ph diphenyl ketone. Whilst unaffected by hot $\text{Na}_2\text{S}_2\text{O}_4$, the blue solutions in hot EtOH are decolorised by Zn dust and NH_3 in N_2 , probably with formation of pyrrolinoanthranols which immediately revert to the radicals in presence of air. They are oxidised by $\text{K}_3\text{Fe}(\text{CN})_6$ in presence of NH_3 with loss of the H atom attached to N to pyrrolinoanthrones which readily pass back into the radicals by auto-reduction. Like the hydrofurananthroxyls they consume 3Br or 3OH respectively when titrated with Br or KMnO_4 and H_2SO_4 , corresponding with the three points of attraction (at the univalent O and the two *meso*-C atoms). The main product of the KMnO_4 titration is the 1-aryloxyanthraquinone. When titrated with CrO_3 they absorb 2 equiv. of O with the probable formation of dimeric peroxides. The violet-red *N*-Me derivative is prepared by means of Me_2SO_4 and NaOH. Apart from the absence of acidic properties, it is distinguished from the non-methylated radical by the consumption of 5OH when titrated with KMnO_4 . Red Bz derivatives are formed with BzCl and pyridine. The radical nature persists in both types of derivatives, thus demonstrating the unusual stability of these radicals.

H. WREN.

Reactions of ω -chloroacetophenone and ω -chloro-*p*-methylacetophenone with phenylhydrazine and its substituted derivatives. A. P. J. HOOGVEEN (Rec. trav. chim., 1931, 50, 669—678).—Phenacyl chloride (I) and the appropriate phenyl-

hydrazine give 1:3-diphenyl- Δ^2 -1:2-diazene (A., 1920, i, 96), 1-*o*-tolyl-, m. p. 147.2°, 1-*p*-tolyl-, m. p. 159.8°, and 1-*p*-nitrophenyl-, m. p. 173° (decomp. ?), -3-phenyl- Δ^2 -1:2-diazene. From ω -chloro-*p*-methylacetophenone (II), 1-phenyl-, m. p. 158.8 (decomp.), 1-*o*-tolyl-, m. p. 143.5° (decomp.), 1-*p*-nitrophenyl-, m. p. 121° [? 201° (decomp.), abstractor] [by-product, m. p. 287°], 1-*p*-bromophenyl-, m. p. 173° (decomp.), -3-*p*-tolyl- Δ^2 -1:2-diazene and 1:3-di-*p*-tolyl- Δ^2 -1:2-diazene, m. p. 177° (decomp.), are similarly prepared. (I) may be determined by titration of the ionised halogen formed by treating it at 60° with aq.-alcoholic Na₂S. Di-*p*-tolylacetyl sulphide, from (II) and Na₂S, has m. p. 88°. J. D. A. JOHNSON.

Labile nature of the halogen atom in organic compounds. XIV. Reactivity of halogen derivatives of 5-alkylbarbituric acids. A. B. COX, A. K. MACBETH, and S. W. PENNYCUIK (J.C.S., 1931, 1870—1874; cf. A., 1927, 575).—The halogen atom in 5-bromo-5-alkylbarbituric acids is reactive, as the compound cannot exist in an enolic form, and interaction with N₂H₄ to form the alkylbarbituric acid, HBr, and N₂ is quant. These bromo-compounds are reduced catalytically by the Pt electrodes of a conductivity cell, but only very slowly with polished electrodes. Modified directions are given for the prep. of 5-alkylbarbituric acids, and the following derivatives are obtained from them by adding Br to their aq. solutions: 5-bromo-5-methyl- (I), m. p. 190°, K 1.08 \times 10⁻⁷; 5-bromo-5-ethyl-, m. p. 202°, K 2.25 \times 10⁻⁷; 5-bromo-5-*n*-propyl-, m. p. 163.5°, K 2.51 \times 10⁻⁷; 5-bromo-5-isopropyl-, m. p. 163°, K 1.96 \times 10⁻⁷; 5-bromo-5-*n*-butyl-, m. p. 109°, K 2.76 \times 10⁻⁷; 5-bromo-5-isoamyl-, m. p. 175°, K 2.98 \times 10⁻⁷; 5-bromo-1:3-diphenyl-5-benzyl-barbituric acid, prep. in AcOH, m. p. 195°. (I) and N₂H₄ form 5-methylbarbituric hydrazide, m. p. 240°.

R. S. CAHN.

Oxygen ethers of barbital [5:5-diethylbarbituric acid]. A. W. DOX (J. Amer. Chem. Soc., 1931, 53, 2741—2744).—2:4:6-Trichloro-5-*sec*-butylpyrimidine is converted by the requisite NaOalk into 2:4:6-trimethoxy-, b. p. 245—250°, -triethoxy-, b. p. 260—264°, -tripropoxy-, b. p. 285—290°, and -tributoxy-, b. p. 310—315°, -5-*sec*-butylpyrimidine. 2:2:4:6-Tetrautoxy-, b. p. 180—183°/3 mm., and 2:2:4:6-tetraethoxy-5:5-diethylidihydropyrimidine, b. p. 122—123°/3 mm. (hydrolysed by conc. HCl at 140—150° to α -ethylbutyric acid and NH₄Cl) are prepared similarly from the 2:2:4:6-tetrachloro-derivative (this vol., 742). H. BURTON.

Stereochemistry of NN'-dipyrryls. Resolution of 2:5:2':5'-tetramethyl-1:1'-dipyrryl-3:3'-dicarboxylic acid. XVI. C. CHANG and R. ADAMS (J. Amer. Chem. Soc., 1931, 53, 2353—2357).—Condensation of Et 1-amino-2:5-dimethylpyrrole-3:3'-dicarboxylate with Et hexane- β -s-dione- γ -carboxylate in boiling MeOH gives Et 2:5:2':5'-tetramethyl-1:1'-dipyrryl-3:3'-dicarboxylate, hydrolysed by 10% EtOH-KOH to the corresponding acid (cf. A., 1904, i, 614). This was resolved by means of its brucine salts [d., m. p. 153—157°, [α]_D²⁰ -73.2° in pyridine; l., m. p. 293—304° (optically impure)] into d., m. p. 218—219°, [α]_D²⁰ +27.5° in pyridine, and l-2:5:2':5'-

tetramethyl-1:1'-dipyrryl-3:3'-dicarboxylic acid, m. p. 220—221°. These are very resistant to racemisation, the *d*-form being unchanged by boiling with pyridine for 24 hr., and only partly racemised by boiling with 0.1N-NaOH for 84 hr. H. A. PIGGOTT.

Rearrangement of quinazolones into triazole derivatives. III. G. HELLER with R. MECKE (J. pr. Chem., 1931, [ii], 131, 82—89).—The presence of a triazole ring in the product of rearrangement of 3-benzamido-2-phenyl-4-quinazolone (A., 1928, 1381) is proved by its decarboxylation at 350° to 1:2:3-triphenyl-1:3:4-triazole. Reduction of this quinazolone with Zn and 90% AcOH removes the NHBz group, and gives 4-hydroxy-2-phenylquinazoline. 3-Acetamido-4-quinazolone, m. p. 206°, is obtained by action of 95% HCO₂H on *o*-aminobenzacethydrizide at 100°, or by direct acetylation; it is stable to 2N-NaOH at 100°, as also is 3-acetamido-2-methyl-4-quinazolone. The Bz, m. p. 194°, and Bz₂, m. p. 205°, derivatives of 3-aminoquinazolone, prepared by benzylation in AcOH and pyridine, respectively, and in the case of the former, by action of HCO₂H on the appropriate hydrazide, are completely hydrolysed by 2N-NaOH and acids. *o*-Aminobenzhydrazide gives with MeCHO an ethylidene derivative, m. p. 150° (Bz derivative, m. p. 207°), which cannot be further condensed to a quinazoline, but its Bz derivative (from the benzyolated hydrazide) readily yields 3-benzamido-4-keto-2-methyltetrahydroquinazoline, m. p. 193°, stable to acids, but hydrolysed by dil. alkalis. 3-Ethylidene-amino-2-phenyl-4-quinazolone has m. p. 137°.

H. A. PIGGOTT.

Reaction between 2:4:6-trichloropyrimidine and dimethylaniline. S. KAWAI and T. MIYOSHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 16, 20—23).—2:4:6-Trichloropyrimidine reacts with boiling NPhMe₂ to give MeCl and 2:4:6-trimethylanilino-pyrimidine, m. p. 133—134°, also formed using NHPhMe. J. D. A. JOHNSON.

Condensation of β -hydroxyethylguanidine and acetoacetic ester. S. KAWAI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 16, 25—28).—The product of the interaction of β -hydroxyethylguanidine and Et acetoacetate is proved to be 4-keto-6-methyl-2:3-cycloethyleneiminotetrahydropyrimidine, $\text{CH}_2 \begin{matrix} \text{N}=\text{C}-\text{NH}-\text{CMe} \\ \text{CH}_2-\text{N}-\text{CO}-\text{CH} \end{matrix}$, decomp. 310° (picrate, m. p. 234°), since it is obtained together with 6-methyluracil and β -chloroethylamine on heating 2- β -hydroxyethylimino-4-keto-6-methyltetrahydropyrimidine, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{N}:\text{C}-\text{NH}-\text{CMe}$ / $\text{NH}-\text{CO}-\text{CH}$, m. p. 204—205° (picrate, m. p. 198—199°; hydrochloride, m. p. 165—166°), with conc. HCl at 140—148°. J. D. A. JOHNSON.

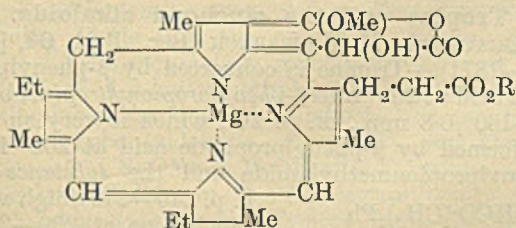
Ring closure of *o*-aminophenylsemicarbazides to benzotriazines. P. C. GUHA and F. ARNDT [with H. SKZYPCZIK and P. S. MAYURANATHAN] (J. Indian Chem. Soc., 1931, 8, 199—202).—Dihydro-1:2:4-benzotriazines are unstable, passing rapidly by atm. oxidation into benzotriazines (cf. A., 1928, 158), contrary to previous statements (A., 1925, i, 1461; 1928, 1263). Reduction of *o*-nitrophenylsemicarbazide (I) and *o*-nitrophenylthiosemicarbazide by the

method previously described gives *o*-phenylenediamine, and not 3-amino-1:2-dihydro-1:2:4-benzotriazine. With a slight excess of SnCl_2 and HCl , (I) yields 3-amino-1:2:4-benzotriazine. R. S. CAHN.

Decomposition of uric acid by various charcoal preparations. S. ZYLBERTAL (Biochem. Z., 1931, 236, 131—137).—The samples of charcoal may be divided into those which, although adsorbing uric acid, scarcely oxidise it at all, those which contain metal (Fe) the oxidation by which is inhibited by CN' , and those samples which are free from metal oxidation by which is not inhibited by CN' . The oxidation proceeds in presence both of O_2 and of methylene-blue but in the latter case is considerably inhibited by CN' .

P. W. CLUTTERBUCK.

Chlorophyll series. V. Structure of chlorophyll-A. J. B. CONANT, E. M. DIETZ, C. F. BAILEY, and S. E. KAMERLING (J. Amer. Chem. Soc., 1931, 53, 2382—2393; cf. this vol., 745).—The participation of an external oxidising agent in the allomerisation of chlorophyll necessitates correction of the formula of chlorin *f* (cf. this vol., 368) to that of a dihydrochlorophyrin. Oxidation of Me phæophorbide *a* with $\text{K}_3\text{Mo}(\text{CN})_8$ in COMe_2 gives Me dehydrophæophorbide *a*, sinters 260—265°, and some phæopurpurin 7. Hot, rapid hydrolysis of the former gives unstable chlorins, converted by diazomethane into Me_2 phæopurpurin 7; further hydrolysis gives chlorin *f* and oxalic acid. Chlorin *f* is more conveniently prepared by bubbling O_2 through a solution of Me phæophorbide *a* in conc. MeOH-KOH at 0°, and heating the product to boiling in a stream of N_2 . Oxidation of chlorin *e* with $\text{K}_3\text{Mo}(\text{CN})_8$ gives chlorin *k* [monoMe ester (diazomethane), m. p. 146—147° (decomp.)]; chlorin *e* Me_2 ester is not oxidised by this reagent. The formula:



is suggested for chlorophyll *a* ($\text{R}=\text{phytyl}$) and phæophorbide *a* ($\text{R}=\text{H}$; 2H in place of Mg). The absorption of dehydrochlorophyll *a* in the visible spectrum differs slightly according to its mode of prep. [O_2 or $\text{K}_3\text{Mo}(\text{CN})_8$], and the same differences are found in the phæophytins.

H. A. PIGGOTT.

Phylloporphyrin. L. MARCHLEWSKI (Rocz. Chem., 1931, 11, 529—531).—Polemical against Willstätter.

R. TRUSZKOWSKI.

Hæmins and the relationship between hæmins and chlorophyll. H. FISCHER (Z. angew. Chem., 1931, 44, 617—623).—A lecture.

Local anæsthetics containing the morpholine ring. J. H. GARDNER and E. O. HAENNI (J. Amer. Chem. Soc., 1931, 53, 2763—2769).—Tri(hydroxyethyl)amine hydrochloride is heated at 200—205°/40 mm., and the resultant product (after removal of unchanged material) hydrolysed by KOH in EtOH to

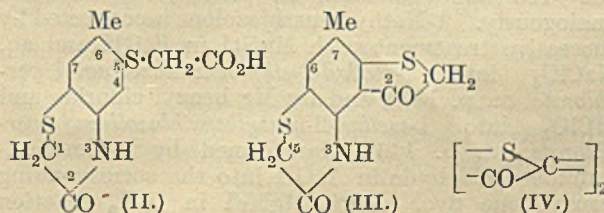
N- β -hydroxyethylmorpholine, b. p. 118—120°/24 mm. (benzoate hydrochloride, m. p. 204.6—205.8°; *p*-nitrobenzoate hydrochloride, m. p. 214.6—215.4°; *p*-aminobenzoate hydrochloride, m. p. 225.8—226.2°). γ -Aminopropyl alcohol, $\beta\beta'$ -dichlorodiethyl ether, and K_2CO_3 at 120—170° give *N*- γ -hydroxypropylmorpholine, b. p. 134—136°/24 mm. (benzoate hydrochloride, m. p. 190.1—190.5°; *p*-nitrobenzoate hydrochloride, m. p. 232.8—233.2°; *p*-aminobenzoate hydrochloride, m. p. 193.3—193.7°). The benzoates and *p*-aminobenzoates possess considerable local anæsthetic activity and low toxicity.

H. BURTON.

Condensation of aldehydes with *o*-aminothiophenols, benzthiazolines, and benzthiazoles. H. P. LANKELMA and P. X. SHARNOFF (J. Amer. Chem. Soc., 1931, 53, 2654—2657).—Substituted 5-chlorobenzthiazolines, obtained in 70—90% yield from 4-chloro-2-aminothiophenol and the appropriate aldehyde in pyridine, are oxidised by FeCl_3 in EtOH to the corresponding benzthiazoles. The following are new: 5-chlorobenzthiazoline, m. p. 168—169° (2-Me, m. p. 61°; 2-Et, m. p. 60°; 2-hexyl, m. p. 51—52°; 2-Ph, m. p. 127°, and 2-*o*-chlorophenyl, m. p. 81°, derivatives); 5-chlorobenzthiazole, m. p. 106° (2-Et, m. p. 56—57°, and 2-*o*-chlorophenyl, m. p. 136—137°, derivatives).

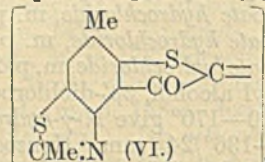
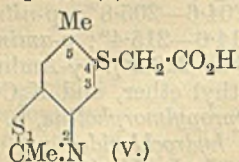
H. BURTON.

Condensed thiazine- and thiazole-thionaphthen derivatives. E. RIESZ, R. POLLAK, and A. WITTELS (Annalen, 1931, 487, 264—269).—Methods of prep. are described for compounds containing the thionaphthen ring system condensed with a thiazole or thiazine ring. The colour of the thioindigoid dyes prepared is deepened by the presence of the extra ring. *p*-Toluidine-2:5-disulphonyl chloride (I) is reduced by Zn dust and HCl in AcOH to the corresponding Zn dimercaptide, which with NaOH and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ gives 5-carboxymethylthiol-2-keto-6-methylbenzthiazine (II), m. p. 228°. This with ClSO_3H at 0—10° gave the thiazine-thionaphthen derivative (III), characterised by its *p*-dimethylaminoanil, bluish-green (prepared by condensation with *p*-nitrosodimethylaniline in aq.-alcoholic KOH at 45°). (II) with ClSO_3H at 30—40° gives the thiazine-thioindigo derivative (IV), bluish-green, which gives a green vat and dyes therefrom in bluish-grey tones. Aceto-*p*-toluidide-2:5-disulphonyl chloride,



m. p. 125° [from (I) by prolonged boiling with AcCl], with Zn dust and HCl in AcOH yields the corresponding Zn dimercaptide, which with NaOH and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ gives 4-carboxymethylthiol-1:5-dimethylbenzthiazole (V), m. p. 146°, which with ClSO_3H at 30° gives the thiazole-thioindigo derivative (VI). This dyes bluish-green shades, not fast to acids. Chloroaceto-*p*-toluidide-2:5-disulphonyl chloride, m. p.

118° [from (I) and boiling $\text{CH}_2\text{Cl}\cdot\text{COCl}$], similarly gave



(V). On treating (V) with Me_2SO_4 , and then boiling for 10 min. with Ac_2O and *p*-dimethylaminobenzaldehyde, 4-carboxymethylthiol-2-*p*-dimethylaminostyryl-5-methylbenzthiazole-2-methosulphate (VII), violet, m. p. 204°, was obtained, which dyes red-dish-violet shades, not fast to acids. Treatment of (V) with Et_2SO_4 , and subsequent boiling with anisaldehyde and a drop of piperidine in EtOH, and addition of aq. KI gave similarly 4-carboxymethylthiol-2-*p*-methoxystyryl-5-methylbenzthiazole-2-ethiodide, m. p. 201°, bright red, which dyes wool and cotton mordanted with tannin orange-yellow tones.

Unusual mode of formation of the simplest thiocyanins. W. KÖNIG, W. KLEIST, and J. GÖTZE (Ber., 1931, 64, [B], 1664—1675).—*as-p*-Tolylethylthiocarbamide is converted by Br in CHCl_3 into 2-imino-5-methyl-1-ethylbenzthiazolin,

$\text{C}_6\text{H}_4\text{Me} \left\langle \begin{array}{c} \text{S} \\ \text{NEt} \end{array} \right\rangle \text{C:NH}$, m. p. 104° [hydrobromide, m. p. 291—292° (decomp.) after darkening. 2-Imino-1-ethyl- β -naphththiazolin, m. p. 130°, and 2-imino-1:7-trimethylenebenzthiazolin [hydrobromide, m. p. 328° (decomp.)], are similarly prepared, whereas *N*-thiocarbonyl-1-methylindolin yields only resinous matter. 2-Imino-5-methyl-1-ethylbenzthiazolin is transformed by NaNO_2 in AcOH into 2-nitrosoimino-5-methyl-1-ethylbenzthiazolin, m. p. 141° (decomp.) when rapidly heated, which passes in boiling $\text{C}_6\text{H}_4\text{Me}_2$ into N_2 and 5-methyl-1-ethylbenzthiazolone, $\text{C}_6\text{H}_4\text{Me} \left\langle \begin{array}{c} \text{S} \\ \text{NEt} \end{array} \right\rangle \text{CO}$, m. p. 58°. 2-Nitrosoimino-1-ethyl- β -naphththiazolin, m. p. 158° (decomp.), 2-nitrosoimino-1:7-trimethylenebenzthiazolin, m. p. 149° (decomp.), 1-ethyl- β -naphththiazolone, b. p. 200°/5 mm., m. p. 124°, and 1:7-trimethylenebenzthiazolone, b. p. 182—185°/about 3 mm., m. p. 77°, are obtained analogously. 1-Methylbenzthiazolone is converted by successive treatment with MgEtI in EtOH and aq. NaClO_4 into 1-methyl-2-ethylbenzthiazolium perchlorate, m. p. 137°, and by Mg benzyl chloride and HClO_4 into 1-methyl-2-benzylbenzthiazolium perchlorate, m. p. 146°, transformed by *p*-dimethylaminobenzaldehyde in AcOH into the corresponding benzylidene dye. With MgMeI in C_6H_6 reaction follows a different course, 1:1'-dimethylthiocyanin iodide, m. p. 293° when rapidly heated, being produced, accompanied apparently by evolution of CH_4 ; the corresponding perchlorate, m. p. 310—311°, is described. The dye can also be prepared by treating benzthiazolone with MgMeI and subsequently with Fischer's base. 5:5'-Dimethyl-1:1'-diethylthiocyanin iodide, m. p. 290° [corresponding perchlorate, m. p. 317° (decomp.) after darkening at 290°], is analogously

obtained. 2:5-Dimethyl-1-ethylbenzthiazolium perchlorate, identified as 5:5'-dimethyl-1:1'-diethylcarbothiocyanin iodide, is isolated from the product of the incomplete action of MgMeI on 5-methyl-1-ethylbenzthiazole in Et_2O . 1:1'-Diethyl-4:5:4':5'-dibenz-2:2'-thiocyanin iodide, m. p. 310°, and 1:7:1':7'-ditrimethylenethiocyanin iodide, darkening at 300°, but not molten below 360° (corresponding perchlorate, m. p. above 360°), are prepared similarly. 5-Methoxy-1:1'-dimethylthiocyanin iodide appears to be formed in small amount by treating the methylene base from 5-methoxy-1:2-dimethylbenzthiazolium iodide with MgMeI in C_6H_6 and subsequently with 1-methylbenzthiazolone. 5-Chloro-1-methyl-2-methylenebenzthiazoline with MgMeI and subsequently with benzthiazolone affords 5-chloro-1:1'-dimethyl-2:2'-thiocyanin iodide, m. p. 288—289°. 1:1':8:10-Tetramethyl-2:2'-streptomono-vinyleneethiocyanin perchlorate is derived from 1-methyl-2-ethylbenzthiazolium iodide and Et orthoformate in AcOH.

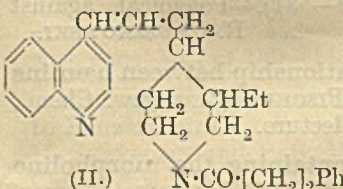
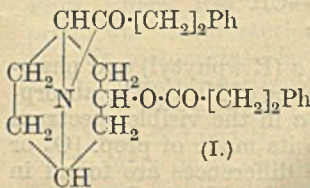
as-p-Tolylethylthiocarbamide, m. p. 99°, is prepared from *N*-ethyl-*p*-toluidine hydrochloride and aq. KCNS. *as-β*-Naphthylethylthiocarbamide, m. p. 155°, *N*-thiocarbonyl-1-methylindolin, m. p. 104°, and 2-thiocarbonyltetrahydroquinoline, m. p. 141°, are analogously derived.

Sparteine isovalerate. F. MERCIER and L. J. MERCIER (Compt. rend., 1931, 192, 1590—1593).—Sparteine isovalerate, $[\text{CH}_2\text{Pr}^\beta\text{-CO}_2\text{H}]_2, \text{C}_{15}\text{H}_{26}\text{N}_2, 2\text{H}_2\text{O}$, m. p. 45.5—46°, from isovaleric acid and sparteine in Et_2O solution, is feebly levorotatory and possesses the physiological properties of the free base.

F. R. SHAW.

Action of organic acids on tertiary amines.

III. Tropine and the cinchona alkaloids. J. VON BRAUN and K. WEISSBACH (Ber., 1931, 64, [B], 1864—1871).—Tropine is converted by β -phenylpropionic acid at 200° into β -phenylpropionyltropine, b. p. 158—160°/0.8 mm., m. p. 20°, which is very slowly transformed by β -phenylpropionic acid at 200° into β -phenylpropionmethylamide and the substance (I), b. p. 240—242°/high vac. Cinchonine at 200—210° is transformed into its β -phenylpropionate, b. p. 352—355°/0.15 mm., very extensively decomposed by further heating with the acid. Deoxydihydrocinchonine reacts readily with β -phenylpropionic acid at 200° giving lepidine and the product (II), b. p. 300—303°/0.15 mm. (dihydro-compound, b. p. 300—303°/0.15 mm.), slowly hydrolysed by 20% H_2SO_4 at 100° into β -phenylpropionic acid and the base $\text{C}_{19}\text{H}_{24}\text{N}_2$, m. p. 202—204°/0.1 mm. (chloroplatinate, decomp. 300—310° after darkening at 250°); the dihydro-base, $\text{C}_{19}\text{H}_{26}\text{N}_2$, b. p. 202—204°/0.1 mm. (chloroplatinate, decomp. 275—290°), and the hexahydro-base are described.



Deoxycinchonine behaves similarly to its dihydro-compound towards β -phenylpropionic acid giving a little lepidene and a *product*, $C_{28}H_{30}ON_2$, b. p. 318—325°/0.2 mm., which is saturated and yields a saturated base, $C_{19}H_{22}N_2$, b. p. 215—220°/0.2 mm., m. p. 174—177° after softening at about 167°, $[\alpha]_D^{25} + 99.24^\circ$ [Ac compound, m. p. 194—196° after softening at 185°; *methiodide*, decomp. 230°; Bz and *p*-nitrobenzoyl derivatives; it is reduced by Na and EtOH to the di-sec. base, $C_{19}H_{26}N_2$, b. p. 210—212°/0.2 mm. [Ac₂ derivative, b. p. 250—260°/0.3 mm. (slight decomp.)]. Cinchene is scarcely affected by β -phenylpropionic acid. Deoxyquinine reacts less completely than deoxycinchonine, giving methoxyepidine and the substance $C_{29}H_{32}O_2N_2$, b. p. about 340°/0.3 mm., which is saturated and yields a non-cryst. sec.-tert. diamine.

H. WREN.

Hydrocupreidine derivatives. I. S. GHOSH and N. R. CHATTERJEE (J. Indian Chem. Soc., 1931, 8, 257—260).—The following ethers of dihydrocupreidine were prepared by addition of the appropriate alkyl iodide to a solution of the alkaloid and the calc. amount of KOH in EtOH and either keeping for 1 month, or boiling for 3 hr. with a little Cu: *Pr* ^{β} ether, m. p. 181°, giving a blue fluorescence in dil. H_2SO_4 (*dihydrochloride*, m. p. 249° to a brown liquid); *Bu* ^{β} ether, an oil [*dihydrochloride*, m. p. 211° (decomp.)]; *isoamyl ether*, m. p. 168°, fluorescent in dil. H_2SO_4 (*dihydrochloride*, m. p. 229°); *sec. octyl ether*, an oil [*dihydrochloride*, m. p. 227° (decomp.)].

R. S. CAHN.

Synthesis of aporphine alkaloids. I. H. KONDO and S. ISHIWATA (Ber., 1931, 64, [B], 1533—1540).— β -Phenylethylamine is converted by homoisoyl chloride in C_6H_6 into *N*-*p*-methoxyphenylacetyl- β -phenylethylamine, m. p. 95°, converted by $POCl_3$ in boiling PhMe into the non-cryst. 1-*p*-anisylmethyl-3:4-*dihydroisoquinoline*, reduced by Zn and HCl in EtOH to 1-*p*-anisylmethyl-1:2:3:4-tetrahydroisoquinoline isolated as the *hydrochloride*, m. p. 215°. Benzylaldehyde, m. p. 53°, and $MeNO_2$ in presence of NaOMe in MeOH afford β -nitro- α -3-benzyl-*oxyphenylethylene*, m. p. 93°, electrolytically reduced to β -3-benzyl-*oxyphenylethylamine* (*hydrochloride*, m. p. 180°; *hydrobromide*, m. p. 183°). With 2-nitrohomoveratroyl chloride the base yields the non-cryst. amide, transformed by PCl_5 in $CHCl_3$ into 6-benzyl-*oxy-1-2'-nitro-3':4'-dimethoxybenzyl-3:4-dihydroisoquinoline*, m. p. 130° [*hydrochloride*, m. p. 210° (decomp.)]; *methiodide*, m. p. 142—143°; *sulphate*, m. p. 63°], electrolytically reduced to 6-benzyl-*oxy-1-2'-amino-3':4'-dimethoxybenzyl-3:4-dihydroisoquinoline* (*hydrochloride*, m. p. 223°). Treatment of the dehydro-base with

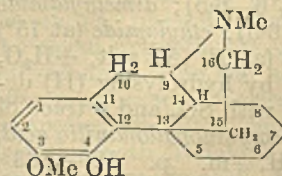
$NaNO_2$ in 2*N*- H_2SO_4 followed by Cu powder and reduction of the product with Zn and HCl yields 6-hydroxy-3:4-dimethoxynoraporphine (I), m. p. 125° (*hydrochloride*, m. p. 265°). The synthesis is preferably effected through β -nitro- α -3-carbethoxyphenylethylene, m. p. 83°, obtained from *m*-carbethoxyphenylbenzaldehyde and $MeNO_2$.

β -3-Benzyl-*oxyphenylethylamine* and *p*-methoxy-

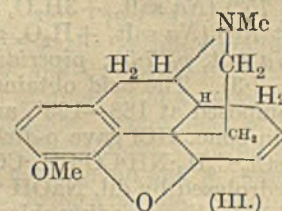
phenylacetyl chloride give *N*-*p*-methoxyphenylacetyl- β -3-benzyl-*oxyphenylethylamine*, m. p. 96°, converted by PCl_5 in $CHCl_3$ into 6-benzyl-*oxy-1-p-anisylmethyl-3:4-dihydroisoquinoline*, m. p. 97° (*hydrochloride*, m. p. 135°), catalytically reduced in 10% AcOH in presence of $PdCl_2$ to 6-hydroxy-1-*p*-anisylmethyl-1:2:3:4-tetrahydroisoquinoline (*hydrochloride*, m. p. 223°). The following compounds are incidentally described: β -nitro- α -*m*-bromophenylethylene, m. p. 59—60°, electrolytically reduced to β -*m*-bromophenylethylamine (*hydrochloride*, m. p. 225°; *hydrobromide*, m. p. 235—236°); with 2-nitrohomoveratroyl chloride the base gives *N*-2-nitrohomoveratryl- β -*m*-bromophenylethylamine, m. p. 78°, converted by $POCl_3$ in boiling PhMe into β -*m*-bromophenylethylamino- α -2-nitro-3:4-dimethoxyphenylethylene, m. p. 134—135°, which is catalytically reduced to β -*m*-bromophenylethylamino- α -2-nitro-3:4-dimethoxyphenylethane, m. p. 110—111°. 3-Bromo-4-methoxybenzaldehyde and $MeNO_2$ yield β -nitro- α -3-bromo-4-methoxyphenylethylene, m. p. 108—109°, and thence β -3-bromo-4-methoxyphenylethylamine (*hydrochloride*, m. p. 215—216°; *hydrobromide*, m. p. 213°). *N*-2-Nitrohomoveratryl- β -3-bromo-4-methoxyphenylethylamine, m. p. 104—105°, is converted by $POCl_3$ in boiling PhMe into β -[β -3-bromo-4-methoxyphenylethylamino]- α -2-nitro-3:4-dimethoxyphenylethylene, m. p. 147—148°.

H. WREN.

Deoxycodine. I. II. Dihydrodeoxycodines. L. F. SMALL and F. L. COHEN (J. Amer. Chem. Soc., 1931, 53, 2214—2226, 2227—2244).—Interaction of α -chlorocodine with $MgMeI$ or $MgEtI$ in Et_2O gives deoxycodine A (I: the identifying letters are assigned by the authors), also obtained from α -chlorocodine (*hydrogen d-tartrate*, $[\alpha]_D^{25} - 219.3^\circ$ in H_2O) by reduction with Zn and EtOH (cf. A., 1920, i, 757), and a little iodocodine [*hydrochloride* (+2 or 2.5 H_2O), m. p. 190—191°; *methiodide*, m. p. 187—188°]; iodocodine, but not β -chlorocodine (*H d-tartrate*, $[\alpha]_D^{25} + 8.3^\circ$ in H_2O), also reacts with $MgMeI$ to form (I). The “dihydrodeoxycodine” obtained by Freund (A., 1920, i, 757) by electrolytic reduction of α - or β -chlorocodine absorbs 4H on catalytic reduction to β -tetrahydrodeoxycodine, and is therefore named deoxycodine B (II) (+ $\frac{1}{2}H_2O$), m. p. 119—120° (*hydrochloride*; *hydriodide*, m. p. 245°). The “dihydrodeoxycodine” prepared by interaction of chlorodihydrocodine with NaOMe in MeOH at 140° (G.P. 414,598) is similarly proved to be deoxycodine C (III) (+ H_2O), m. p. 105—106° [*hydriodide* (+ H_2O), m. p. 160—165° (sinters at 135—140°); *hydrochloride* (+ H_2O), m. p. 114°; *methiodide*, m. p. 236—240°]; it is insol. in aq. alkalis, does not form a Me ether or an Ac derivative, and is generally without phenolic properties. The absence of geometrical isomerism at C_{14}



(I.) and (II.)



(III.)

requires the existence of two “phenolic” deoxycodines according as the double linkings are at C_5

and C₇ or C₆ and C₈ and four "non-phenolic" forms of which (III) represents one.

II. "α-Tetrahydrodeoxycodeine" (A., 1920, i, 757) obtained by reduction of α-chlorocodide or deoxycodeines A or B with Na and 95% EtOH or electrolytically, is actually a *dihydrodeoxycodeine* (A), b. p. 160—170°/1 mm., m. p. 134—136° (+½H₂O), [α]_D²⁰ -27.1°, -26.7° in EtOH (*methiodide*, m. p. 250—251°). It is reduced by H₂ and PtO₂ in MeOH to "β"-tetrahydrodeoxycodeine. The following additional *dihydrodeoxycodeines* are described: B (+½H₂O), m. p. 128—131°, [α]_D²⁰ -106.9° [*hydrochloride*, m. p. 154—156° (decomp.); *hydriodide*, m. p. 255—256° (sinters 244—246°); *methiodide*, m. p. about 175°], produced by electrolytic reduction of deoxycodeine C; C (+½H₂O), m. p. 109—111°, [α]_D²⁰ -61.6° in 96% EtOH [*hydrochloride*, m. p. 241—242° (sinters 157—163°); *hydriodide*, m. p. 242—243°; *methiodide*, m. p. 245—246°], accompanies A in the product of electrolytic reduction of chlorodihydrocodide (*loc. cit.*), and has previously been confused with deoxycodeine B: D, m. p. 106—107°, [α]_D²⁰ -82.5° [*H tartrate*, m. p. 123—125°; *hydriodide*, m. p. 250—251° (decomp.); *methiodide*, m. p. 256°] is obtained by reduction of β-chlorocodide with H₂ and Pd-BaSO₄ (A., 1921, i, 124), and is the only non-phenolic dihydrodeoxycodeine yet known; E, m. p. 139—140°, is prepared by electrolytic reduction of bromocodine (A., 1924, i, 122). All of these dihydro-derivatives pass on complete reduction into β-tetrahydrodeoxycodeine, which is therefore the only known tetrahydro-derivative; consequently it is extremely unlikely that isomerism can occur at C₁₄, and five isomeric dihydrodeoxycodeines only, all of which are now known, can exist. Measurement of [α] is more trustworthy as a means of comparison in this series than the method of mixed m. p.

H. A. PIGGOTT.

Derivatives of *p*-arsanilic acid. II. *p*-Arsonomalonanilic acid and related compounds. G. T. MORGAN and E. WALTON (J.C.S., 1931, 1743—1748; cf. this vol., 636).—Compounds of the type (I) have been prepared. In many cases the Na salts have trypanocidal action in mice. The *p_H* quoted below refer to aq. solutions. (I)

p-H₂O₃As·C₆H₄·NH·CO·CH₂·CO·NRR' [·CO₂Et (II)] *Et p*-arsonomalonanilate (II), *cryst.* (Na salt, +H₂O, *p_H* 6), could not be obtained from CH₂(CO₂Et)₂ and *p*-arsanilic acid, but was prepared from carbethoxyacetyl chloride (improved prep.), *p*-arsanilic acid, and NaOH. This yielded the following *cryst.* derivatives of type (I) when condensed with the appropriate amine under the conditions stated: *methylamide* (in the cold) (Na salt, +H₂O, *p_H* 6—6.5); *amide* (0.880 aq. NH₃ at 75°) (Na salt, +3H₂O, *p_H* 6—6.5); *dimethylamide* (at 75°) (Na salt, +H₂O, *p_H* 6.5); *ethylamide* (at 75°) (Na salt, *p_H* 7.5); *piperidide* (at 0°) (Na salt, +H₂O, *p_H* 7.3). The *acid* obtained by hydrolysing (II) decomposed at 188—193°, and with SO₂ and a trace of I in conc. HCl gave *p*-dichloroarsinomalonanilic acid, AsCl₂·C₆H₄·NH·CO·CH₂·CO₂H, m. p. 128—133°, hydrolysed by dil. NaOH to *p*-arsinomalonanilic acid. This or the preceding chloride was converted by SOCl₂ at 20° into the trichloride, which with NH₂Ph at 0°, and subsequent hydrolysis by dil. NaOH gave *p*-

arsinomalonanilide, oxidised by H₂O₂ to *malonanilide-p*-arsinic acid (I; R=H: R'=Ph) (Na salt, +2.5H₂O, *p_H* 8.5). Malonyl chloride (improved prep.), and *p*-arsanilic acid yielded *malonanilide-pp'*-diarsinic acid (*p*-H₂O₃As·C₆H₄·NH·CO)₂CH₂, darkening on drying (Na salt).

Malonanilino-n-propylamide-p-arsinic acid, *cryst.* (Na salt, *p_H* 6.5) was prepared from (II) and cold aq. NH₂Pr^a. Succinanilino-*p*-arsinic acid and cold alcoholic NH₂Pr^a gave *succinanilino-n-propylamide-p*-arsinic acid, *cryst.* (Na salt, Na₂ salt, *p_H* 10).

R. S. CAHN.

Mercury derivatives of cyclohexyl- and benzylphenols. J. W. HAUGHT, C. E. GARLAND, and H. A. H. PRAY (J. Amer. Chem. Soc., 1931, 53, 2697—2700).—The following derivatives of *o*- and *p*-benzyl- and *o*- and *p*-cyclohexyl-phenols are prepared by the usual methods: *diacetoxymercuro-o*-benzylphenol, *decomp.* 115—125°, *diacetoxymercuro-*, *decomp.* 110—115°, *dichloromercuro-*, *decomp.* 128—134°, and *anhydromercurohydroxymercuro-*, *decomp.* 245—250°, *p*-benzylphenols; *diacetoxymercuro-*, *decomp.* 135—140°, *dichloro-*, *decomp.* 155—160°, and *dihydroxy-*, *decomp.* 230—235°, *mercurio-o*-cyclohexylphenols; *diacetoxymercuro-*, *decomp.* 105—110°, *dichloro-*, *decomp.* 225—230°, and *dihydroxy-*, *decomp.* 255—260°, *mercurio-p*-cyclohexylphenols.

H. BURTON.

Effect of heat on the chemical composition of proteins. I. Elementary composition and diamino-acids. K. YAMAFUJI (Bul. Sci. Fak. Terkultura Kjusu, 1930, 4, 101—107).—When muscle proteins are heated at 140° in sealed tubes at varying *p_H* the reaction tends to approach neutrality. The NH₃ and H₂S evolved increase with a higher *p_H*. Cystine, arginine, lysine, and NH₂-N generally decrease slightly, although there is a slight increase of arginine at *p_H* 3.4.

P. G. MARSHALL.

Sources of error in organic elementary analysis. VIII. Ignition of the combustion tube and origin of the water occurring thereby. J. LINDNER (Ber., 1931, 64, [B], 1560—1567; cf. A., 1930, 940).—Pure CuO (granular or wire-form), finely-divided Ag, and PbCrO₄ readily yield their H₂O when ignited in air. Less ready evolution of H₂O is observed from the asbestos filling. Hard glass tubes in the initial stages of heating yield H₂O in noticeable amount, which gradually diminishes to a small quantity depending on the temp. of ignition. Quartz behaves similarly at temps. usual in combustion analysis, but yields markedly smaller amounts than those obtained with hard glass. Asbestos, air-dried or transiently ignited, gives much larger amounts of H₂O, but complete removal could not be effected. The H₂O slowly attracted by thoroughly ignited asbestos can be reduced to its former degree only by protracted ignition.

H. WREN.

Detection of carbon disulphide. S. L. MALOWAN (Z. anal. Chem., 1931, 84, 406—407).—A note on previous work (this vol., 638).

H. F. GILLBE.

Conductivity method for the analysis of binary mixtures of the volatile fatty acids. E. I. FULMER, E. E. MOORE, and R. L. FOSTER (J. Physical Chem., 1931, 35, 1227—1231; cf. J. Bact., 1930, 19,

5).—For binary mixtures of formic, acetic, propionic, and *n*-butyric acids the antilog. of $\kappa \times 10^3$ is a linear function of % composition; this can be used as a basis for analysis.
L. S. THEOBALD.

Colour reaction of ephedrine. J. SIVADJIAN (J. Pharm. Chim., 1931, [viii], 14, 61—63; cf. A., 1930, 1460).—A reply to Hartung and others (this vol., 724). The peculiar reddish-violet colour is specific for compounds of the ephedrine type. Ephedrine and ψ -ephedrine may be distinguished from each other.
R. K. CALLOW.

Determination of citrates, salicylates, and benzoates by the mercurimetric method. A. IONESCU-MATIU and (MME.) POPESCO (J. Pharm. Chim., 1931, [viii], 14, 54—61).—The citrate (Na or Mg) is treated with HgSO_4 solution, oxidised by KMnO_4 , and the ppt. of complex Hg salt is dissolved in HNO_3 - H_2SO_4 and Hg determined by adding Na nitroprusside and titrating with NaCl (cf. A., 1927, 687; 1928, 1230). Salicylates and benzoates give ppts. of the Hg salts directly and Hg is determined in the same way. Aspirin may be determined after hydrolysis.
R. K. CALLOW.

Determination of sulphosalicylic acid. E. PRSCHEVALSKI and V. PESCHKOVA (Trans. Inst. Pure Chem. Reag., 1931, 10, 8).—The free H_2SO_4 is determined by BaCl_2 in the usual manner, and the total SO_4 after oxidising with KMnO_4 .
E. S. HEDGES.

Colorimetric determination of tryptophan. T. RUEMELE (Z. anal. Chem., 1931, 84, 81—89).—A crit. study of the method of Tillmans and Alt (A., 1926, 189). Accurate results are obtained by adherence to standardised conditions. Not more than 2 drops of a 2% CH_2O solution should be used and 45 min. should elapse after this has been added before comparison of the colours is made.
A. R. POWELL.

Potassium ferrocyanide as a microchemical reagent for the identification of strychnine. V. D. GNESIN (Farm. Zhur., 1930, 293—295).—Characteristic crystals are described.
CHEMICAL ABSTRACTS.

Anhydrous distillation method for the determination of certain metals in organic compounds. I. Mercury. E. P. FENIMORE and E. C. WAGNER.—See this vol., 1025.

Biochemistry.

Determination of respiratory capacity by micro-determination of iron in the blood. J. M. CLAVERA (Anal. Fis. Quím., 1931, 29, 392—398).—The method of Fontès and Thivolle for the determination of Fe in blood may be used for determining the respiratory capacity, which is equal to 40 times the Fe content (in mg. per c.c.). The error is less than 2%.
H. F. GILLBE.

Deformability and wetting properties of leucocytes and erythrocytes. S. MUDD and E. B. H. MUDD (J. Gen. Physiol., 1931, 14, 733—751).—A microscopical study of the behaviour of blood-cells at an oil-water interface. The surface of the leucocyte is hydrophilic, that of the erythrocyte hydrophobic.
A. COHEN.

Staining of reticulocytes by brilliant-cresyl-blue. Influence of solutions of substances. C. W. HEATH and G. A. DALAND (Arch. Int. Med., 1931, 48, 133—145).—The staining of reticulocytes (rabbit and man) by brilliant-cresyl-blue is inhibited by liver extracts, NH_2 -acids, and a variety of org. and inorg. substances to an extent which varies with their concentrations. The inhibitory influence is not related to the efficacy of the liver extracts in anæmia, and is decreased by long contact between blood-cells and inhibitors. The effects are probably due to changed permeability of the cells under the influence of the inhibitors.
A. COHEN.

Determination of hæmoglobin in blood. O. ORIAS (Compt. rend. Soc. Biol., 1930, 105, 305—306; Chem. Zentr., 1931, i, 2240).—A comparison of methods.
A. A. ELDRIDGE.

Simplification of the Osgood-Haskins hæmoglobin method. E. E. OSGOOD and H. D. HASKINS

(J. Lab. Clin. Med., 1931, 16, 482—486).—A solution of acid hæmatin is used as a standard.
CHEMICAL ABSTRACTS.

Crystalline forms of hæmin, and conditions of their preparation. K. LINDENFELD (Rocz. Chem., 1931, 11, 532—542).—Hæmin is obtained in hexagonal plates on adding a CHCl_3 -pyridine solution to 80% AcOH containing NH_4Cl or NaCl at 60°; similar polymorphs of the ordinary Teichmann form are obtained from bromo-, iodo-, and thiocyno-hæmin in a similar way. The polymorphs are unstable, and are rapidly converted into Teichmann crystals at 100°.
R. TRUSZKOWSKI.

Physical properties of normal blood-sera of man and some mammals, and of serum-proteins isolated by acetone. C. ACHARD, A. BOUTARIC, and M. DOLADILHE (Compt. rend., 1931, 193, 271—276).—Colloidal suspensions of the proteins in an equal vol. of H_2O have almost the same optical density and viscosity as whole serum; addition of salts and the extracts increases the optical density and decreases the no. of particles. The no. of particles per g. of dried protein is sensibly the same in the sera from man, horse, and ox.
C. C. N. VASS.

Fractionation of serum-proteins and absorption spectra of the fractions. J. GRÓH and E. FALTIN (Z. physiol. Chem., 1931, 199, 13—24).—The mean extinction coeffs. for the serum-globulin and -albumin from the horse and ox agree, but the differences observed between samples from a particular species are often considerable. Fractional precipitation with $(\text{NH}_4)_2\text{SO}_4$ yields fractions showing a steady decrease in coeff., the tryptophan and to some extent the tyrosine contents showing a parallel diminution. None of the fractions is homogeneous.
J. H. BIRKINSHAW.

Protein coagulation and its reversal. Serum-albumin. M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1931, 14, 725—732).—The prep. of sol. cryst. serum-albumin from a denatured product obtained by the action of acid COMe_2 on the native protein is described. It appears that the more sol. is the denatured protein, the more easily is denaturation reversed. A. COHEN.

Temperature stability and denaturation of serum-albumin. K. O. PEDERSEN (Nature, 1931, 128, 150—151; cf. A., 1930, 1197).—Heat treatment of serum-albumin within the p_{11} -stability region forms aggregation products which vary in size and no. according to p_{11} , temp., time of heating, and the nature of the salts in solution. Removal of these products leaves an unchanged portion of serum-albumin. Heat treatment of amandin forms some smaller particles with a large portion unchanged. Outside the p_{11} -stability region ($p_{11} < 3.8$) serum-albumin is split up into smaller particles by heating, and mobilities expected for denatured serum-albumin are obtained. Serum-albumin solutions at p_{11} 3.5 are changed by ultra-violet light. L. S. THEOBALD.

Osmotic pressure of colloids. XVI. Daily fluctuation and arterio-venous difference of the osmotic pressure of the colloids of blood-serum. E. KYLIN (Arch. exp. Path. Pharm., 1931, 161, 91—103).—The average osmotic pressure exerted by the colloids of arterial blood during a fasting period is 343 mm. H_2O and that of venous blood 337 mm. After food the arterial colloidal osmotic pressure rises to 355—359 mm., whilst the venous osmotic pressure rises after food taken with little H_2O and falls when much H_2O is taken. P. G. MARSHALL.

Use of interferometer for serum-protein and protein fraction determinations. W. J. DIECKMANN (J. Lab. Clin. Med., 1931, 16, 513—519).—Methods are described. CHEMICAL ABSTRACTS.

Determination of blood-proteins by a direct micro-Kjeldahl method. R. S. HUBBARD (J. Lab. Clin. Med., 1931, 16, 500—503).—The digested material is nesslerised directly; precipitation of the reagent is prevented by the use of Na K tartrate. CHEMICAL ABSTRACTS.

Occurrence of proteolytic enzymes in serum. Criticism of Yokota's work. H. J. FUCHS and M. VON FALKENHAUSEN (Biochem. Z., 1931, 237, 87—89).—The results of Yokota (this vol., 641) are shown to be erroneous, due to an imperfect removal of proteolytic enzymes from the fibrin. F. O. HOWITT.

Chemical nature of the depressor substance of blood. K. ZIFP (Arch. exp. Path. Pharm., 1931, 160, 579—598; cf. A., 1930, 811).—Defibrinated blood is freed from protein by precipitation with trichloroacetic acid, and the depressor principle is isolated from the filtrate by successive precipitation of its Hg, Pb, and Ba salts. It is identical with adenylic acid. A. COHEN.

Spectrophotometric determination of allantoin in the blood of mammals and in the seed of plants. R. FOSSE, A. BRUNEL, and P. E. THOMAS (Compt. rend., 1931, 193, 7—11; cf. this vol., 976).—

The concentration of allantoin in the sera of the ox, horse, sheep, and pig varies from 10.7 to 26.9 mg. per litre. In 40 out of 50 plants the allantoin content of the seed varied from 0.02 to 0.41 g. per kg., but reached 1.78 g. per kg. in *Phaseolus mungo* and 3.3 g. per kg. in *Dolichos sinensis*. C. C. N. VASS.

Acetylcholine in ox-blood. II. C. BISCHOFF, W. GRAB, and J. KAPFFHAMMER (Z. physiol. Chem., 1931, 199, 135—168; cf. A., 1930, 1464).—In 29 out of 32 animals examined the blood was shown by biological test to contain acetylcholine. The essential conditions for successful testing are (a) the filtrate from the blood-EtOH mixture after evaporation in vac. must not be alkaline, (b) after deproteinisation the solution must not be kept long and must be maintained at a low temp. Of the three protein precipitants trichloroacetic acid, sulphosalicylic acid, and $\text{H}_3\text{P}_2\text{O}_7$, the last is preferred, since it gives a more suitable p_{11} . J. H. BIRKINSHAW.

Blood-ammonia. L. STANOJEVITCH (Bull. Soc. Chim. biol., 1931, 13, 579—587).—Blood drawn directly into the reagents contains 0.026 mg. $\text{NH}_3\text{-N}$ per 100 c.c. $\text{NH}_3\text{-N}$ increases during muscular work but falls to its initial val. after 2 hr. rest. On autolysis *in vitro* the rate of formation of $\text{NH}_3\text{-N}$ varies with temp.; the precursor is thought to consist of 2 substances, one of which decomposes at room temp. in 24 hr., whilst the other requires a higher temp. and has a variable time factor. C. C. N. VASS.

Effect of muscle extracts on blood-sugar in the rabbit. F. AMANTEA (Arch. Farm. sperim., 1931, 52, 189—196).—Injection of extract of ox-muscle has in general a slight hypothermic action on guinea-pigs. The injection of muscle extracts into rabbits has a variable effect on the temp.; homologous extracts lower the blood-sugar, whilst extracts from other animals have little effect. R. K. CALLOW.

Determination of cholesterol in blood-plasma and -serum. J. C. FORBES (J. Lab. Clin. Med., 1931, 16, 520—521).—The cholesterol is extracted without heat in presence of "doucil," a water softener. CHEMICAL ABSTRACTS.

Influence of nerve excitation on the cholesterol and fat content of blood flowing from the extremities. J. SCHEFFER and G. BĀRDOŠ (Biochem. Z., 1931, 236, 493—499).—Excitation of the ischiadic nerve in the dog increases the cholesterol content of the blood in the femoral or saphenous vein and, to a smaller extent, in that of the femoral artery. Simultaneous excitation of the cruralis nerve inhibits this increase. The total fat does not rise parallel with the cholesterol level so that the quotient total fat/cholesterol decreases during stimulation, which brings about liberation of cholesterol from subcutaneous and bone-marrow tissue. F. O. HOWITT.

Dichlorofluorescein as an adsorption indicator for the determination of blood-chloride. A. E. OSTERBERG (Proc. Staff Meetings Mayo Clinic, 1930, 5, 300).—Plasma or serum (2 c.c.), COMe_2 (7 c.c.), and H_2O (to 10 c.c.) are centrifuged; 5 c.c. of the solution is treated with the indicator (Kolthoff, Lauer, and Sunde), and titrated with $N/3456\text{-AgNO}_3$. CHEMICAL ABSTRACTS.

Blood-phosphorus in man. M. JAVILLIER and M. FABRYKANT (Bull. Soc. Chim. biol., 1931, 13, 687—696).—The mean vals. in mg. per litre for venous blood collected at rest while fasting were, total P 358.4, inorg. P 36.6, lipin-P 115.7, nucleoprotein-P 26.5. In disease total P was 183—1055, lipin-P 53—268, and inorg. P 23—60. C. C. N. VASS.

Titrimetric determination of inorganic phosphorus in blood-serum. L. CANNARO (Biochem. Z., 1931, 237, 136—138).—From 1 c.c. (not deproteinised) Ca is removed by $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and phosphate precipitated as MgNH_4PO_4 in presence of Na citrate. The ppt. is converted into NH_4 phosphomolybdate, which is dissolved in 3 c.c. of 0.02N-NaOH and titrated with 0.02N-HCl. Vals. for some pathological sera are given. F. O. HOWITT.

Possible transition of inorganic to organised matter. M. COPISAROW (Kolloid-Z., 1931, 56, 67—71).—A discussion of published work on inorg. structures resembling organised matter in form. E. S. HEDGES.

Paracrystalline organisms. F. RINNE (Kolloid-Z., 1931, 56, 71—77).—Sepia spermatozoa are gel-like, paracryst., living organisms, which constitute a transition between artificial liquid crystals and organised matter. E. S. HEDGES.

Cholesterol content of shrimp waste. R. F. ABERNETHY and F. C. VILBRANDT (J. Amer. Chem. Soc., 1931, 53, 2796—2797).—Shrimp oil (this vol., 272) contains 19.08% of cholesterol. H. BURTON.

Cholesterol and protoplasm structure. IX. Summary of I—VIII. G. PFEIFFER (Biochem. Z., 1931, 236, 457—463).—In a survey of the amounts of cholesterol and its derivatives in various tissues (cf. A., 1929, 90; 1930, 945, 1204; this vol., 507, 644, 975) the functions of these compounds are discussed with reference to interfacial and protective colloid action, O_2 adsorption, H_2 -acceptor action, synthetic processes, and their bearing on protoplasmic structure and immuno-behaviour. F. O. HOWITT.

Modification of the Kumagawa-Suto method for the determination of the lipin content of organs. E. LEBORDE and ENVER (Bull. Soc. Chim. biol., 1931, 13, 712—713).—The operation is carried out in one stage, avoiding the evaporation to dryness of the EtOH-extract prior to hydrolysis with EtOH-KOH. C. C. N. VASS.

Colour reactions of the nucleic acids. P. THOMAS (Z. physiol. Chem., 1931, 199, 10—12).—A tryptophan reagent (0.1% in 50% aq. HCl) is recommended for the detection of thymus-nucleic acids since it gives characteristic colour reactions with these and with the monosaccharides. J. H. BIRKINSHAW.

Camel flesh. G. A. MAKARYTSHEV (Z. Fleisch-Milchhyg., 1931, 41, 181—182, 207—212; Chem. Zentr., 1931, i, 2406).—The flesh contained H_2O 75.51—79.90, protein 18.68—21.37, fat 0.80—2.52, ash 0.51—0.86%, and gave a positive reaction for glycogen. A. A. ELDRIDGE.

Comparative copper determinations in hen embryos. A. LOESCHKE (Z. physiol. Chem., 1931,

199, 125—128).—The Cu content of the liver of the embryo is only about $\frac{1}{2}$ to $\frac{1}{3}$ that of the whole egg but the percentage is 12—20 times as great. J. H. BIRKINSHAW.

Sulphur content of some South African wools. F. N. BONSMMA (J. Text. Inst., 1931, 22, T305—313).—There is a considerable variation in the S content of wools from different sheep fed on the same diet, but although the S content is largely an inheritable characteristic, it may be altered by, e.g., limitation of the cystine supply in the natural diet. As long as the demand for cystine for the production of wool by the animal is satisfied by its food, the wool maintains the normal S content, but when the supply is inadequate a reduction in S content follows. B. P. RIDGE.

Biochemistry of sulphur. X. Cystine content of meat and fish. M. X. SULLIVAN and W. C. HESS (U.S. Pub. Health Rep. Suppl., 1931, no. 94, 13 pp.).—Cystine was determined in meat and fish (haddock, halibut, and salmon) using fresh or COMe_2 - Et_2O dehydrated defatted material and also hydrolysed samples. The colorimetric method of Sullivan (A., 1930, 488) gives results comparable with those by the iodometric method of Okuda (A., 1929, 730; 1191), but lower than those by the colorimetric method of Folin (*ibid.*, 1093). Higher vals. (0.26% for wet material) are found for fish than for meat (0.19%) which, however, has a slightly higher glutathione content. F. O. HOWITT.

Separation of iodine from thyroid gland pulp by ultra-violet irradiation and from iodised protein by irradiation with X-rays. F. LIEBEN and H. KRAUS (Biochem. Z., 1931, 236, 182—186).—I is liberated from suspensions of human thyroid gland pulp under the action of ultra-violet light (0.5—2.7% of the total I being set free) and from iodised caseinogen and thyroxine under the action of X-rays (less than 1% of the total I set free). P. W. CLUTTERBUCK.

Detection and determination of glucosamine. F. ZUCKERKANDL and L. MESSINER-KLEBERMASS (Biochem. Z., 1931, 236, 19—28).—A method for the determination of 1—5 mg. of glucosamine depends on the red colour produced when glucosamine monoacetate is treated with alkali and Ehrlich's reagent, the limits of error being not greater than 6%. Ovumucoid contains only half of its carbohydrate as glucosamine, the remainder consisting probably of mannose (up to 10%). P. W. CLUTTERBUCK.

Haliotis-indigo, the blue pigment of the shells of *Haliotis californiensis*. N. SCHULZ and M. BECKER (Biochem. Z., 1931, 236, 99—106).—The separation and purification of the pigment are described and preliminary tests place it in the indigo group. P. W. CLUTTERBUCK.

Histological and chemical examination of the gills of *Anodonta cygnea*, Lin. M. DUBUIS-SON and J. VAN HEUVERSWYN (Arch. Biol., 1931, 41, 37—74).—Certain concretions found in the gills of *A. cygnea* contain Fe, Mn, and CaCO_3 . Their formation and function in relation to the yellowish-brown pigment of the tissue are discussed. A. G. POLLARD.

Elimination of choline from lecithin and the choline content of cerebrospinal fluid. I. H. PAGE and E. SCHMIDT (*Z. physiol. Chem.*, 1931, 199, 1—9).—Lecithin is not hydrolysed by boiling in EtOH or when kept for a longer period at 37°. It is only slowly attacked in aq. emulsion at p_H 5.6—8.2. Fresh serum or brain extract has no action on it. The choline content of cerebrospinal fluids was 0.1—1.0 mg. per litre except in a case of Lues univ. ac., when 1.3 mg. was attained. J. H. BIRKINSHAW.

Determination of pancreatic enzymes in duodenal contents. E. HOLLANDER (*J. Lab. Clin. Med.*, 1931, 16, 460—465).—The steapsin and trypsin are determined by measuring the time (normally 5 min.) necessary for the neutralisation of 1 c.c. of 0.1N-NaOH by the fatty or NH_3 -acids formed by the action of 1 c.c. of duodenal contents on olive oil or gelatin, respectively. The amylopsin activity is determined by determining the amount (normally 1.9 c.c. or less) of substrate required to reduce 5 c.c. of Benedict's quant. sugar reagent after the action of 1 c.c. of duodenal contents on sol. starch. A decrease in the activity of the enzymes is usually associated with disease of the gall bladder.

CHEMICAL ABSTRACTS.

Proteolytic enzymes in intestinal and pancreatic juices. E. LE BRETON, I. MOCOROA, and E. STULZ (*Compt. rend.*, 1931, 193, 79—81).—Only abnormal pancreatic secretions contain erepsin or kinase or both, whereas erepsin and enterokinase are always present in the intestinal juice.

C. C. N. VASS.

Characterisation of semen in legal investigations. R. MARCILLE (*Ann. Chim. anal.*, 1931, [ii], 13, 193—203).—Semen may be detected microchemically by Florence's reagent (1.8 g. I; 2.4 g. KI; 45 c.c. H_2O), which gives characteristic brown, prismatic crystals with choline hydrochloride at a limiting dilution of 1 : 70,000 at room temp. or 1 : 400,000 at 12°. The stain is extracted with water, protein precipitated by EtOH, the filtrate evaporated, and the limiting dilution of the aq. extract which gives a positive reaction is determined. Dried semen gives a positive reaction in a dilution of 1 : 1000 or 1 : 4000, and is thus readily distinguished from other materials containing choline in comparatively small amount. Putrefaction interferes with the test. Bogarius' reagent is not sufficiently sensitive. The microscopical detection of spermatozoa is described.

R. K. CALLOW.

Absorption spectrum of bilirubin in different solvents. P. MÜLLER and L. ENGEL (*Z. physiol. Chem.*, 1931, 199, 117—124).—The absorption of bilirubin in (so-called) alcoholic solution differs from that exhibited in $CHCl_3$ solution (cf. this vol., 644).

J. H. BIRKINSHAW.

Detection and determination of indican in urine. FISCHER and HUPPMANN (*Pharm. Ztg.* 1931, 76, 810—812).—The urine is treated with 10% of basic Pb acetate solution and 11 c.c. of the filtrate are boiled with 10 c.c. of a saturated solution of acenaphthenequinone in AcOH and 2 c.c. of fuming HCl. The red 1-acenaphthene-2'-indoleindigo formed is extracted with hexahydrotoluene and determined

colorimetrically. The prep. of the dye from indoxyl and acenaphthenequinone is described.

R. K. CALLOW.

Photometric determination of acetone in urine. C. URBACH (*Biochem. Z.*, 1931, 236, 164—173).—The method is described and its advantages over other methods are discussed.

P. W. CLUTTERBUCK.

Micro-determination of the organic acids of urine by ether extraction. M. LAFARGUE (*Bull. Soc. Chim. biol.*, 1931, 13, 703—709).—2 c.c. of protein-free urine saturated with $(NH_4)_2SO_4$ and acidified with conc. H_2SO_4 are continuously extracted with EtOH-free Et_2O for 1½ hr., the extract is diluted with H_2O and titrated with 0.02N-NaOH, using cresol-red as indicator.

C. C. N. VASS.

Phenol test for urinary albumin. W. B. CLAPP and B. COHEN (*New England J. Med.*, 1930, 203, 1237—1238).—A ring test, employing saturated aq. PhOH containing glycerol (d 1.045), detects albumin in a concentration of 0.004%.

CHEMICAL ABSTRACTS.

Excretion of uric acid. J. NEEDHAM (*Nature*, 1931, 128, 152—153).—Facts concerning the development of the chick embryo are quoted in support of the view that a circulation of base as well as of H_2O takes place in the excretion of uric acid (cf. this vol., 976).

L. S. THEOBALD.

p_H Values in routine urine analysis. O. B. PRATT and H. O. SWARTOUT (*J. Lab. Clin. Med.*, 1931, 16, 471—475).—Misleading vals. are discussed.

CHEMICAL ABSTRACTS.

Distribution of amino-acids in blood in anæmia; criticism of the new Folin method of determination of amino-acids in the blood. A. SIMON (*Arch. exp. Path. Pharm.*, 1931, 160, 599—609).—An increase in the ratio of NH_2-N in blood-corpuses to that in the plasma is found in dogs suffering from anæmia and after splenectomy. The ratio of the concentration of diffusible NH_2-N in corpuses to that in the plasma is greater in canine than in human anæmia. Folin's method for the determination of NH_2 -acid (A., 1930, 630, 1305) is criticised, since it gives low results due to absorption of NH_2 -acids by the contracted cells.

B. LEVIN.

Catalase action and glutathione content of red blood-corpuses in anæmia. E. BACH and E. BACH (*Biochem. Z.*, 1931, 236, 174—181).—The catalase content and the reducing power in the cold (caused chiefly by the glutathione content) in various types of anæmia are investigated. In true pernicious anæmia a parallel increase takes place in both catalase and glutathione contents of the cells. In secondary anæmia the catalase and glutathione contents are not increased. In acute loss of blood, the relative glutathione content of human red cells is increased, and the catalase content is also increased in the cells of lower animals.

P. W. CLUTTERBUCK.

Effect of adrenaline-free suprarenal extract on the specific dynamic action of foodstuffs. A. E. KOEHLER (*Science*, 1931, 74, 78).—In cases of asthenia, continued administration of the extract results in a diminution of its beneficent effect and a

diminution or disappearance of the sp. dynamic action of foodstuffs.

L. S. THEOBALD.

Cancer research and the scientific method. E. McDONALD (Science, 1931, 74, 55—60).—An address.

L. S. THEOBALD.

Hormones in cancer. F. BISCHOFF, L. C. MAXWELL, and H. J. ULLMANN (Science, 1931, 74, 16).—With one possible exception, none of the well-established hormones or glandular products affects the rate of growth (or final mortality) of transplantable rat sarcoma or carcinomata.

L. S. THEOBALD.

Respiration of Jensen sarcoma and mouse carcinoma. B. KISCH (Biochem. Z., 1931, 237, 226—243).—The respiration-increasing action of certain substances [salts with bivalent and trivalent elements, "omega" (A., 1930, 949, 1036), glycine, and alanine] is greater with normal than with tumour tissue from the same rat. The respiration-inhibiting action of high concentrations of Al salts, borates, and NH_2 -acids occurs both with normal and tumour tissue. Hence it appears that tumour tissue has reached the max. rate of respiration for the experimental conditions.

F. O. HOWITT.

Mitogenetic spectrum analysis. I. N. KANNEGIESSER. II. Carcinoma and cornea epithelium. L. GURWITSCH (Biochem. Z., 1931, 236, 415—424, 425—431).—I. Blood glycolysis and three different types of oxidation were examined by the method of spectrum analysis of mitogenetic radiation. Typical spectra are obtained, that of glycolysis possessing a range of 190—200 and 212—220 $\text{m}\mu$ and that of oxidation 223—234 $\text{m}\mu$.

II. The duplex nature of mitogenetic radiation of carcinoma is due to glycolytic and proteolytic action. That of the epithelium of the cornea of rabbit is normally glycolytic, but is proteolytic during inanition.

F. O. HOWITT.

Carcinogenic potency of mineral oils. C. C. TWORT and J. M. TWORT (J. Ind. Hygiene, 1931, 13, 204—226).—A revised method of expressing carcinogenic potency is described. Refined Scottish shale lubricating oil was found to be more potent than any refined petroleum-well oil. The potency of crude shale oil did not decrease until the retorting temperature fell below 400° . The potency of refined petroleum lubricating oil may vary as much as 30 times in different samples. Potency is decreased by addition of lanolin or sperm oil; saponifiable oils showed no activity. In general the more saturated mineral oils are less potent. The fluorescence of oils may be related to their potency. Chrysene has definite carcinogenic activity.

R. K. CALLOW.

Production of dental caries in rats fed on an adequate diet. C. A. HOPPERS, P. A. WEBBER, and T. L. CANNIFF (Science, 1931, 74, 77—78).—Dental caries in rats is not due primarily to a deficiency of vitamin or mineral salts, but is probably caused by bacterial decomp. of foodstuffs lodged in the teeth.

L. S. THEOBALD.

Partition of potassium in healthy or pathological muscle. A. LEULIER, B. POMMÉ, and R. DELAYE (Compt. rend., 1931, 193, 202—204).—There is a diminution of K in the musculature affected by

certain amyotrophic conditions arising from cerebral or spinal lesions.

C. C. N. VASS.

Acid-soluble phosphorus of blood in normal individuals and diabetics. R. MEIER and E. THOENES (Arch. exp. Path. Pharm., 1931, 161, 119—140).—The mean total acid-sol. P of blood in normal man is 55 mg. per 100 c.c., made up by inorg. P 8.5, easily hydrolysable esters 12.0, and esters hydrolysed with difficulty 34.5 mg. 0.1N-HCl will hydrolyse 13% in 3 hr. The lowering of total acid-sol. P in diabetes, which is most noticeable in the state of coma (to 35.8 mg. per 100 c.c.), occurs largely at the expense of the esters which are hydrolysed only with difficulty, the changes which these esters undergo being independent of the H_2O content of the serum. Insulin treatment brings about a lowering of inorg. P, increases the fraction of esters hydrolysed with difficulty, and produces a temporary decrease in the easily hydrolysable fraction. Phosphoric esters occur entirely in the corpuscles.

P. G. MARSHALL.

Initial hypoglycæmia after extirpation of the pancreas. H. HORSTERS (Arch. exp. Path. Pharm., 1931, 160, 692—698).—A discussion of the cause of the hypoglycæmia observed in dogs within a few hr. after pancreatectomy (cf. this vol., 758).

A. COHEN.

Formation in articular exudates of fibrin apart from blood-fibrinogen; rôle of white cells. M. PIETTRE and B. CELAN (Compt. rend., 1931, 193, 83—85).—The exudate formed in polyarthritis in the calf contains fibrin in three forms: free, mixed with the formed elements, and dispersed in the liquid phase. The formation of the reticulum proceeds as when white cells are treated with dil. HCl or distilled H_2O .

C. C. N. VASS.

Occurrence of heavy metals in human gallstones. R. SCHÖNHEIMER and W. HERKEL (Klin. Woch., 1931, 10, 345—346; Chem. Zentr., 1931, i, 2218—2219).—Cu, Zn, Mn, and Fe were found in considerable quantities.

A. A. ELDRIDGE.

Hæmophilia. C. LA F. BIRCH (Science, 1931, 74, 16—17).—Introduction of the female sex hormone (ovarian extract) into two young males rendered them symptom-free for several months. The blood platelets are resistant to hypo- and hyper-tonic salt solutions.

L. S. THEOBALD.

Effect of diet on hookworm infestation in dogs. A. O. FOSTER and W. W. CORT (Science, 1931, 73, 681—683).—Dogs fed on a diet deficient in vitamins and inorg. salts develop hookworm infestations, but recover when fed on an adequate diet.

L. S. THEOBALD.

Urinary p_{H} and alveolar carbon dioxide in hyperchlorhydria. C. S. HICKS (Austral. J. Exp. Biol., 1931, 8, 133—138).—Ingestion of food in one case was immediately followed by secretion of an acid urine which gradually became more alkaline. Alveolar CO_2 changes ran parallel to the urinary p_{H} .

P. G. MARSHALL.

Intelligence and body chemistry. G. J. RICH (Science, 1931, 74, 21—22).—No significant correlations between blood-Ca and -P and intelligence in children could be found (cf. this vol., 977).

L. S. THEOBALD.

Colloid chemistry of insanity. I. W. D. BANCROFT and G. H. RICHTER (J. Physical Chem., 1931, 35, 1606—1623).—The effects of different reagents on the nervous system are discussed, and it is suggested that mental disorders are of two types, the one resulting from increased and the other from decreased dispersion of the colloids of the nervous system.

L. S. THEOBALD.

Bilirubin liver-function test. I. I. R. JANKELSON and S. L. GARGILL (New England J. Med., 1931, 204, 547—549).—Blood-bilirubin is determined at 5 min. and 3 hr. intervals following intravenous injection of bilirubin.

CHEMICAL ABSTRACTS.

Cinchophen oxidation test of the function of the hepatic cells. S. S. LICHTMAN (Arch. Int. Med., 1931, 48, 98—125).—A colorimetric determination of "oxycinchophen" in urine is based on the yellow colour produced by HCl, which is sensitive in dilutions of 0.0002%. Following oral administration of 0.45 g. of "cinchophen," the 24 hr. excretion of "oxycinchophen" is used as a test of liver function. In normal subjects this excretion is 30—100 mg., but higher vals. (about 200 mg.) are given for cases of various liver disorders.

A. COHEN.

Ration for the production of rickets in chicks. E. B. HART, O. L. KLINE, and J. A. KEENAN (Science, 1931, 73, 710—711).—A ration containing 19—20% of protein, 0.9—1% Ca, and 0.5—0.6% P is detailed.

L. S. THEOBALD.

Histochemical investigation of the initial lesions of experimental pulmonary silicosis. A. POLICARD (Compt. rend., 1931, 193, 197—199).—In white rats breathing rock dust containing 82% SiO₂ the particles are filtered by the alveoli. The particles of SiO₂ are attacked by the cellular juices and the resulting fibrosis with its degenerated cytoplasm rich in SiO₂ constitutes an excellent medium for the tubercle bacillus.

C. C. N. VASS.

Serum-calcium and -inorganic phosphorus during parathyroid tetany. A. VON BEZNAK (Biochem. Z., 1931, 236, 362—371).—Strychnine convulsions in normal and parathyroidectomized dogs result in an increase in blood-Ca and -inorg. P. In venous blood of the contracted muscle, the inorg. P is greater than in resting muscle whilst the Ca content is unchanged. The tetany of parathyroidectomy produces a decrease of muscle-creatinephosphoric acid with a concomitant increase of inorg. P.

F. O. HOWITT.

Cell metabolism. J. JÁNY and C. SELLEI (Biochem. Z., 1931, 236, 348—361).—An exact criterion of cell metabolism is provided by the energy quotients $W_{CO_2}^a/W$ and $W_{CO_2}^a/W_{O_2}$, where $W_{CO_2}^a$ is the heat from aerobic glycolysis of the tissue for 1 hr., $W_{CO_2}^a$ that from anaerobic glycolysis, W_{O_2} the basic heat of respiration, and W the total heat evolution under aerobic conditions, so that $W = W_{O_2} + W_{CO_2}^a$. Changes in these quotients for various tissues indicate that the kidney cortex has little glycolytic function and possesses typically aerobic metabolism, whilst the medulla produces sufficient heat by glycolysis to support anaerobic metabolism. Grey cerebral cortical tissue is more highly glycolytic, yet is not suited for

anaerobic existence. Tissue from rat carcinoma exhibits amongst all tissues considered the greatest adaptation for glycolysis and anaerobiosis.

F. O. HOWITT.

Basal-metabolic rates of vegetarians. G. WAKEHAM and L. A. HANSEN (Science, 1931, 74, 70—71).—Basal-metabolic rates in young women who have been vegetarians for 5 years or more are less than in non-vegetarians.

L. S. THEOBALD.

Metabolic experiments on rabbits with hormone preparations. H. HORSTERS (Z. ges. exp. Med., 1930, 73, 167—179; Chem. Zentr., 1931, i, 2354).—Determinations of blood-albumin, -P, -Ca, -NaCl, and -cholesterol, urinary P₂O₅ and NaCl, and faecal P₂O₅ are recorded.

A. A. ELDRIDGE.

Relation of life to electricity. IV. Electromotive action of homologous fatty acids; exhaustion as an electrochemical sequence of a chemical splitting of higher molecular compounds. R. BEUTNER and J. LOZNER (Protoplasma, 1931, 12, 380—393; cf. this vol., 866).—Solutions of homologous fatty acids in fats and in amyl acetate gradually decrease in stability, e.m.f., and p_H with decreasing mol. wt. These changes are shown to accompany the exhaustion of living tissue with the gradual breakdown of high-mol. compounds.

A. G. POLLARD.

Bile acid : fat ratio of intestinal contents and its relation to fat absorption. O. FÜRTH and H. MINIBECK (Biochem. Z., 1931, 237, 139—158).—The cholic acid : total fats ratio was determined in the intestinal contents of infants, cream-fed cats, and fat-fed rats, vals. of $\frac{1}{8}$ — $\frac{1}{4}$, $\frac{1}{8}$ — $\frac{1}{20}$, and $\frac{1}{15}$ — $\frac{1}{8}$, respectively, being obtained. Thus rats are best adapted for fat absorption. The results indicate that the dissolving action of bile acids on fat does not follow *in vitro* experiments, but is increased by the presence of small amounts of phosphatides and that, especially with increased fat ingestion, the bile acids convey fat into the blood- and lymph-streams and then return to the intestinal lumen for further use.

F. O. HOWITT.

Fat and glycogen metabolism of resting and exercised rats. T. OSUKA (Z. physiol. Chem., 1931, 199, 81—92).—The increased total fat of resting rats receiving an addition of yeast to their diet is found in parts other than the liver; the increased glycogen is present in the liver. With adequate diet, the total body-fat is the same for exercised rats whether they receive yeast or not, but is smaller than for resting rats. Exercise does not affect the liver-fat. The glycogen of the yeast-fed exercised rats is higher than in absence of yeast. Exercise promotes glycogen storage in the liver at the expense of the body-fat.

J. H. BIRKINSHAW.

Glycolysis and amylolysis in muscle after fatigue. E. BECCARI (Biochem. Z., 1931, 236, 113—121).—Fatigue of muscle causes a decrease in glycolytic but does not affect amylolytic power. The effect is independent of the p_H changes.

P. W. CLUTTERBUCK.

Biochemistry of fatigue. I. Influence of "training" on the lactic acid content of muscle after work. A. PALLADIN, L. PALLADIN, and E. PERSOVA (Biochem. Z., 1931, 236, 268—275).—Mus-

cular activity by frequent electrical stimulation affects rabbit muscle so that, unlike "untrained" muscle, no increase of lactic acid content occurs on further stimulation. Hence lactic acid formation is not a trustworthy criterion of work performance. Stimulation of "untrained" muscle results in a decrease of creatinephosphoric acid and a more than correspondingly greater formation of H_3PO_4 , indicating a simultaneous degradation of hexosephosphate. In "trained" muscle stimulation produces formation of creatinephosphoric acid, indicating a synthesis; comparison with the data of Ferdmann and Feinschmidt (A., 1929, 1193), however, points to a fission of the acid on excitation of "trained" muscle. H_3PO_4 is increased to a smaller extent than in "untrained" muscle.

F. O. HOWITT.

Muscular contraction without formation of lactic acid ("alactacidic"). V. HENRIQUES and E. LUNDSGAARD (Biochem. Z., 1931, 236, 219—225).—The latent period, contraction time, course of contraction, maximal tension developed, and the action current for the contraction of muscle, the lactic acid formation of which has been completely inhibited by iodoacetic acid, are the same as for normal muscle and the rôle of lactic acid formation in muscular contraction should be regarded as of a secondary nature.

P. W. CLUTTERBUCK.

Energetics of muscular contraction when formation of lactic acid is prevented. O. MEYERHOF, E. LUNDSGAARD, and H. BLASCHKO (Biochem. Z., 1931, 236, 326—347; cf. A., 1930, 1312).—In muscle poisoned with iodoacetic acid the amount of heat liberated for a definite amount of creatinephosphoric acid hydrolysis is not const. For weak stimulation the calorific equiv. is 160 g.-cal. per g. of liberated H_3PO_4 . With anaërobic resting muscle higher vals. are obtained, extensive hydrolysis giving a final val. of about 450 g.-cal. Hence when lactic acid formation is prevented a heat-supplying reaction independent of phosphagen hydrolysis occurs. Part of the excess heat is due to hydrolysis of adenylypyrophosphoric acid and part to the evolution from resting anaërobic muscle. 80% of the heat due to contraction alone is accounted for by phosphagen hydrolysis.

F. O. HOWITT.

Poisoning of frog muscle-extract by iodoacetate. K. LOHMANN (Biochem. Z., 1931, 236, 444—456).—The hexosediphosphoric acid of Harden and an aldosemonophosphoric acid of the Embden type were isolated from the musculature of the intact iodoacetate-poisoned frog. Formation of phosphoric ester in frog muscle-pulp or -extract is less on addition of iodoacetate than on that of fluoride. Inhibition of lactic acid formation from glycogen and hexosediphosphate is a well-marked time reaction. In completely poisoned muscle-extracts H_3PO_4 liberation from hexosediphosphate is almost completely whilst esterification of glycogen is only partly inhibited. Et urethane inhibits the poisoning action of iodoacetate. With high concentrations of iodoacetate lactic acid formation from hexosediphosphate is inhibited before that from glycogen, whilst with that from methylglyoxal inhibition is much less marked.

F. O. HOWITT.

Formation of lactic acid and hydrolysis of creatinephosphoric acid in anaërobic activity of muscle. O. MEYERHOF and W. SCHULZ (Biochem. Z., 1931, 236, 54—86).—The time course of lactic acid formation with short (2 sec.) tetanus in N_2 and O_2 at high and low temp., and of the isometric coeffs. of decomp. of phosphagen and of lactic acid formation for short tetani and for series of single twitches at different temps. in normal and curarised muscle is investigated and the results are shown to remove some of the essential discrepancies between the findings of the chemical and myothermic methods. With max. contraction and with indirect stimulation in short tetanus, a considerable part of the lactic acid arises after relaxation and independently of the temp. (4° and 18°). The lactic acid formation within and immediately following tetanus is the same in an O_2 -saturated as in an anaërobic muscle. The lactic acid time coeffs. with and without recovery confirm the older results of Embden rather than those of the author and remove the contradiction between the appearance of positive anaërobic heat and the simultaneous endothermic resynthesis of creatinephosphoric acid, the energy for the latter being accounted for by the energy of exothermic formation of lactic acid. The K_{mL} val. for a single twitch is independent of the stimulation interval, but for a short series of twitches is dependent on the total tension developed (no. of stimuli), being for 30—60 stimuli 255×10^6 , for 120 stimuli 150×10^6 , and for complete fatigue 115×10^6 . With a high degree of curarisation (trimethyloctylammonium iodide) the K_{mL} value for 30—60 twitches is 180×10^6 . The K_Z val. for the decomp. of phosphagen in curarised muscle is considerably increased. The increase of the K_{mL} val. of curarised muscle is equiv. in energy val. to the lowering of the K_{mL} val. in the same muscle. Within the tetanus, O_2 is without influence on the decomp. of phosphagen.

P. W. CLUTTERBUCK.

Breakdown and resynthesis of phosphagen in frozen and thawed muscles. E. KREPS (Proc. Roy. Soc., 1931, B, 108, 545—552).—As with glycogen (A., 1929, 1102), the max. rate of breakdown of phosphagen in frozen frogs' muscles occurs at -2.6° . On thawing, phosphagen is recovered completely if the muscles are frozen for 24 hr. at a temp. not lower than -1.5° . There is no recovery below -2.5° , and partial recovery at intermediate temp. owing to variations in muscle fibres. Recovery is dependent on O_2 .

A. COHEN.

Oxygen uptake of frozen and thawed muscles. E. C. SMITH (Proc. Roy. Soc., 1931, B, 108, 553—559).—The O_2 uptake of frozen frogs' muscles decreases to zero at -4° . The initial O_2 uptake is recovered on thawing muscles frozen 24 hr. at a temp. not lower than -2.4° . When frozen below -3° , muscles can recover only 10% of the O_2 uptake of muscles in resting condition. Loss of contractility and ability to synthesise glycogen and phosphagen is not due to destruction of the respiratory function, since oxidation of lactic acid is still possible in irreversibly frozen muscle.

A. COHEN.

Creatine-creatinine metabolism. I. Urinary creatinine and diet. K. EIMER (Z. ges. exp. Med.,

1930, 74, 738—749; Chem. Zentr., 1931, i, 2357).—A large increase in the intake of meat causes increased urinary creatinine and N, but not creatine.

A. A. ELDRIDGE.

Liver and nitrogen metabolism. F. GOEBEL (Med. Doświad. Spolecz., 1929, 10, 16 pp.; Chem. Zentr., 1931, i, 2357).—The N distribution in the normal dog's urine is: urea 85.2—89.6, NH_3 3.4—4.6, oxyproteic acids 1.3—1.8, Et_2O -sol. 2.7—4.0; with Eck's fistula the NH_3 :N: urea-N ratio and the total N were disturbed, and the oxyproteic acid was increased.

A. A. ELDRIDGE.

Structure of mentholglycuronic acid obtained by feeding menthol. A. DA CRUZ (Compt. rend. Soc. Biol., 1930, 105, 815—816; Chem. Zentr., 1931, i, 2222).—Fission of biosynthetic mentholglycuronic acid with β -glucosidase gives *d*-glycuronic acid.

A. A. ELDRIDGE.

Utilisation of pentosans in the animal organism. O. FÜRTH and P. ENGEL (Biochem. Z., 1931, 237, 159—188).—The total carbohydrate content of the liver of rats fed with various diets was determined. Fats and proteins are not good glycogen formers. Cellulose freed from sol. carbohydrate and pectin, galactose, hydropectan, and crude arabinose (hydrolysed cherry-gum) exhibit weak but definite glycogen formation. Cherry- and tragacanth-gums are without action. Orally introduced xylan in 5 phloridzinised rabbits gave an increase in sugar excretion and *D/N* ratio in only 2 cases. In adrenalectomised and partly starved rabbits oral administration of xylan when the urinary sugar is nil results in the appearance of reducing sugar in the urine. Hence pentosans are utilised and transformed into reducing sugars by the organism.

F. O. HOWITT.

Intermediary carbohydrate metabolism. IX. Intravenous galactose assimilation under the influence of hormones, hunger, and feeding. X. The first phase of dextrose assimilation. M. WIERZUCHOWSKI (Biochem. Z., 1931, 237, 92—102, 103—128).—IX. The assimilation of galactose administered intravenously to normal dogs at the rate of 2 g. per kg. per hr. for 10 hr. is not affected by the type of feeding, by hunger, or by adrenaline or thyroxine administration. An average of 25.36% is metabolised and 74.64% excreted in the urine. Insulin, however, increases the assimilation, the galactosuria being reduced throughout the experimental period.

X. The first phase of assimilation of dextrose administered intravenously to dogs at the rate of 2 g. per kg. per hr. is attended by a blood-sugar curve which exhibits (a) a rise, (b) a flat portion, and (c) a fall. This first phase, which is sp. for dextrose, is eliminated by increasing the daily administration of carbohydrate. It appears only once during the period of dextrose administration despite any variation in rate and is not influenced by performance of work, which also has no action on the degree of dextrose assimilation. Insulin administration affects the phase mainly during the period of (a), simultaneous adrenaline administration resulting in a normal phase. 1 γ of the latter hormone nullifies the assimilation of an average of 27.7 mg. of dextrose.

F. O. HOWITT.

Influence of exclusive and mixed diet, and of addition of salts on the urinary excretion and the composition of blood. W. VON MORACZEWSKI and S. GRZYCKI (Arch. exp. Path. Pharm., 1931, 160, 703—719).—The proportions of the substances excreted in the urine of dogs fed on a mixed diet, or on one composed exclusively of fat, carbohydrate, or protein, vary. Diuresis is increased by overfeeding of fat or carbohydrate. The latter also increases the excretion of creatinine, which is also increased by the addition to all the diets of salts such as KCl and NH_4Cl . A parallel effect is also observed with the excretion of P. The alkali reserve of the blood is lowered on a diet of fat, whilst addition of salts has a similar effect. Fat in the diet increases the amount of blood-Ca. Overfeeding, generally, leads to an increase in the amounts of NH_3 and uric acid excreted.

B. LEVIN.

Mineral metabolism in infancy. III. Substitution of cow's milk for human milk in infant feeding. S. V. TELFER (Glasgow Med. J., 1930, 33, 265—284).—With cow's milk the intake of Ca, Mg, and P is much greater than with human milk; the mineral retention (except of Fe) is increased, but the proportionate mineral retention falls. The fat is less effectively utilised. The urinary H_3PO_4 is greater with cow's milk.

CHEMICAL ABSTRACTS.

Calcium requirements of dairy heifers. J. B. LINDSEY, J. G. ARCHIBALD, and P. R. NELSON (J. Agric. Res., 1931, 42, 883—896).—Heifers on a high-Ca ration showed higher Ca-storage but lower % retention than those on a low-Ca ration. A high Ca content in the ration was necessary to ensure adequate P-storage. The Mg balance averaged a small positive value for high-Ca rations and a small negative value for low-Ca rations. The intake of all elements per unit wt. and the retention per unit wt. showed a similar, proportional decline with increasing age. The 2:1 ratio of Ca:P retained, irrespective of the ratio of the intake, was very uniform for both types of ration and for animals of all ages. The storage of mineral substances was definitely lower with animals on low-Ca ration, but no ill effects were observed.

A. G. POLLARD.

Sulphur and growth. L. BINET and J. MAGRON (Compt. rend., 1931, 193, 115—117).—0.1% aq. $\text{Na}_2\text{S}_2\text{O}_4$ promotes the growth of *Lepidum sativum* and the metamorphosis of the tadpole.

C. C. N. VASS.

Toxicity limit of ozone. F. TOUL (Coll. Czech. Chem. Comm., 1931, 3, 333—335).—Concentrations of 0.05—0.07% of O_3 in air have no effect on the larvæ of *Tenebrio molitor*; above 0.12%, O_3 is definitely toxic.

H. BURTON.

Effects of dilution on the lethal properties of a poison. T. N. SETH (J. Pharm. Exp. Ther., 1931, 42, 333—341).—In measurements of the time taken for the heart of the tadpole to cease beating when the animal is placed in solutions containing a poison such as HgCl_2 in varying concentrations, it is observed that an increase in the dilution of the poison causes, up to a point, a decline in its lethal properties. Further dilution enhances its lethal effect, but still further dilution again decreases the effect. It is

suggested that the lethal effect of a poison which dissociates in solution depends on both the undissociated mols. and the ions formed.

B. LEVIN.

Modifications of the alcohol and water contents of the blood following administration of alcohol and water. A. GALAMINI and G. LAMANNA (*Atti R. Accad. Lincei*, 1931, [vi], 13, 143—148).—While fasting, different individuals show different H_2O contents of the blood, the max. usually occurring at about 11 a.m. Administration of small quantities (200—300 c.c.) of H_2O causes lowering of the H_2O content of the blood, sometimes preceded by a slight increase. Lowering of the H_2O content is produced also by ingestion of EtOH or of large amounts of dextrose in the form of grapes, although the amount of H_2O introduced in the latter case may be relatively high. When Marsala is taken at intervals, the EtOH content of the blood shows, not a regular increase, but successive increments, sometimes interrupted by decreases. The H_2O content of the blood varies inversely to the EtOH content.

T. H. POPE.

Etiology and therapeutic modifiability of the specific toxic action of methyl alcohol. E. KEESER (*Arch. exp. Path. Pharm.*, 1931, 160, 687—691).— CH_2O is found in the abdominal fluid and vitreous body of rabbits poisoned with MeOH, and is formed by the action of fresh vitreous body (calf) on MeOH. In the latter case, the addition of $(NH_4)_2CO_3$ leads to the formation of hexamethylenetetramine. The organs of rabbits receiving MeOH and $(NH_4)_2CO_3$ show less injury than those of rabbits receiving MeOH alone. The results support the view that the toxic effects of MeOH are due to CH_2O formation.

A. COHEN.

Blood-lipins and fixation of ethyl chloride by whole blood. L. SCOTTI-FOGLIENI (*Compt. rend. Soc. Biol.*, 1931, 105, 959—960; *Chem. Zentr.*, 1931, i, 2219—2220).—Blood-lipins do not influence the amount of EtCl retained; the amount is more probably determined by the red corpuscles.

A. A. ELDRIDGE.

Insulin and the blood-sugar level under ether anaesthesia. H. ESCHWEILER (*Arch. exp. Path. Pharm.*, 1931, 161, 21—33).—Injection of insulin $\frac{1}{2}$ hr. before the beginning of anaesthesia is of advantage in counteracting the hyperglycaemic effect of Et_2O , since the administration of the anaesthetic coincides with the hypoglycaemic stage of insulin action.

P. G. MARSHALL.

Influence of magnesium chloride on the narcotic and toxic effects of sodium barbital. H. G. BARBOUR and W. F. TAYLOR (*J. Pharm. Exp. Ther.*, 1931, 42, 321—331).—When 2 parts of $MgCl_2$ and 1 part of Na-barbital are injected simultaneously into rabbits, the min. lethal dose is much higher than that calc. by a simple summation of the two separate effects, the $MgCl_2$ exercising a "protective antagonism." Similarly, $MgCl_2$ injected simultaneously with Na-barbital may hasten the onset of narcosis, and lessen its duration, with no corresponding increase in toxicity.

B. LEVIN.

Toxicology of benzene. A. M. TSCHERNIKOV, I. D. GADASKIN, and F. V. KOVSCHAR (*Arch. exp. Path. Pharm.*, 1931, 161, 214—228).—A detailed

account of the symptoms of acute C_6H_6 poisoning (dilatation of the pupils, fall in blood-pressure, paralysis of the respiratory centre, etc.) is given and these are compared with the results of PhOH poisoning. PhOH in the blood is determined colorimetrically by coupling with diazotised *p*-nitroaniline.

P. G. MARSHALL.

Resorption of salicylic acid following intratracheal or subcutaneous injection. W. BLUME and P. BREUNIG (*Arch. exp. Path. Pharm.*, 1931, 161, 181—195).—Salicylic acid (Na salt) is rapidly absorbed from the trachea, making its appearance in the blood in 1 min. and the urine in 10 min. The max. concentration occurs in 3 min. in the blood and in 1 hr. in the urine. Absorption occurs less rapidly after subcutaneous injection.

P. G. MARSHALL.

Influence of quinone on cells. G. LEJHANEC, I. A. PARFENTJEV, and B. SOKOLOFF (*J. Pharm. Exp. Ther.*, 1931, 42, 343—353).—Benzoquinone added to a 36% aq. suspension of yeast (p_H 9.3) increases the O_2 consumption in a dilution of 1 in 500,000. This effect is more marked in salt solution (p_H 5.6) than in H_2O . At the same time, the life of the cells is shortened, and their multiplication inhibited.

B. LEVIN.

Mechanism of antglycosuric action of santonin. A. LEULIER and A. ROCHE (*Compt. rend.*, 1931, 193, 81—82).—In the rabbit, 2 hr. after injection santonin exerts an action antagonistic to that of phloridzin; the action lasts for 5—6 hr. and is probably due to an elevation of the dextrose threshold val. of the kidney.

C. C. N. VASS.

Active principle of guarana. G. BERTRAND and B. CARNEIRO (*Compt. rend.*, 1931, 193, 276—278).—The active principle is caffeine. β -Guarinine, described by Nierenstein (1910) is impure caffeine.

C. C. N. VASS.

Biological determination of morphine. L. MAIER (*Arch. exp. Path. Pharm.*, 1931, 161, 163—172).—Straub's morphine reaction (*Biochem. Z.*, 1912, 39, 216) forms a basis for its biological determination. By injection of crude neutral organ extracts (in forensic cases) into mice as little as 0.02 mg. can be detected.

P. G. MARSHALL.

Neutralisation of [toxicity of] strychnine sulphate. A. C. MARIE (*Compt. rend. Soc. Biol.*, 1930, 105, 744—745, 846—847; *Chem. Zentr.*, 1931, i, 2226).—Strychnine is detoxicated for mice by $NaMnO_4$. Guinea-pigs are not trustworthy test-animals. Strychnine is also detoxicated for mice by admixture with guinea-pig's blood and dried horse adrenals. The protective action is attributed to the colouring matter of the blood.

A. A. ELDRIDGE.

Effect of vomicine on blood-sugar. E. RUCKOLDT (*Arch. exp. Path. Pharm.*, 1931, 161, 59—63).—Intravenous administration of vomicine to rabbits causes a rise in blood-sugar (to > 200 mg. per 100 c.c.) which is independent of convulsions caused by this drug and is unaffected by adrenalectomy when large doses are given. Administration of ergotamine prevents this rise in blood-sugar, which is also reduced by the action of adrenaline.

P. G. MARSHALL.

Curare-diabetes in the frog. E. GEIGER (*Arch. exp. Path. Pharm.*, 1931, 161, 88—90).—Contrary to

the conclusions of Langendorff (Pflüger's Archiv, 1887, 139) curare never produces glycosuria following extirpation of the liver. Small doses are more lethal in frogs with extirpated livers than in normal animals (0.3 mg. per 100 g.), whilst the paralysing dose is almost the same (0.05 mg. per 100 g.).

P. G. MARSHALL.

Pharmacology of hops. H. STEIDLE (Arch. exp. Path. Pharm., 1931, 161, 154—162).—Both hop dust and hop oil produce symptoms of paralysis in frogs, the toxicity varying according to the locality from which the material is obtained, the season, and the duration of storage.

P. G. MARSHALL.

Toxicity of aluminium compared with that of iron, nickel, and other metals. G. BERTRAND and S. SERBESCU (Compt. rend., 1931, 193, 128—131).—The toxicities of Cu, Ni, Cd, Co, Zn, Mn, Fe^{II}, Fe^{III}, and Al have been contrasted by intraperitoneal injections of the cryst. sulphates or chlorides into guinea-pigs, the time of survival being measured. The toxicity of Al is comparable with that of Fe and less than that of Cu and Ni.

C. C. N. VASS.

[Blood-]coagulating action of inorganic and organic calcium salts. R. DOURIS and M. PLESSIS (Compt. rend. Soc. Biol., 1930, 105, 757—759; Chem. Zentr., 1931, i, 2220).—For equal amounts of Ca, the rapidity of coagulation diminished in the order: chloride, hypophosphite and benzoate, lactate and acid malate.

A. A. ELDRIDGE.

Partition of gallium in the organism. C. LEVADITI, J. BARDET, A. TCHAKIRIAN, and A. VAISMAN (Compt. rend., 1931, 193, 117—119).—Ga has been determined spectrographically and colorimetrically in the ash of the tissues and blood of the rabbit after intramuscular injection of Ga tartrate. Ga gives with resorcinol and NH₃ a bluish-violet colour the intensity of which depends on the quantity of resorcinol; for the same amount of reagent the rate of development of the colour is proportional to the amount of Ga present. Ga remains in the organism at least 69 days after injection; it circulates in the blood, accumulates first in the kidney and liver, but is rarely present in the brain.

C. C. N. VASS.

Toxicity of several allotropic modifications of germanic oxide. J. H. MULLER (J. Pharm. Exp. Ther., 1931, 42, 277—297).—The min. lethal dose of the colloidal form when injected intraperitoneally into guinea-pigs is 400 mg. per kg. body-wt., and that of the cryst. form is 300 mg. per kg. A marked tolerance is developed by its administration in sub-lethal amounts.

B. LEVIN.

Amalgam [toxicity] question. P. BORINSKI (Zahnärztl. Mitt., 1929, 4 pp.; Chem. Zentr., 1931, i, 2225).—Absorption of Hg occurs from dental amalgams, chiefly in the first 3 months, but also during 15 months or longer. Little difference between Cu and Ag amalgams was observed.

A. A. ELDRIDGE.

Occurrence of small quantities of mercury in urine and faeces. P. BORINSKI (Klin. Woch., 1931, 10, 149—153; Chem. Zentr., 1931, i, 2225).—Hg (up to 10⁻⁵ g. per day) was excreted by 56% of (75) persons who had not been in contact with Hg, or

those carrying old dental amalgam fillings. Markedly higher results were obtained with persons carrying new fillings or those otherwise brought into contact with Hg. Nearly all foodstuffs contain traces of Hg; it is estimated that the daily intake from this source is 5 × 10⁻⁶ g.

A. A. ELDRIDGE.

Salt effects on eggs and nauplii of *Artemia salina*. L. E. BOONE and L. G. M. BAAS-BECKING (J. Gen. Physiol., 1931, 14, 753—763).—The hatching of eggs of the brine shrimp is not affected by the reaction of its environment between *p*_H 2.0 and 13.0. The highly toxic effect of K salts is slightly antagonised by Na salts, in which nauplii are formed, and to a smaller extent by Mg and Ca.

A. COHEN.

Salt effects on swarms of *Dunaliella viridis*. Teod. L. G. M. BAAS-BECKING (J. Gen. Physiol., 1931, 14, 765—779).—The organism may be grown in *M*—4*M*-NaCl solutions at *p*_H 6—9 without decrease in the size of the cells. It is sensitive to the toxic effects of Ca and Mg, which are, however, antagonistic. The Mg : Ca ratio which permits development of the organism rises from 4—5 in *M*-NaCl to 20 in 4*M*-solution.

A. COHEN.

Colloid chemistry of the nervous systems. I. Sodium thiocyanate therapy. I. W. D. BANCROFT and J. E. RUTZLER, jun. (J. Physical Chem., 1931, 35, 1185—1211).—Further examples of the antagonistic effect of NaCNS on the physiological action of certain drugs support the reversible coagulation theory of narcosis (this vol., 513). NaCNS alleviates the effects of strychnine and other drugs on rabbits (this vol., 649), but "nembutal" and EtOH are not antagonised to any marked degree. Na poisoning may be produced by too much NaCNS in the presence of a strong narcotic. Na tartrate augments the action of morphine hydrochloride, whilst NaCNS antagonises it, indicating the existence of a lyotropic series of ions connected with the peptisation of colloids coagulated by morphine. A theory based on the peptisation of coagulated protein colloids of the brain for relief of drug addiction is proposed.

L. S. THEOBALD.

X-Radiation and regeneration in *Amblystoma*. E. G. BUTLER (Science, 1931, 74, 100—101).—X-Radiation prevents normal regeneration of the fore-limb of the embryo of *Amblystoma* at any stage of development, but has no apparent effect on normal growth and differentiation.

L. S. THEOBALD.

"Omega"-catalysis of oxidative glycine fission. B. KISCH (Biochem. Z., 1931, 236, 380—386).—In the oxidative deamination of glycine by "omega"-catalysis (cf. A., 1930, 949, 1036) added phosphate functions as a buffer and is replaceable by NaHCO₃. "Omega"-catalysis is ineffective for alanine, dihydroxyphenylalanine, glutamic acid, taurine, and also for glycine Et ester and glycylglycine, indicating that these latter compounds are neither hydrolysed nor directly deaminated under the experimental conditions. Thus the "omega"-catalyst exhibits a marked specificity of action similar to that of enzymes.

F. O. HOWITT.

Inhibiting effect of oxidase on the reduction of sulphur by potato and gladiolus juice. J. D. GUTHRIE (Contr. Boyce Thompson Inst., 1931, 3,

125—130).—Treatment of potato tubers or gladiolus corms with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ reduces the ability of the expressed juices to reduce S to H_2S . This effect is increased by boiling the juice or carrying out the reaction in an atm. of N_2 . Addition of unboiled juice decreases the H_2S production from boiled juice. Fresh juice probably contains oxidase which oxidises either H_2S as formed or the reducing agents responsible for its formation.
A. G. POLLARD.

Influence of reaction of medium on the re-generation of peroxidase inactivated by heat. S. PRONIN (Biochem. Z., 1931, 236, 107—112).—Re-generation of heat-inactivated peroxidase of horseradish occurs most completely in neutral solution.
P. W. CLUTTERBUCK.

Molecular statistics of an enzyme action. J. B. S. HALDANE (Proc. Roy. Soc., 1931, B, 108, 559—567).—Mathematical treatment of available data leads to the following results. About 2×10^5 mols. of H_2O_2 are destroyed per mol. of catalase; the mean life of the active enzyme-substrate mol. is about 10^{-7} sec., and the velocity coeff. for its formation exceeds 7×10^6 .
A. COHEN.

Dismutation of methylglyoxalacetic acid into *d*- α -hydroxyglutaric acid by an enzyme of animal cells. S. FUJISE (Biochem. Z., 1931, 236, 237—240).—Methylglyoxalacetic acid is converted by animal glyoxalase into *d*- α -hydroxyglutaric acid, the yield being 78.3—86.7%.
P. W. CLUTTERBUCK.

Crystalline amylase. M. L. CALDWELL, L. E. BOOHER, and H. C. SHERMAN (Science, 1931, 74, 37).—Isotropic, elongated crystals of amylase, n 1.54 (approx.), showing slight double refraction, have been obtained from carefully-buffered aq. EtOH solutions of pancreatic amylase. Formation and yield are both dependent on p_{H} , and the smallness and instability of the crystals necessitate a special technique.
L. S. THEOBALD.

Synthetic action of amylase on dextrans of various origin. S. NISHIMURA (Biochem. Z., 1931, 237, 133—135).—Achrondextrin prepared by the action of α -amylase (pancreatic extract) on starch is much more readily polymerised by the synthetic action of purified amylase (cf. this vol., 653) than are those prepared by the action of β -amylase (malt) or acid hydrolysis on starch, the synthetic action being followed by I coloration.
F. O. HOWITT.

Effect of thiocyanates on amylase activity. I. Potato amylase. F. E. DENNY. II. Salivary amylase. L. P. MILLER (Contr. Boyce Thompson Inst., 1931, 3, 277—285, 287—296).—I. The saccharogenic activity of expressed potato juice was decreased by Na and K thiocyanates. The amylolytic activity was much less affected. Similar effects were obtained with dialysed juice. No stimulative action was observed. The stimulation of sprouting and the decreased starch content of potatoes following immersion in thiocyanate solutions are not the results of direct action on the amylase.

II. With all concentrations of KCNS, the activity of salivary amylase was increased at high p_{H} and decreased at low p_{H} , with varied intermediate effects. With increasing concentration of KCNS the optimum

p_{H} for starch hydrolysis by the dialysed amylase in the presence of phosphate buffers moved to the alkaline side. With NaCl in the normal concentration found in saliva and at p_{H} 6.6, addition of KCNS up to 0.06M produced no effect. In the absence of NaCl amylase activity was increased.
A. G. POLLARD.

Effect of potassium cyanide on the amylase activity of potato juice. F. E. DENNY (Contr. Boyce Thompson Inst., 1931, 3, 297—307).—Small additions of KCN to potato juice increased the amylase activity in slightly acid solution (p_{H} 6—7), the effect decreasing as the neutral point was approached. Dialysis of the juice almost prevented the action of KCN. The fraction of potato juice necessary to the activating effect of KCN diffuses through collodion more slowly than reducing sugars.
A. G. POLLARD.

Cholam diastase. I. Electrodialysis and electro-osmosis. D. NARAYANAMURTI and R. V. NORRIS (Proc. XV Indian Sci. Cong., 1928, 166).—The activity of cholam malt diastase can be increased, and the ash and protein contents decreased, by electro-dialysis. In electro-osmotic experiments the ratio of liquefying power to saccharifying power was different in different fractions.

CHEMICAL ABSTRACTS.

Enzymic processes in germinating barley. I. Development of diastatic activity. J. WEICHERTZ and R. ASMUS (Biochem. Z., 1931, 237, 20—72).—Germinating barley grains were examined histologically by normal and polarised light. The development of diastatic activity during germination indicates a progressive liberation of diastase due to proteolytic action of papain. The diastatic activity of grain extracts when papain is added, however, is seldom attained under natural conditions. The activity-time curve is determined by the type and age of the barley. The greater is the diastatic activity the greater is the stimulating action on it by the following substances: Et_2O , EtOH, MeOH, Et and Ph urethanes, MeCHO, saponin, Hg-chlorophenol and -nitrophenol, HgCl_2 , and H_3PO_4 . The following are inhibitory: CHCl_3 , EtCl, chloral hydrate, Pr, Bu, and amyl alcohols, HCN, NH_2Ph , CS_2 , eosin, methylene-blue, and tannin. Stimulation is due to increase in cell permeability, which runs parallel with both development of diastatic activity and readiness of germination.

F. O. HOWITT.

Cyclising enzymes. O. FERNÁNDEZ and B. PIZARROSO (Anal. Fis. Quim., 1931, 29, 369—373).—Unsuccessful attempts have been made to detect plant enzymes which might transform hexoses and methylpentoses into inositol or phloroglucinol.

H. F. GILLBE.

Chondrosulphatase. C. NEUBERG and E. HOFMANN (Naturwiss., 1931, 19, 484—485).—The enzyme decomposes chondroitinsulphuric acid and the ester sulphates of the mustard-oil glucosides.
A. J. MEE.

Specificity of phosphatase. J. TAPADINHAS (Compt. rend. Soc. Biol., 1930, 105, 811—813; Chem. Zentr., 1931, i, 2345).—Phosphatase from *Euphorbia pulcherrima*, Wild, readily (78%) splits monobornyl-orthophosphoric acid, whilst diphenylpyrophosphoric acid is split only to the extent of 29%.

A. A. ELDRIDGE.

Crystalline pepsin. III. Preparation of active crystalline pepsin from inactive denatured pepsin. J. H. NORTHROP (J. Gen. Physiol., 1931, 14, 713—724; cf. A., 1930, 1317).—The activity of pepsin solutions, inactivated at p_H 10.5, is partly recovered by titration to p_H 5.4 and keeping for 24—48 hr. at 22°. The inactivation and its reversal are not due to an inhibitory substance. The reactivated pepsin is isolated from solution by fractional precipitation with $MgSO_4$ after partial precipitation of inactive protein by H_2SO_4 . It has the same physical characteristics and activity as the original material, providing further evidence that the proteolytic activity is a property of the mol. itself. A. COHEN.

Action of pepsin on solutions of monoaminoacids alone or in mixtures. A. BLANCHETIÈRE (Compt. rend., 1931, 193, 256—257).—In the hydrolysis of glycine and alanine by pepsin, the initial rapid rate of disappearance of NH_2-N , as determined by Sørensen's method, soon decreases. Since the solution always gives a positive Abderhalden and Kamm reaction part at least of the NH_2-N which disappears is diketopiperazine- N , and accordingly the diketopiperazines produced in the enzymic hydrolysis of proteins are at least in part degradation products. Glycerol has an adverse action in peptide synthesis. The carbamate method of determining NH_2-N gives higher results than Sørensen's method.

R. BRIGHTMAN.

Examination of pepsin according to the [Dutch] pharmacopœia. C. G. VAN ARKEL (Pharm. Weekblad, 1931, 68, 657—660).—The amounts of residue of coagulated egg albumin left after the action of various pepsin solutions have been determined.

S. I. LEVY.

Tryptic digestion of iodoproteins. G. BARKAN and G. KINGISEFF (Arch. exp. Path. Pharm., 1931, 160, 610—627).—The ultrafiltrate from the tryptic digestion of an iodoprotein contains, besides a preponderating amount of organically bound I, a small amount of iodide. Two I fractions are present in the ultrafiltrate, one precipitable by Ag^+ in acid solution, and the other not. These two fractions appear to be mutually convertible and in equilibrium. The bearing of these results on earlier work is discussed.

B. LEVIN.

Edestin as substrate for nephelometric determination of proteolytic enzymes. K. G. STERN (Biochem. Z., 1931, 236, 464—473).—The use of edestin and nephelometric measurement following precipitation by sulphosalicylic acid is recommended for the investigation of proteolytic enzymes.

F. O. HOWITT.

Specific action of metallic salts on the urease of the amoebocytes of *Limulus*. L. LOEB and I. LORBERBLATT (Biochem. Z., 1931, 236, 298—311).—The sp. relation between metal constituents of inorg. salts and the activity of urease prepared from the amoebocytes of the blood-serum of *Limulus* (king crab) is not due to any influence on the cell protoplasm. The activity of urease extracted by $CaCl_2$ solution is decreased by presence of 0.5M-NaCl, and the earlier is the addition of NaCl the greater is the inhibition. This phenomenon occurs with other metallic salts.

Hence definite metallo-urease compounds are formed and are stabilised with age so that replacement of the metal by another becomes more difficult with passage of time. Combination probably occurs, not with the urease, but with a co-enzyme or protein.

F. O. HOWITT.

Antiurease. J. B. SUMNER and J. S. KIRK (Science, 1931, 74, 102).—Rabbits have been immunised to cryst. urease by graded injections of this substance. Serum from these animals strongly inhibits the power of the urease to hydrolyse urea.

L. S. THEOBALD.

Influence of structure on the kinetics of desmolases. System: uric acid, surviving liver. S. J. PRZYLECKI and E. MYSTKOWSKI (Biochem. Z., 1931, 236, 122—130).—The greater part of the uric acid of tissue is present in the sorbed condition, the amounts being regulated by an equilibrium between the free and sorbed acid. Decomp. of uric acid takes place entirely within the cell. Addition of $PrOH$ (by a reversible reaction) causes almost complete elution of sorbed uric acid and so accelerates the action of uricase, and it also increases the permeability of the cell to uric acid.

P. W. CLUTTERBUCK.

Kinetics of the action of uricase. M. Z. GRYNBERG (Biochem. Z., 1931, 236, 138—163).—The decomp. of uric acid with shaken suspensions of uricase is much more rapid in O_2 than in air. Addition of boiled uricase solutions slightly inhibits, but of filtered boiled uricase solution and of saturated solutions of allantoin has no effect on the reaction velocity. The reaction involves the utilisation of 1 atom of O and 1 mol. of H_2O and the formation of 1 mol. of CO_2 . The absorption of O_2 and the oxidation of uric acid do not depend on, but the R.Q. decreases with, the age of the enzyme extract. The decomp. of uric acid is proportional, within limits, to the amount of uricase, and increases with the concentration of uric acid. Addition of small amounts of $PrOH$ and $BuOH$ accelerates and of large amounts inhibits the reaction. The inhibition is proportional to the amount of alcohol and independent of the amount of uric acid and is reversible with $BuOH$, but irreversible with $PrOH$.

P. W. CLUTTERBUCK.

p_H sensitivity of respiring and fermenting yeast. The shift of fermentation to respiration. K. TRAUTWEIN and J. WASSERMANN (Biochem. Z., 1931, 236, 35—53).—The dependence of fermentation and respiration on the p_H is determined for 2 top and bottom yeasts. The respiration of top is usually greater than of bottom yeast. The respiration- and fermentation- p_H curves at first run parallel; the respiration and fermentation optima practically fall together, but in the later portions, the respiration curve flattens out and proceeds asymptotically to the x axis. At p_H 8 fermentation practically ceases, but from this point respiration proceeds with almost const. velocity up to p_H 10.8 and then suddenly decreases and ceases at p_H 11.8.

P. W. CLUTTERBUCK.

Oxidation-reduction potential of complex iron compounds in yeast. T. B. COOLIDGE (Nature, 1931, 128, 223).— $(NH_4)_2SO_4$ precipitates protein, cytochrome "c," and a complex Fe compound from

an alkaline yeast-extract. The Fe compound, separated by ultra-filtration, has an oxidation potential which lies close to that at which the spectrum of cytochrome "c" appears. The Fe is not present as Fe⁺⁺ or Fe⁺⁺⁺. L. S. THEOBALD.

Phytochemical reduction of oxaloacetic acid to malic acid. S. FUJISE (Biochem. Z., 1931, 236, 231—236).—Oxaloacetic ester added to a yeast fermentation of sucrose is reduced to L-malic acid.

P. W. CLUTTERBUCK.

Dismutation of thienylglyoxal. S. FUJISE (Biochem. Z., 1931, 236, 241—246).—In contact with fresh unwashed yeast, thienylglyoxal [p-nitrophenyl-hydrazone, m. p. 234°; semicarbazone, m. p. 222° (decomp.)] is dismutated to 1- α -thienylglycollic acid, m. p. 84.5—85°, α_D^{20} —98.07°.

P. W. CLUTTERBUCK.

Acetoacetic acid and yeast. E. FRIEDMANN (Naturwiss., 1931, 19, 400).—Fermenting yeast transforms acetoacetic acid into d- β -hydroxybutyric acid in presence or absence of dextrose, both reactions being influenced by bromo- or iodo-acetic acid. A second acid is also formed.

F. O. HOWITT.

Action of monoiodoacetic acid on respiration and fermentation. P. B. JENSEN (Biochem. Z., 1931, 236, 211—218).—The fermentation of dextrose and dihydroxyacetone by *S. Ludwigii* is inhibited by a concentration of 1/5000 of the acid, but to a much smaller extent than the dextrose fermentation by pressed yeast. Formation of dextrose could not be detected when the dihydroxyacetone fermentation is inhibited by iodoacetic acid. Fermentation of pyruvic acid by pressed yeast is also inhibited by the acid, but much more feebly than the dextrose fermentation. The methylene-blue reduction by the yeast and by the Schardinger enzyme is only slightly affected by the acid.

P. W. CLUTTERBUCK.

Effect of iodine on the carbon dioxide production of fermentation yeasts. K. SCHARRER and G. CLAUS (Arch. Mikrobiol., 1930, 1, 343—364).—The activity of yeasts was slightly decreased by treatment with 0.006—0.01% I as KI, stimulated with 0.01—2.5% I, and reduced by higher concentrations. NaI gave similar results. No stimulation occurred with KIO₃ and with 0.001% I in this form fermentation was reduced. Slightly increased activity was produced by 0.0001—0.0005% of KIO₄ with a subsequent decrease at higher concentration. Elementary I had a smaller inhibitory effect than KIO₃ or KIO₄.

A. G. POLLARD.

Influence of magnesium and calcium chlorides on some fermentations. E. KEESER (Arch. exp. Path. Pharm., 1931, 160, 663—686).—The effect of the addition of CaCl₂ and MgCl₂, on, e.g., the fermentation of yeast and the hydrolysis of gelatin by trypsin depends on the concentration in which they are added as well as on the p_H . The bearing of the results on the theory of enzymes is discussed. B. LEVIN.

Action of sea-water on alcoholic fermentation. L. SANZO and F. PIRRONE (Atti R. Accad. Lincei, 1931, [vi], 13, 140—143).—When added to dextrose solutions in proportions below 20%, sea-H₂O accelerates alcoholic fermentation appreciably (20—24% for

13% of the H₂O), proportions above 20% causing marked retardation. The accelerative influence is greatest with freshly collected sea-H₂O and decreases somewhat to a const. val. after about 48 hr. if the H₂O is kept before being added to the sugar solution.

T. H. POPE.

Action of marine algæ on the alcoholic fermentation of sugar solutions. F. PIRRONE (Atti R. Accad. Lincei, 1931, [vi], 13, 137—140).—In the fresh state, or still more when dry, addition of *Ulva lactuca* (L.), Lejol, to dextrose solution greatly increases its rate of alcoholic fermentation, as measured by the amount of CO₂ liberated, the max. effect being obtained if the alga is dried in presence of ultra-violet rays. The action is due to org. substances, sol. in H₂O, EtOH, or Et₂O at room temp.

T. H. POPE.

Action of bile salts on some fermenting organisms. F. BOAS and G. NEUMÜLLER (Arch. Mikrobiol., 1930, 1, 35—59).—Addition of bile salt to nutrient media reduced the tolerance of *S. cerevisiæ* to NaCl (0.6—0.8M), but accelerated the growth of the organism where the NaCl concentration was small (0.3M). Similar effects occurred with relatively high concentrations of NaCl (1—1.6M) in nutrients containing a biocatalyst. With *S. anamensis* the crit. NaCl concentration at which stimulation ceased was lower. The effect of bile salts on *Torula* was less intense.

A. G. POLLARD.

Growth-promoting substance of yeast. N. NIELSEN (Biochem. Z., 1931, 237, 244—246).—Aq. extracts of yeast contain a substance which promotes the growth of *Avena* coleoptiles. It is sol. in EtOH or Et₂O, insol. in light petroleum, thermolabile, and probably identical with "rhizopin" extractable from fungi.

F. O. HOWITT.

Growth regulators from bacteria. P. B. JENSEN (Biochem. Z., 1931, 236, 205—210).—Three of four micro-organisms isolated from saliva were able, on growing on a meat-peptone-agar medium, to form substances which accelerate the growth of the coleoptile of *Avena*. The power of forming these growth-promoting substances is widespread amongst bacteria.

P. W. CLUTTERBUCK.

Amœboid motion as the product of protein swelling. S. W. WHITEHOUSE (Science, 1931, 73, 325—326).—HCl, lactic acid, AcOH, H₂SO₄, urea, p-phenylenediamine, and NaOH solutions of sufficient concentration cause the formation of pseudopodia and movement of the amœba towards the reagent. The effectiveness of the reagent concerned is in the same order as its action on protein. Inorg. salts inhibit movement of the amœba, stimulated by acid, in the order trivalent cations > bivalent > univalent.

L. S. THEOBALD.

Molecular organisation in amœbic protoplasm. A. A. SCHAEFFER (Science, 1931, 74, 47—51).—Data which support the view that the protoplasm of amœbæ consists primarily of sp. mols. organised into patterns are presented.

L. S. THEOBALD.

Phototropic sensitivity of *Phycomyces* as related to wave-length. E. S. CASTLE (J. Gen. Physiol., 1931, 14, 701—711).—The max. growth

response of the sporangiophores of *Phycomyces* is observed on exposure to light of wave-length 400—430 m μ . This is discussed in relation to the absorption spectrum of the photo-sensitive substance.

A. COHEN.

The yield law and *Aspergillus niger*. R. MEYER (Arch. Mikrobiol., 1930, 1, 277—303).—The mathematical treatment of experimental data of nutrient-growth curves is criticised. The slope (tangential) of the N-growth curve for *A. niger* is independent of the P present, and *vice versa*. The N-curve in the presence of high P concentration shows a point of inflexion near the origin, and the abscissal val. of the max. increases and, later, decreases as the proportion of P is raised.

A. G. POLLARD.

Autolysis of *Aspergillus niger*. G. BEHR (Arch. Mikrobiol., 1930, 1, 418—444).—In acid media with (NH₄)₂SO₄ as a source of N, autolysis of *A. niger* occurs at p_{H} 1 and is characterised by relatively small losses of wt. of mycelium, the elimination of protein, peptone, polypeptide, NH₂-acids, and NH₃, an increased chitin content, and the production of yellow pigment. Neutral autolysis occurs at p_{H} 6.5 approx. There is a rapid destruction of mycelium with the production of NH₃, but no other N compounds, complete destruction of chitin, and the formation of humic substances and a violet pigment. There is no evidence that org. acids are the products of a deamination process.

A. G. POLLARD.

Distribution of magnesium in fungus mycelium. A. RIPPEL and G. BEHR (Arch. Mikrobiol., 1930, 1, 271—276).—No Mg could be extracted from the mycelium of *Aspergillus niger* by means of org. solvents (EtOH, Et₂O, CS₂, CHCl₃, COMe₂). During growth and autolysis changes in the Mg and ash contents of the mycelium were not proportional. During autolysis in acid media the Mg decreased much less rapidly than the ash content.

A. G. POLLARD.

Action of carbon dioxide on heterotrophes. A. RIPPEL and F. HEILMANN (Arch. Mikrobiol., 1930, 1, 119—136).—The accelerated growth of *Aspergillus* resulting from increasing concentration of CO₂ may be represented by a typical nutrient-growth curve. The effect of CO₂ was more marked in acid media.

A. G. POLLARD.

Influence of acetate and phosphate on the activity of the amylase of *Aspergillus oryzae*. M. L. CALDWELL and M. G. TYLER (J. Amer. Chem. Soc., 1931, 53, 2316—2320).—The amylase has an activity dependent on p_{H} , and the nature and concentration of the buffer. An increase of NaOAc concentration from 0.01 to 0.1N leads to a slight decrease not observed with Na₂HPO₄ as buffer provided the p_{H} is suitably adjusted. The max. activity is shown at p_{H} 5.3—5.5 in 0.01N-NaOAc, which is recommended for measurements with this enzyme.

H. A. PIGGOTT.

Colouring matter of *Penicilliosis*, Solms-Laubach. A. BLOCHWITZ (Ber. deut. bot. Ges., 1931, 49, 319—323).—The solution of the colouring matter in Et₂O and EtOH is intense yellow. Alkalis produce a blood-red colour and the colouring matter by this treatment loses its solubility in Et₂O and becomes sol.

in H₂O. The solubility in CHCl₃ is similarly affected and the substance is therefore acidic. An EtOH solution gradually becomes blood-red on keeping, due to the formation of an ester. P. G. MARSHALL.

Biochemistry of micro-organisms. I. Introductory. H. RAISTRICK and W. RINTOUL. II. Quantitative methods and technique of investigation of the products of metabolism of micro-organisms. J. H. BIRKINSHAW and H. RAISTRICK. III. Quantitative examination by the carbon balance-sheet method of the types of products formed from dextrose by species of *Aspergillus*. J. H. BIRKINSHAW, J. H. V. CHARLES, H. RAISTRICK, and J. A. R. STOYLE. IV. Quantitative examination by the carbon balance-sheet method of the types of products formed from dextrose by species of *Penicillium* (including *Citromyces*). J. H. BIRKINSHAW, J. H. V. CHARLES, A. C. HETHERINGTON, H. RAISTRICK, and C. THOM. V. Quantitative examination by the carbon balance-sheet method of the types of products formed from dextrose by species of *Fusarium*. J. H. BIRKINSHAW, J. H. V. CHARLES, H. RAISTRICK, and J. A. R. STOYLE. VI. Quantitative examination by the carbon balance-sheet method of the types of products formed from dextrose by miscellaneous species of fungi. J. H. BIRKINSHAW, J. H. V. CHARLES, A. C. HETHERINGTON, and H. RAISTRICK. VII. Kojic acid (5-hydroxy-2-hydroxymethyl- γ -pyrone). J. H. BIRKINSHAW, J. H. V. CHARLES, C. H. LILLY, and H. RAISTRICK. VIII. Determination of kojic acid. J. H. BIRKINSHAW and H. RAISTRICK. IX. Production of mannitol from dextrose by species of *Aspergillus*. J. H. BIRKINSHAW, J. H. V. CHARLES, A. C. HETHERINGTON, and H. RAISTRICK. X. Determination of mannitol in fermentation solutions. H. RAISTRICK and W. YOUNG. XI. Citromycetin, a new yellow colouring matter produced from dextrose by species of *Citromyces*. A. C. HETHERINGTON and H. RAISTRICK. XII. New methoxydihydroxytoluquinone produced from dextrose by species of *Penicillium* of the *P. spinulosum* series. J. H. BIRKINSHAW and H. RAISTRICK. XIII. New type of mucilaginous material, luteic acid, produced from dextrose by *Penicillium luteum*, Zukal. H. RAISTRICK and M. L. RINTOUL. XIV. Production and chemical constitution of a new yellow colouring matter, citrinin, produced from dextrose by *Penicillium citrinum*, Thom. A. C. HETHERINGTON and H. RAISTRICK. XV. Molecular structure of citrinin. F. P. COYNE, H. RAISTRICK, and R. ROBINSON. XVI. Production from dextrose by *Penicillium spiculisporum*, Lehman, of a new polybasic fatty acid, C₁₇H₂₈O₆ (the lactone of γ -hydroxy- $\beta\delta$ -dicarboxypentadecic acid). P. W. CLUTTERBUCK, H. RAISTRICK, and M. L. RINTOUL. XVII. Products of dextrose metabolism formed by various species of fungi (*Helminthosporium*, *Clasterosporium*, etc.). J. H. BIRKINSHAW and H. RAISTRICK. XVIII. Biochemical characteristics of species of *Penicillium* responsible for the rot of citrus fruits. J. H. BIRKINSHAW, J. H. V. CHARLES, and H. RAISTRICK.

(Phil. Trans., 1931, B, 220, 1—10, 11—26, 27—54, 55—92, 93—98, 99—126, 127—138, 139—152, 153—172, 173—208, 209—244, 245—254, 255—268, 269—296, 297—300, 301—330, 331—354, 355—367).—I. The types of products formed by a large number of moulds were examined quantitatively by the C balance-sheet method in order to select those organisms giving considerable yields of products other than mycelium and CO₂. The selected moulds were then grown on a larger scale for detailed investigation. A Czapek-Dox synthetic medium was used, with dextrose as sole source of C. Pure and authenticated cultures only were employed. The results show that (1) the C balance sheets may be used as a biochemical method of classification in some families of moulds; (2) the first stage of the breakdown of dextrose may be a Cannizzaro reaction with production of mannitol and gluconic acid; (3) the mould products are very sp.; (4) moulds show remarkable powers of synthesis. Many of the products resemble the lichen acids.

II. The mould is cultivated and aerated daily in a closed system retaining all products of metabolism. The volatile products and CO₂ are absorbed in H₂SO₄ and KOH, respectively. The O₂ absorbed (and hence the R.Q.) is determined by analysis of the vitiated air. After the incubation the mycelium is separated from the solution and dried. The compounds in solution are divided into the classes (1) residual dextrose, (2) CO₂ in solution, (3) volatile acids, (4) non-volatile acids, (5) volatile neutral compounds, (6) non-volatile neutral compounds (including synthetic compounds). C is determined in each class by wet combustion (in 1 and 2 by calculation), a balance sheet is constructed, and C unaccounted for obtained by difference.

III—V. The C balance sheets for a large number of species of each of the genera *Aspergillus*, *Penicillium*, and *Fusarium* are arranged in groups, the species in each group having similar characteristics. In the case of the *Aspergilli*, the groups follow closely the accepted morphological classification of Thom and Church. With the *Penicillia* a less close agreement is found. Thom's diagnoses of the species employed are given in an appendix. With the *Fusaria* only a rough biochemical classification was attainable. Their main characteristic is the production of large amounts of EtOH. With each genus a selection was made of organisms suitable for intensive investigation; many of these were found in the *Penicillia*.

VI. C balance sheets were prepared for a number of miscellaneous species and selections made for further examination. The family *Dematiaceæ* includes the largest proportion of interesting species.

VII. The best yield of kojic acid was obtained with *A. parasiticus*, Speare, although it is formed by most species of the *A. flavus-oryzæ* group, and is claimed as a diagnostic test for this group. It is also given by *Penicillium daleæ*, Zaleski. Kojic acid is obtained from starch, sucrose, lactose, dextrose, lævulose, galactose, xylose, arabinose, mannitol, and glycerol.

VIII. Kojic acid may be determined by oxidation with alkaline I as in the Willstätter-Schudel method for aldose, if 90 min. are allowed for reaction and at least 4 times the theoretical amount of I is used. 1 Mol. of kojic acid requires 10 I. Allowance is made for dextrose present as determined polarimetrically.

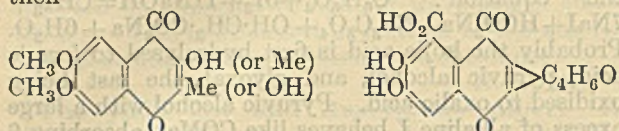
The products of reaction agree quantitatively with the equation: $C_6H_6O_4 + 5I_2 + 11NaOH = CHI_3 + 7NaI + HCO_2Na + Na_2C_2O_4 + OH \cdot CH_2 \cdot CO_2Na + 6H_2O$. Probably the kojic acid is first hydrolysed to formic acid, pyruvic alcohol, and glyoxal, the last being oxidised to oxalic acid. Pyruvic alcohol with a large excess of alkaline I behaves like COMe₂, absorbing 6 I, but yields OH·CH₂·CO₂H and CHI₃.

IX. Three groups of *Aspergilli*, white species, *A. elegans*, and *A. nidulans*, gave considerable yields of mannitol (shown as "C unaccounted for" in the balance sheets). Good yields are not obtained unless aëration is restricted. Two white species, *Ac* 55 and *Ac* 56, both give about 40% "unaccounted for"; with *Ac* 55 this is mostly mannitol, but *Ac* 56 also produces glycerol in fair amount. A mycelium of *Ac* 55 may be used to ferment a fresh quantity of dextrose solution supplied in place of the exhausted medium, yields of mannitol approaching 50% of the dextrose fermented being thus obtained. Other metabolic products are small amounts of succinic and malic acids from *Ac* 55 and malic acid and glycogen from *Ac* 56.

X. A method for determination of mannitol consists in the removal of residual dextrose by yeast fermentation, purification with Pb(OAc)₂, removal of glycerol by Et₂O-EtOH extraction, and measurement of rotation in presence of 6% borax. Tables are given connecting rotation with amount of mannitol present. The *Ac* val. gives a confirmation. A rapid method, carried out in presence of dextrose, is based on the observation that 0.9% dextrose with 6% borax is optically inactive; below 0.9% it is lævorotatory (min. at 0.5%). The solution is adjusted to 0.9% or 0.5% dextrose and 6% borax and the rotation interpreted by means of tables.

XI. Various strains of *Citromyces* give a yellow dye. The acidified filtered solution on evaporation deposits *citromycetin* (I), C₁₄H₁₀O₇·2H₂O, darkens at 263°, m. p. 283—285° (decomp.), anhyd. at 150°, gives an olive-green colour with FeCl₃ [*Ac*₂ derivative, m. p. (from abs. EtOH) 223—224° (decomp.), (from aq. KOAc with HCl) 235—236° (decomp.); *K* salt, C₁₄H₉O₇·K·H₂O; *Ba* salt, (C₁₄H₉O₇)₂Ba·3H₂O; *hydrobromide*; *Me* ester of *O-Me*₂ derivative, m. p. 178°; *O-Me*₂ derivative, m. p. 217—218° (decomp.)]. Boiling (I) with dil. acid gives CO₂ and a monobasic acid, *citromycin* (II), C₁₃H₁₀O₅, darkens 255—260°, m. p. 285—290° [*Ac*₂ derivative, m. p. 221—222°; *K* salt, C₁₃H₁₀O₅·K; *hydrobromide*; *hydriodide* (also obtained from HI and (I) and all Zeisel determinations); *O-Me*₂ derivative, m. p. 225—227° (with Me₂SO₄), also +H₂O, m. p. 183—185° (with MeI and KOH)]. 1 Mol. of (I) absorbs 8 I in alkaline solution. Hydrolysis of (I) with 33% aq. KOH under N₂ liberates COMe₂, CO₂, AcOH, and a small amount of 3 : 5 : 6-trihydroxyphthalic acid. Hydrolysis of the *Me* ester of *O*-dimethylcitromycetin with KOH in EtOH gives a *hydroxydimethoxybenzopyrone* (III), m. p. 177—180°, a *hydroxydimethoxyphthalic acid* (IV), m. p. 181—182° (decomp.) (*dimethoxyethoxyphthalic anhydride*, m. p. 195—196°), and a *product*, m. p. 242—243°. Boiling HI converts (IV) into 2-hydroxyquinol-5-carboxylic acid, m. p. 214—215° (decomp.), which on sublimation yields hydroxyquinol. (IV) is probably 3-hydr-

oxy-5:6-dimethoxyphthalic acid. (III) and (I) are then

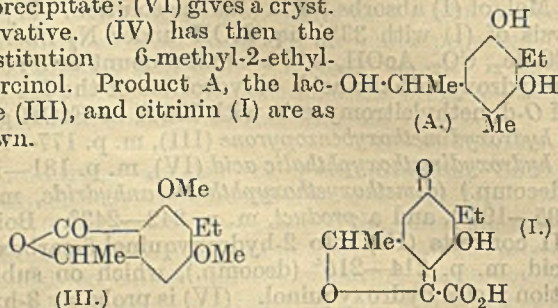


XII. Certain strains of *P. spinulosum* produce large amounts of citric acid and a dihydroxymethoxytoluquinone (I), m. p. 202—203.5°, purplish-black crystals (Ac_2 derivative, m. p. 139.5°), which is reduced by Zn and HCl to the corresponding quinol (Ac_1 derivative, m. p. 192.5—194°). NH_2OH has no action on (I).

XIII. *P. luteum*, Zukal, produces a colloidal material, luteic acid (Na salt, $[\alpha]_{5461} -47^\circ$), which on hydrolysis with $N-H_2SO_4$ gives dextrose and malonic acid. Hydrolysis with 0.25*N*-Ba(OH)₂ gives malonic acid and a polysaccharide, luteose, $[\alpha]_{5461} -46.4^\circ$, yielding dextrose on acid hydrolysis. The polysaccharide unit of luteic acid is a condensation product of 2 mols. of dextrose with 1 of malonic acid with loss of 2 mols. of H₂O, in which one CO₂H group is free, whilst the other is combined and the CHO groups are linked in such a way as to destroy their aldehydic properties.

XIV. *P. citrinum* yields a yellow colouring matter, obtained cryst. on acidification of the metabolism solution (optimum temp. for production 28—32°). Citrinin (I), C₁₃H₁₄O₅, m. p. 166—170° (decomp.), $[\alpha]_{5461} -42.8^\circ$ [Ac derivative, an oil; Et_2 derivative, b. p. 170—210°/1 mm.; Br compound, m. p. 121°; phenylhydrazide, m. p. 207° (decomp.)], is a monobasic acid, which on reduction gives dihydrocitrinin, not isolated [Ac_2 derivative darkens at 200°, m. p. 322—323° (decomp.)]. Hydrolysis of (I) with 2*N*-H₂SO₄ gives 1 mol. of CO₂, 1 mol. of HCO₂H, and two isomerides, C₁₁H₁₆O₃, product A, m. p. 128—130°, $[\alpha]_{5461} -43.7^\circ$ [Ac_3 (with Ac₂O and NaOAc), m. p. 90—91°; Ac_2 derivative (with Ac₂O and pyridine), Me_2 , b. p. 136—138°/1 mm., Me , m. p. 144—147°, and $AcMe_2$, b. p. 136—138°/1 mm., derivatives], and, in small amount, its racemate B, m. p. 169—170°. Oxidation of the Me_2 compound of A with alkaline KMnO₄ gave a dimethylated product (III), C₁₃H₁₆O₄, m. p. 122—124°, probably a lactone. Fusion of A with KOH gives a phenolic substance, C₉H₁₂O₂ (IV), m. p. 97—99° (Me_2 , b. p. 89—91°/1 mm., and Me , m. p. 63—65° derivatives). Oxidation of the Me_2 derivative of (IV) yields a product (V) C₈H₇(OMe)₂·CO₂H, m. p. 97—99°, and a product (VI) C₇H₅(OMe)₂·CO₂H, m. p. 142—146°.

XV. From colour reactions the Me_2 compound of (IV) is a methylethylresorcinol Me_2 ether. The Me_2 ether of orsellinic acid with Br gives 2:6- (or 2:4)-dibromo-orsinol Me_2 ether, m. p. 168—169°, (V) gives no precipitate; (VI) gives a cryst. derivative. (IV) has then the constitution 6-methyl-2-ethylresorcinol. Product A, the lactone (III), and citrinin (I) are as shown.



XVI. *P. spiculisporum*, Lehman, produces succinic acid and γ -hydroxy- $\beta\delta$ -dicarboxypentadecolactone (I), m. p. 145—146°, $[\alpha]_{5461} -14.76^\circ$ (Na salt, $[\alpha]_{5461} +14.98^\circ$). Hydrolysis with dil. NaOH opens the lactone ring, giving the hydroxytricarboxy-acid (II), m. p. 134—135° [Ac derivative, unstable], reconverted into (I) on heating. (I) or (II) at 180° eliminates 1 or 2H₂O, respectively, and gives dehydrated I (III), m. p. 41°, hydrolysed by alkali to an isomeride of (I), a tricarboxylic acid (IV), m. p. 87°, which reverts to (III) at 100°. With diazomethane (I) yields an Me_2 ester (V); with diazoethane (II) gives an Et_2 ester (VI). (V) with aq. NH_3 gives a Me ester diamide, m. p. 178.5°, and Me_2 ester amide, m. p. 78.5°. Fusion of (I) with KOH gives lauric, oxalic, and succinic acids and CO₂. Oxidation of (I) with acid KMnO₄ or of (II) with KMnO₄ in COMe₂ yields γ -ketopentadecolic acid (VII), m. p. 92.6°, which by Clemmensen reduction gives pentadecolic acid. Oxidation of NH_4 pentadecolate with H₂O₂ gave (VII). (VII) was synthesised as follows: *n*-octyl iodide was condensed with Et malonate to *Et n*-octylmalonate, b. p. 169°/17 mm.; *n*-octylmalonic acid, m. p. 108°, decomp. 140°, was heated to remove CO₂, thus forming *n*-decoic acid, m. p. 31°. *Et n*-decoate, b. p. 131°/17 mm., was reduced with Na to decyl alcohol, b. p. 127°/16 mm., and the latter with HI gave decyl iodide, b. p. 132°/15 mm. Condensation of the iodide with Et acetoacetate in presence of Na yielded *Et α* -acetyl-*n*-dodecoate, b. p. 170°/16 mm.; the latter with γ -carbomethoxypropionyl chloride and Na gave (VII). (VII) was also isolated from the metabolism solution.

XVII. The main metabolic products of *Helminthosporiumgeniculatum* are EtOH and mannitol; subsidiary products are glycerol and MeCHO. A *Clasterosporium* species gives mannitol and EtOH with smaller amounts of glycerol, MeCHO, succinic and probably malic acid. *Aspergillus Wentii* produces gluconic acid (present as free acid and lactone) and small amounts of mannitol and glycerol, but no EtOH. *Fumago vagans* gives gluconic acid, smaller amounts of glycerol and succinic acid, but no mannitol. It also produces a polysaccharide, $[\alpha]_{5461}^{18} +217^\circ$, composed entirely of dextrose units. A strain of *Penicillium chrysogenum* forms gluconic acid and mannitol.

XVIII. *Penicillium digitatum*, Saccardo, gives EtOAc in fair amount together with EtOH and a polysaccharide, $[\alpha]_{5461}^{30} +299^\circ$, $[\alpha]_{5461}^{18} +270^\circ$, composed entirely of dextrose units. *Penicillium italicum*, Wehmer, yields a product giving an emerald-green colour with FeCl₃ and a purple colour with bleaching-powder solution. These colour tests are of value for diagnosis of the species. J. H. BIRKINSHAW.

Tannin-decomposing micro-organisms. A. RIPPEL and J. KESELING (Arch. Mikrobiol., 1930, 1, 60—77).—Of a no. of moulds examined, only *Penicillium*, *Citromyces*, and *Aspergillus* were able to utilise tannin as a sole source of C. Tannase production by fungi occurred only in the presence of tannin, but was not associated with the ability to utilise tannin. A. G. POLLARD.

Effect of iron, zinc, and copper on the growth and pigmentation of moulds. O. METZ (Arch. Mikrobiol., 1930, 1, 197—250).—The general

effect of Fe, Zn, and Cu on pigmentation, growth, and spore production was similar for numerous fungi examined, but characteristic minor differences among individual species occurred. Details of these effects and of variations produced in the p_{H} , NH_3 and sugar contents of the media are recorded. A. G. POLLARD.

Hypothesis of mitogenetic radiation acting on the multiplication of bacteria. (MLLE.) CHOUCROUN (Compt. rend., 1931, 192, 1674—1677).—The work of Sewertzova (Ann. Inst. Pasteur, 1931, 46, 337) on the activation of *B. mesentericus* by the yeast *Nadsonia* has been confirmed; if the sheet of Pb is enclosed between two quartz plates which form the base of the culture flask the dissymmetry of multiplication of the bacteria no longer obtains. Mitogenetic action is thus due to a material effect which is propagated only along certain substances.

C. C. N. VASS.

Biological gas reactions. I. Carbon monoxide. F. FISCHER, R. LIESKE, and K. WINZER (Biochem. Z., 1931, 236, 247—267).—The bacterial reduction of CO to CH_4 in presence of H_2 necessitates a 10:1 ratio of H_2 :CO for total reduction. With higher CO content the reaction takes place in two stages, viz., $CO + H_2O = CO_2 + H_2$ and $CO_2 + 4H_2 = CH_4 + 2H_2O$, which, after an initial incubation period, proceed simultaneously with a possible concomitant reduction of CO directly to CH_4 . Part of the CH_4 is not liberated, but is utilised in synthetic processes of the cell, small amounts of org. acids, aldehydes, and higher hydrocarbons being detectable. Bacteria appear to be able to assimilate CO_2 directly, but not CO. Comparison is made between the biological reduction of CO and that by inorg. catalysis.

F. O. HOWITT.

Formation of hydrogen sulphide in the rabbit's intestine in relation to diet. M. DEGANELLO (Arch. Farm. sperim., 1931, 52, 181—184).—Sulphides may be detected in the fæces of rabbits fed on cabbage, bran, and hay, and free H_2S appears after 15 days. With a diet of bran and hay no H_2S is formed. With a diet of cabbage alone the formation of H_2S is observed in the large intestine, but the amount decreases in the rectum.

R. K. CALLOW.

Proteolytic enzymes of gelatin-liquefying bacteria. A. I. VIRTANEN and J. TARNANEN (Naturwiss., 1931, 19, 397).—*B. fluorescens liquefaciens* secretes a proteinase which hydrolyses caseinogen and gelatin with little increase of NH_2-N . Filtration of the centrifugate of a 15—20-hr. culture results in a liquid containing all this enzyme. The bacteria cells contain peptone- and dipeptide-splitting enzymes which do not readily pass out from the normal cell and also an enzyme reversibly eliminating NH_3 from aspartic acid, giving rise to fumaric acid.

F. O. HOWITT.

Molybdenum as a catalyst in the biological fixation of nitrogen. H. BORTELS (Arch. Mikrobiol., 1930, 1, 333—342).—The growth of *Azotobacter chroococcum* in an N-free nutrient was stimulated by the addition of 0.0005% of Na_2MoO_4 .

A. G. POLLARD.

Immunising action of diphtheria antitoxins purified with aluminium hydroxide. S. SCHMIDT

and A. HANSEN (Compt. rend. Soc. Biol., 1930, 105, 334—336; Chem. Zentr., 1931, i, 2220).—The prep. may be purified with $Al(OH)_3$ without loss of antitoxic power.

A. A. ELDRIDGE.

Refractometric determination of proteins. I. Numerical value of the refractive index constant α for antitoxic globulins. T. D. GERLOUGH and W. WHITE (J. Physical Chem., 1931, 35, 1328—1335).—For the diphtheria, tetanus, scarlet-fever, and erysipelas antitoxic globulins the increment in n corresponding with a change in protein concentration of 1 g. per 100 c.c. (constant α) has the value 0.00184 for concentrations between 3 and 17 g. per 100 c.c. NaOH lowers n . Euglobulin, pseudoglobulin, albumin, and pneumococcus antibody have the same value for α .

L. S. THEOBALD.

Determination of the size of sub-visible virus by centrifuging. Small-pox vaccine and fowl-plague viruses. H. BECHHOLD and M. SCHLESINGER (Biochem. Z., 1931, 236, 387—414).—The determination of the size of sub-visible viruses by methods of dispersivity and centrifuging is discussed. Centrifuging at 10,000 r.p.m. permits a determination of size up to a diameter of 0.05 μ and by fractional centrifuging a discrimination of various particle sizes is possible. Filtration through membranes calibrated by filtration of known organisms indicates a diameter of 0.2 μ for small-pox vaccine virus, whilst centrifuging gives 0.21—0.23 μ and for fowl-plague virus 0.12—0.13 μ . That these vals. refer to the actual agent is indicated by the changes in concentration on fractional centrifuging.

F. O. HOWITT.

Colorimetric and potentiometric methods for p_{H} determination of solid bacteriological media, using a dilution method based on the buffer equation. M. W. LISSE, O. G. JENSEN, and R. P. TITSLER (J. Bact., 1931, 21, 383—394).—Agar media may be diluted sevenfold (and remain liquid) without change of p_{H} . The effect of the drift of quinhydrone electrodes is eliminated by the extrapolation of vals. obtained after successive intervals of time. Quinhydrone vals. average 0.16 p_{H} lower than those of the H_2 electrode. Colorimetric methods using bromothymol-blue gave accurate vals.

A. G. POLLARD.

Physical properties and bactericidal power of solutions of certain phenyl-substituted acids. T. C. DANIELS and R. E. LYONS (J. Physical Chem., 1931, 35, 2049—2060).—The bactericidal activity of a number of Ph-substituted acids shows a marked parallelism with the solubility, the distribution coeff. between oil and H_2O , and the adsorption by activated C. The power of reducing the surface tension of H_2O is of only secondary importance. Data are given for m. p., solubility, $[H^+]$ of 0.01—0.002N solutions, viscosity, and surface tension of solutions of the acids; *p*-phenylhexoic acid has m. p. 16°. H. F. GILLBE.

Adrenal cortical hormone. G. A. HARROP, J. J. PFEIFFNER, A. WEINSTEIN, and W. W. SWINGLE (Science, 1931, 73, 684).—Normal and bilaterally adrenalectomised dogs show no characteristic changes in blood constituents or in respiratory metabolism when treated with adequate doses of cortical extract. Blood non-protein-N and urea rise, however, and

respiratory metabolism falls when a healthy bilaterally adrenalectomised animal is deprived of adequate supplies of the extract. The serum-K concentration steadily rises, secretion of urine diminishes, and urinary N and urea are suppressed. Excretion of creatine and creatinine diminishes later. Changes in blood-creatinine do not occur until the animal is very ill.

L. S. THEOBALD.

Effects of cortico-adrenal extract on the gonads. E. L. COREY and S. W. BRITTON (*Science*, 1931, 74, 101—102).—The extract, prepared by Swingle and Pfflner's method, produces precocious sexual maturity in the albino rat, especially in the female.

L. S. THEOBALD.

Determination of adrenaline in the adrenals. T. KONSCHIEGG (*Klin. Woch.*, 1931, 10, 408—409; *Chem. Zentr.*, 1931, i, 2219).—Zanfrognini's method gives low results, which depend on the time elapsing between filtration and determination. The max. is reached in 3—4 days; values then obtained accord with those afforded by other methods.

A. A. ELDRIDGE.

Electrodialysis of adrenaline. W. DEVRIENT, S. THYSSEN, and B. SOKOLOFF (*J. Pharm. Exp. Ther.*, 1931, 42, 299—319).—Among the reduction products at the cathode, obtained by the electrolysis of adrenaline in acid or alkaline solution, using varying c.d., were detected cyclic alcohols and ketones, cresol, quinol, and NHMe_2 , whilst in the oxidation products at the anode were found diketoquinone, quinhydrone, PhCHO , methylaminoacetopyrocatechol, and an unidentified red product. The last is presumed to be an unstable oxidation product, formed from 2 mols. of adrenaline, which acts as an autocatalyst in the anodic oxidations, its catalytic action being more marked under the influence of light. The highest degree of oxidation was obtained between p_{H} 6.9 and 7.2.

B. LEVIN.

Connexion between blood-cholesterol and adrenaline-sensitivity. M. VON BABARCY (*Arch. exp. Path. Pharm.*, 1931, 160, 699—702).—There is no definite relation between blood-pressure response to adrenaline and blood-cholesterol. Since the latter is influenced by several factors, a relationship between it and the vegetative nervous system is not precluded.

A. COHEN.

Action of insulin on adrenaline secretion. H. POLL (*Naturwiss.*, 1931, 19, 397—398).—The intervals required for the disappearance of the $\text{K}_2\text{Cr}_2\text{O}_7$ reaction for adrenaline in physiological saline solutions containing adrenaline-secreting ganglionic cells of the leech in presence of various amounts (10—60 units) of insulin were determined. The results, which give a logarithmic curve, are discussed mathematically.

F. O. HOWITT.

Significance of the suprarenal cortex in the prevention of insulin shock. D. H. BÖGGILD (*Biochem. Z.*, 1931, 236, 372—379).—Characteristic blood-sugar curves of normal and adrenalectomised dogs after intravenous insulin injection following starvation and carbohydrate-feeding are given. With massive insulin dosage adrenaline production by the organism does not affect the precipitous fall of blood-

sugar, but contributes towards the rapid recovery to the normal level.

F. O. HOWITT.

Mechanism of insulin action. I. Ammonia formation during muscular activity. H. SCHWARZ and M. TAUBENHAUS (*Biochem. Z.*, 1931, 236, 474—492).—Muscular work in man induces an increase in blood- NH_3 which, however, does not appear or is substantially less when insulin is previously administered. The diminished NH_3 -production is a reversible process; administration of sugar inhibits this action of insulin, which is probably due to an inhibition of adenylic acid degradation. The relation between the blood-sugar-lowering action of insulin and the change of NH_3 metabolism following work together with the possible analogous changes in creatinephosphoric acid are discussed.

F. O. HOWITT.

Mechanism of insulin action. H. SCHWARZ and M. TAUBENHAUS (*Klin. Woch.*, 1931, 10, 313—314; *Chem. Zentr.*, 1931, i, 2355).—In slightly fatiguing work a marked increase in blood- NH_3 occurs unless insulin is injected. The increase is connected with the decomp. of adenylic acid to inosic acid; the fission is arrested by insulin.

A. A. ELDRIDGE.

Insulin. Effects on normal rabbits protected from hypoglycæmia by ingestion of dextrose. R. F. LOEB, E. G. NICHOLS, and B. H. PAIGE (*Arch. Int. Med.*, 1931, 48, 70—81).—Although there are marked individual differences in the blood-sugar of rabbits receiving the same treatment, it appears that small doses of insulin (7 units per kg. body-wt.) are more effective on hyperglycæmia produced by administration of dextrose than large ones (75 units). Glycogen deposition in the liver is suppressed by insulin in the presence of hyperglycæmia. No histological effects are observed on the adrenals, neither is there a toxic effect on normal rabbits receiving 300—500 units of insulin.

A. COHEN.

Extraction of insulin from blood. S. MAUGERI (*Aten. Parm.*, 1929, 1, 113—117; *Chem. Zentr.*, 1931, i, 2240).—Defibrinated blood (10 c.c.) is rubbed to a homogeneous mass with finely-powdered picric acid (0.08 g.) and COMe_2 (8 c.c.), centrifuged, and the residue is washed with 8 c.c. of 70% COMe_2 followed by 8 c.c. of H_2O . COMe_2 is removed from the liquid in a desiccator, the ppt. formed being centrifuged, washed with Et_2O followed by alcoholic HCl (2 c.c.), and again centrifuged. The acid liquid is then treated with 10 vols. of COMe_2 , the ppt. (containing insulin) being centrifuged, washed with Et_2O , and dried over H_2SO_4 .

A. A. ELDRIDGE.

Insulin reaction of the leucocytes of the blood. W. STOCKINGER and K. KOBER (*Klin. Woch.*, 1931, 10, 389—392; *Chem. Zentr.*, 1931, i, 2219).

A. A. ELDRIDGE.

Mol. wt. of insulin. B. SJÖGREN and T. SVEDBERG (*J. Amer. Chem. Soc.*, 1931, 53, 2657—2661).—A more detailed account of work previously reviewed (this vol., 658).

H. BURTON.

Thyroxine in muscle. B. KOMMERELL (*Arch. exp. Path. Pharm.*, 1931, 161, 141—153).—A myxœdematous condition develops in thyroidectomised dogs fed on a meat-free diet, and a rise in the basal metabolism occurs when meat from a normal animal is

given. No rise occurs when meat from a thyroidectomised animal is administered. Thyroxine occurs, in small amount, in the muscles of normal, but not of thyroidectomised animals. P. G. MARSHALL.

Thyroxine and nutrition. B. KOMMERELL (Arch. exp. Path. Pharm., 1931, 161, 173—180).—The stimulating effect of thyroxine on the basal metabolism of thyroidectomised dogs lasts several days longer with a meat diet than with pure carbohydrate feeding, although the maximal effect obtainable is independent of the type of diet. The R.Q. is similarly affected. P. G. MARSHALL.

Concomitance of male and female sexual hormones. S. LOEWE, H. E. VOSS, and E. ROTHSCCHILD (Biochem. Z., 1931, 237, 214—225).—All sexual hormone preps., including those from one kind of organ, contain both male and female sexual hormones. The ratio of the activity of the female sexual hormone (F.S.H.) to that of the male sexual hormone (M.S.H.), as shown by animal tests, is designated by *Q*, the val. of which varies from 0.15 for M.S.H. preps. to 620 for F.S.H. preps., demonstrating the non-identity of the two hormones. Highly-purified crystalline F.S.H. has the val. for *Q* of 620, indicating a contamination with traces of M.S.H. The F.S.H. from yeast and bile also contains M.S.H.

F. O. HOWITT.

Action of sexual hormones (ovarian and anterior pituitary) on the gas exchange. A. VON ÁRVAY (Biochem. Z., 1931, 237, 199—213).—The typical action on the oestrous cycle of normal and spayed rats due to administration of ovarian preps. is accompanied by an increase in basal metabolism. Anterior pituitary extracts have a similar action in normal female but not in spayed or male rats, indicating a liberation of the ovarian hormone under the influence of the extract, which, however, also exhibits the power to inhibit oestrus and to reduce the O_2 consumption in female rats. This latter effect is not correlated to the inhibition of oestrus, but is a specific metabolic action of the anterior pituitary extract, being apparent also in male and ovariectomised female rats.

F. O. HOWITT.

Carotene and vitamin-A. (MLEL.) D. VAN STOLK, J. GUILBERT, and H. PÉNAU (Compt. rend., 1931, 193, 209—210).—Attempts to fractionate the pigment from carrots are described. Xanthophyll is shown to be absent. A. A. LEVI.

Pure carotene and vitamin-A. D. VAN STOLK, J. GUILBERT, H. PÉNAU, and H. SIMONNET (Bull. Soc. Chim. biol., 1931, 13, 616—633).—A more detailed account of work already noted (this vol., 880).

Relation of the growth-factor to carotene. H. VON EULER, V. DEMOLE, A. WEINHAGEN, and P. KARRER (Helv. Chim. Acta, 1931, 14, 831—833).—The extract, prepared in the usual way, of yellow (autumn) chestnut leaves gave no carotene spectrum, and also showed no marked vitamin-A effect, thus indicating the dependence of the latter on the presence of carotene. The statements that a H_2O -sol. active extract can be prepared from the wheat germ, and that no active substance, but a toxic one, exists in the fat-sol. materials (B., 1925, 520) are not confirmed. H. A. PIGGOTT.

Carotene from lettuce and its relation to vitamin-A. H. S. OLCOVICH and H. A. MATTILL (Proc. Soc. Exp. Biol. Med., 1930, 28, 240—241).—Lettuce (150 kg.) lipins afforded 200 mg. of carotene. When kept at room temp., or in 24 hr. at 105° , the hexagonal crystals became isometric, bleached, and inactive. Carotene is best preserved in Et laurate containing 0.1% of quinol. Vitamin-A-deficient rats were cured of xerophthalmia by daily doses of 0.005 mg. of carotene. CHEMICAL ABSTRACTS.

Vitamin of growth. II. Action of α - and β -carotene on rats. R. KUHN and H. BROCKMANN (Ber., 1931, 64, [B], 1859—1864).—The growth-promoting power of α -carotene is of the same order of magnitude as that of β -carotene. Treatment of carotene with diazomethane has little effect on its growth-promoting power. Within the limits of experimental error, the activity of β -carotene does not depend on its origin from carrot through the di-iodide, from spinach, or from nettle exclusively by fractional crystallisation. β -Carotene from paprika behaves somewhat differently. Pronounced changes in the effect of mixtures of α - and β -carotene are not caused by heating at 110° or by fractional adsorption on fibrous $Al(OH)_3$. It is improbable that a hydrocarbon with properties intermediate between those of α - and β -carotene is present in carrot. *iso*Carotene appears to be inactive. As far as unchanged hydrocarbon persists in the rat, there is no mutual transformation of α - and β -carotene. Preps. of carotene with approx. the same growth-promoting power do not lead to the production of equal quantities of vitamin-A in the liver, as judged by the behaviour towards $SbCl_5$.

H. WREN.

Influence on growth of the isomeric carotenes and their first hydrogenation products. H. VON EULER, P. KARRER, H. HELSTRÖM, and M. RYDBOM (Helv. Chim. Acta, 1931, 14, 839—842).—Both α - and β -carotenes exert a marked influence on the growth of animals, the ratio of their activities being about 8 : 10, but they become more nearly equal as the treatment is continued. Conversion of carotene into its tri-iodide, and decomp. of this with $Na_2S_2O_3$, does not affect its physiological activity. The dihydrocarotenes have the same activities as the corresponding carotenes when given in three times the quantity.

H. A. PIGGOTT.

Behaviour of the vitamin-A content of butter on heating. A. SCHEUNERT and E. WAGNER (Biochem. Z., 1931, 236, 29—34).—The domestic operations of baking, roasting (meat), and browning do not materially decrease the vitamin-A content of butter as shown in feeding experiments with young growing rats. Considerable but not complete injury is caused by heating in an open pan at 160 — 200° for a long time. P. W. CLUTTERBUCK.

Manner of action of the vitamin-B complex.

I. E. ABDERHALDEN. II. E. ABDERHALDEN and V. VLASSOPOULOS (Pflüger's Archiv, 1931, 226, 723—737, 808—815; Chem. Zentr., 1931, i, 2256—2257).—I. Convulsive symptoms in pigeons receiving polished rice can be effectively treated by administration of dried liver, kidney, muscle, or brain of normal pigeons or of those which died or were killed during convul-

sions. The liver is the most efficacious. In many cases thyroxine is effective. So-called vitamin action is probably a complex process.

II. The dehydrase activity of the liver, muscle, and cerebral tissue of pigeons suffering from the effects of an exclusive diet of polished rice is less than that of normally fed or fasting pigeons. If yeast or the above tissues (I) were administered during convulsions the dehydrase activity increased. Lack of vitamin-B or B_1 leads primarily to disturbance of oxido-reduction processes, and the observed symptoms result from defective conversion of metabolic products.

A. A. ELDRIDGE.

Action of rice phosphatase. S. BELFANTI (Giorn. Chim. Ind. Appl., 1931, 13, 270—274).—The deficiency of enzymes like phosphatase, phytase, and those acting on fats and carbohydrates is claimed to be the cause of avitaminosis-B. Vitamin-B is probably identical with these enzymes.

O. F. LUBATTI.

Isolation of the antineuritic vitamin. A. SEIDELL and V. BIRCKNER (J. Amer. Chem. Soc., 1931, 53, 2288—2295).—The method of adsorption on fuller's earth, re-extraction with alkali, benzoylation of the residue after adjustment of the p_H to 3.0 and removal of inorg. salts, and precipitation of the active substance with $COMe_2$ has yielded extracts of the antineuritic vitamin more potent than Jansen and Donath's crystals.

H. A. PIGGOTT.

Irradiated ergosterol. A. WINDAUS (Proc. Roy. Soc., 1931, B, 108, 568—575).—An account of work, in part previously abstracted (this vol., 881). Irradiated ergosterol is treated with maleic anhydride at room temp. for 3 days. The fraction which does not react yields a cryst. highly-antirachitic substance, $C_{27}H_{42}O$, m. p. 122—123°, $[\alpha]_D^{25} +138^\circ$, $[\alpha]_{589}^{25} +169^\circ$ in $COMe_2$, with main absorption band at 265—270 μ . The relationship of this product to "calciferol" (this vol., 881) is discussed. It is thought that the mol. formula, the alcoholic OH group, and double linkings of ergosterol are not changed by conversion into vitamin-D, but that a steric rearrangement occurs.

A. COHEN.

Influence of wave-length in ergosterol irradiation. F. LAQUER (Deut. med. Woch., 1931, 57, 243—244; Chem. Zentr., 1931, i, 2356).—Ergosterol protected from radiation of wave-length less than 280 μ is in large doses at least as toxic as totally irradiated ergosterol.

A. A. ELDRIDGE.

Activation of ergosterol with radium emanation. R. B. MOORE and T. DEVRIES (J. Amer. Chem. Soc., 1931, 53, 2676—2681).—Activation of ergosterol by Nt gives a product which is about 0.01 as potent as that obtained by ultra-violet irradiation. The rate of activation, but not the potency, is increased by stirring.

H. BURTON.

Effects of ultra-violet rays on the vitamin-D content of plants as compared with the direct irradiation of the animal. M. LOJKIN (Contr. Boyce Thompson Inst., 1931, 3, 245—265).—Plants grown under greenhouse conditions do not produce vitamin-D. Ultra-violet rays from the solar spectrum produce very slight antirachitic properties in lettuce, lucerne, spinach, and soya bean. Rays from

Hg-vapour lamps have much greater effect. Cabbage was unaffected by either source of radiation. Cut plants had greater antirachitic properties than whole plants after exposure to Hg lamps. Irradiated plants retained their activity for at least 24 hr. The effects of various light filters are recorded and control experiments with rats described. The min. exposure to ultra-violet rays required to produce vitamin-D in plants is much greater than that requisite for the complete protection of the animal by direct irradiation.

A. G. POLLARD.

Vitamin content of the sour milk preparations yoghurt, kephir, and saya. K. A. FORSTER (Biochem. Z., 1931, 236, 276—297).—Compared (biologically) with the fresh milk from which they were derived, yoghurt is richer in A and D, but contains less B and C, kephir is weaker in A, C, and D and of equal content in B, whereas saya is much richer in A and C and about equal in B and D. An increased vitamin content is due to bacterial synthesis.

F. O. HOWITT.

Structure of protoplasm. W. SEIFRIZ (Science, 1931, 73, 648—649).—Details of the structure of the hyaline protoplasm of onion cells as revealed by the Spierer lens are described.

L. S. THEOBALD.

Physico-chemical studies on proteins. V. Comparative study of the peptisation of the protein complex in various seeds and grains. E. V. STAKER and R. A. GORTNER (J. Physical Chem., 1931, 35, 1565—1603).—The peptisation produced by 0.5M aq. salt solutions has been studied. A lyotropic series of anions is recognisable for most of the protein complexes. With barley, oats, and wheat the order is $KF < K_2SO_4 < KCl < KBr < KI$; with the pea it is $SO_4 < Cl < F < Br < I$; with radish and rape meals the order is the same as for barley, and with mustard meal it is $F < I < SO_4 < Br < Cl$. Legumes show some variation; for the halogens the order is $F < Cl < Br < I$. In the case of maize, millet, and teosinte meals the lyotropic effect is much less pronounced, and for sorghum seeds none could be demonstrated. The effects for Brazil nut, hemp, flax, and sunflower meals are discussed. The peptisation of the various groups of related seeds is distinct and characteristic for each group. Protein "solubility" is in reality protein peptisation and the existence of true plant "albumins" as definite chemical entities is questioned.

L. S. THEOBALD.

Action of bromine on plant-tissues. F. M. WOOD (Ann. Bot., 1931, 45, 421—423).—Plant-tissues which give a pink colour with Cl_2 give a dark red colour with Br. Washing with hot H_2O destroys traces of oxonium salts and renders the sections more transparent. The cortical tissues of *Cycas revoluta*, *Larix europæa*, and *Bambusa* sp. give a blue colour with Na_2HPO_4 after washing with cold H_2O . The use of Cl_2 is preferable to that of Br.

P. G. MARSHALL.

Stimulated development of the winter buds of *Hydrocharis morsus ranae*. L. M. MATSUBARA (Planta [Z. wiss. Biol.], 1931, 13, 695—715).—The dormant period of the winter buds is arrested by fumigation with HCN (gas from 1.0—1.5 g. KCN in 3 litres at 0—5°). Subsequent development occurs

only if the buds are exposed to light. Treatment with AcOH or with H₂ produces a similar but smaller effect.

A. G. POLLARD.

Microchemical and morphological study of the developing endosperm of maize. L. LAMPE (Bot. Gaz., 1931, 91, 337—376).—Changes in the starch, total- and reducing-sugar contents in the developing cells are recorded.

A. G. POLLARD.

Influence of increasing amounts of iodide, iodate, and periodate on germination and early development of culture plants. K. SCHARRER and W. SCHROPF (Biochem. Z., 1931, 236, 187—204).—The influence of increasing amounts of KI, KIO₃, and KIO₄ on germination and development of wheat, rye, barley, and oats in lower moor and sandy clay soil is investigated. Higher doses of I injure germination and further development, iodide having the most and periodate the least injurious effect. The sensitivity of the plants decreases in the following order: oats, wheat, rye, barley. The yield of crop is decreased by high I doses, most strongly with iodide and least with periodate. The injury to germination, embryonic development, and yield on addition of iodide is less in the sandy clay than in the lower moor soil, due to its reaction and colloidal content, the I being largely precipitated by the Ca content.

P. W. CLUTTERBUCK.

Translocation of materials in the vascular bundles of the higher plants. W. SCHUMACHER (J. wiss. Bot., 1930, 73, 770—821; Bied. Zentr., 1931, 60 A, 200—201).—The translocation of N takes place through the sieve tubes of the phloem. Attempts to induce artificial movement through the parenchyma were unsuccessful.

A. G. POLLARD.

Fat metabolism of leaves. I. Detached and starved mature leaves of Brussels sprout (*Brassica oleracea*). A. C. CHIBNALL and P. N. SAHAI (Ann. Bot., 1931, 45, 489—502).—An Et₂O extract of the leaves was similar in composition to that of cabbage leaves. No change in the phosphatides or glycerides occurs in detached leaves, even when these are kept in the dark until the chlorophyll has almost disappeared. Sugars in the lamina increase during such isolation. In leaves kept in the dark a continuous breakdown of protein occurs (22.3—13.2 g. per kg.) despite the abundance of carbohydrate present.

P. G. MARSHALL.

Gas contained in *Valonia utricularis* (Roth), Ag. S. COLLA (Atti R. Accad. Lincei, 1931, [vi], 13, 149—153).—When kept submerged, the gas present in this alga contains CO₂ (2.5—7.1% according to the age of the organism) only in the morning. The content of O₂ increases as the day advances and may reach 70% in very bright weather (cf. A., 1930, 1072).

T. H. POPE.

Katharometer in measurement of respiration. W. STILES and W. LEACH (Ann. Bot., 1931, 45, 461—488).—An apparatus is described for use with a closed glass respiration chamber, by means of which both CO₂ and O₂ changes can be measured. The sensitivity of the moving-magnet galvanometer can be varied, but in actual use a deflexion of 1 mm. corresponds with a change in CO₂ content of 0.007%.

P. G. MARSHALL.

Phæohæmin b. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1931, 235, 240—242).—The prep. of hæmin from phæophorbide b is described; the spectrum is closely related to that of *Spirographis* hæmin (this vol., 109).

P. W. CLUTTERBUCK.

Pigment of the elderberry (*Sambucus nigra*, Linn.). T. J. NOLAN and H. M. T. CASEY (Proc. Roy. Irish Acad., 1931, 40, B, 56—66; cf. A., 1927, 252).—The chlorides of chrysanthemine and "sambucicyanin," a bimol. compound of chrysanthemine and a pentose glucoside of cyanidin, were isolated. The pentose is not rhamnose.

A. A. LEVI.

Formation of anthocyanin pigments in the flower of *Iris germanica*. A. GUILLERMOND (Compt. rend., 1931, 193, 112—114).—Oxyflavonols are the precursors of anthocyanins; occasionally both substances are absorbed in the cells by colloids of unknown constitution.

C. C. N. VASS.

Micro-chemical characteristics and cytological mode of formation of anthocyanin pigments. A. GUILLERMOND (Compt. rend., 1931, 192, 1581—1583).—In certain flowers anthocyanin is present in the vacuoles in true solution or admixed, or as a complex adsorption colloid with the tannins. Anthocyanin arises as a transformation of hydroxyflavonols.

C. C. N. VASS.

Chemical effect of a Mendelian factor for flower colour. R. S. MONCREIFF (Nature, 1931, 127, 974—975).—In *Pelargonium* the effect of the factor which converts salmon-coloured flowers into rose is to substitute cyanin almost completely for pelargonin.

L. S. THEOBALD.

Chlorophyll defect. H. VON EULER and D. RUNEHJELM (Arkiv Kemi, Min., Geol., 1931, 10, A, no. 10, 8 pp.).—Ungerminated barley contains more catalase than barley after several days' germination. That the catalase content of chlorophyll-defective mutants of barley is less than that of normal grains is confirmed (cf. A., 1930, 498). The chlorophyll-defective tissue of certain species of *Pelargonium*, in contrast to barley, contains more total Mg than that normal in chlorophyll.

F. O. HOWITT.

Chlorophyll defect. H. VON EULER and O. MORITZ (Arkiv Kemi, Min., Geol., 1931, 10, A, No. 11, 15 pp.).—A yellow mutant of barley showed no difference in catalase activity between the green and chlorophyll-poor parts of the germinated seed. In chlorophyll-defective cabbage the decrease in catalase activity with age is related to the chlorophyll content, the former decreases both in yellow and white leaves parallel with decrease in ability to turn green, this being true also for the etiolated cotyledons of *Cucurbita*. That no parallelism exists between catalase activity and chlorophyll content is shown by chlorophyll-free tissue being rich in catalase. The tryptophan content of chlorophyll-free cotyledons is higher than normal.

F. O. HOWITT.

Chlorophyll mutants of barley. H. NILSSON (Arkiv Kemi, Min., Geol., 1931, 10, A, No. 12, 34 pp.).—The amylase activities of homo- and hetero-zygotic and white chlorophyll-defective homozygotic barley show no difference. The O₂-consumption of green parts of the embryo is greater than that of the white,

no difference existing between mono- and heterozygotes. Presence of KNO_3 (0.2—0.3%) in the culture media has no influence on the O_2 -consumption. Green leaves have a slightly higher ash than white.

F. O. HOWITT.

Carotenoid of *Citrus aurantium*. P. G. F. VERMAST (Naturwiss., 1931, 19, 442—443).—The properties of xanthophyll from fruits are examined. That from *C. aurantium* is the same as that obtained by Tswett, and has vitamin-A properties.

A. J. MEE.

Sapogenin of guaiacum bark. II. Identity of guagenin with the sugar-beet sapogenin. E. WEDEKIND and W. SCHICKE (Z. physiol. Chem., 1931, 198, 181—184; cf. this vol., 491).—Beet resin-acid, when hydrolysed by dil. H_2SO_4 , yields a sapogenin identical with guagenin. The guagenin regenerated from the Ac derivative gives combustion figures which correspond closely with the formula $\text{C}_{30}\text{H}_{48}\text{O}_3$.

J. H. BIRKINSHAW.

Distribution of saponins. L. ROSENTHALER (Pharm. Zentr., 1931, 72, 417—418).—A discussion of the relationships between terpenes and saponins. The fact that plants which are rich in the one substance are poor in the other is explained by the different initial polymerisation of the C_5 isoprene residue; on the one hand terpenes are formed and on the other sapogenins which by further condensation with sugars give saponins.

E. H. SHARPLES.

Natural polyævans. II. Polyævans of the leaves of *Yucca filamentosa*. III. Formation of polyævans in *Helianthus tuberosus*. H. H. SCHLUBACH and W. FLÖRSHEIM (Z. physiol. Chem., 1931, 198, 153—164; cf. A., 1929, 914).—II. The MeOH extract of dried yucca leaves, after removal of hexoses and sucrose by fermentation, gave a dilævan agreeing in rotation with sinistrin A and yielding 3:4:6-trimethyl-*h*-fructose after methylation and hydrolysis. The yucca product is hydrolysed by yeast enzyme.

III. The leaves of *Helianthus tuberosus* harvested in July and September contain no polyævans, although these are present in the axes (cf. A., 1925, i, 618).

J. H. BIRKINSHAW.

Presence of maclurin in sapwood of the catch-producing acacias. M. NIERENSTEIN (J. Indian Chem. Soc., 1931, 8, 143—145).—Extraction of the sapwood of *Acacia catechu*, *A. catechuoides*, and *A. Sundra* affords maclurin (0.4 g. per kg.) but no quercetin. The biosynthetic relationships of *l*-leuco-maclurin glycol with acacatechin, isoacacatechin, and maclurin are discussed.

J. W. BAKER.

Principal sugar of Kaá-hé-é (*Stevia Rebaudiana*, Bertoni). II. Products of enzymic hydrolysis of stevioside: dextrose and steviol. M. BRIDEL and R. LAVIELLE (Compt. rend., 1931, 193, 72—74).—Stevioside, $\text{C}_{38}\text{H}_{60}\text{O}_{18}$, is hydrolysed by the digestive juices of the edible snail to dextrose and a phenol, steviol, $\text{C}_{20}\text{H}_{30}\text{O}_3$, m. p. 217°; $[\alpha]_D -94.66^\circ$.

C. C. N. VASS.

Rebaudin of Dieterich and impure stevioside. M. BRIDEL and R. LAVIELLE (Bull. Soc. Chim. biol., 1931, 13, 656—657).—The rebaudin of Dieterich is impure stevioside.

C. C. N. VASS.

Biochemistry of *Salix*. III. A new β -glucoside, salipurposide, from the bark of *Salix purpurea*, L. C. CHARAUX and J. RABATÉ (Bull. Soc. Chim. biol., 1931, 13, 590—597).—Extracts of the bark of male and female trees have been prepared and their rotations and reducing powers before and after enzymic hydrolysis determined. *Salicopurposide*, $\text{C}_{21}\text{H}_{22}\text{O}_{10}$, was extracted in 1.87% yield from the bark by 90% EtOH and crystallised from H_2O , $[\alpha]_D^{20} -116.87^\circ$. It is non-reducing, but yields on hydrolysis 42.5% of dextrose and 61.6% of a phenol, *salipurpol*, $\text{C}_{15}\text{H}_{12}\text{O}_5$, m. p. 256.5°. C. C. N. VASS.

Salireposide, new glucoside from the bark of *Salix repens*, L. N. WATTIEZ (Bull. Soc. Chim. biol., 1931, 13, 658—667).—The bark is extracted with 70% EtOH in presence of CaCO_3 . After distillation of the EtOH and removal of chlorophyll, salireposide crystallises on keeping; subsequent treatment with basic Pb acetate ppts. salicoside. Anhyd. *salireposide*, m. p. 206°, $[\alpha]_D +36.78^\circ$, is non-reducing; on hydrolysis with dil. H_2SO_4 it yields dextrose, BzOH, and an unknown phenol.

C. C. N. VASS.

Gaultherioside, a new glucoside obtained from *Gaultheria*. J. RABATÉ and S. RABATÉ (Bull. Soc. Chim. biol., 1931, 13, 604—615).—In addition to monotropitin and sucrose, the EtOH extract of fresh *G. procumbens*, L., contains a mixture of sugars from which after hydrolysis *gaultherioside*, m. p. 185°, $[\alpha]_D -58.07^\circ$ (anhyd.), containing 1.44% H_2O has been isolated. It is non-reducing and on hydrolysis with dil. H_2SO_4 yields dextrose, xylose, and EtOH. It is not hydrolysed by rhamnodiastase. C. C. N. VASS.

Pollen and pollen extracts. VII. Glucoside from certain grass pollens. M. B. MOORE and E. E. MOORE (J. Amer. Chem. Soc., 1931, 53, 2744—2746).—An aq. extract of the pollens of *Dactylis glomerata*, L., and *Phleum pratense*, L., gradually deposits crystals of *dactylin*, $\text{C}_{23}\text{H}_{28}\text{O}_{15}$, m. p. 183—185° (corr.), hydrolysed by 5% H_2SO_4 to 1 mol. of a substance, m. p. 298—300° (corr.; decomp.), and 2 mols. of (probably) a hexose. *Dactylin* is not hydrolysed by emulsin.

H. BURTON.

Pectic substances of the carrot and their decomposition by *Bacillus carotovorus*. H. W. BUSTON and H. F. KIRKPATRICK (Ann. Bot., 1931, 45, 519—525).—The protopectin content of the cortex is approx. twice that of the stele. If the powdered tissue is extracted with boiling $N/75$ HCl, only the protopectin is removed, the middle lamella pectin being unattacked, whilst $(\text{NH}_4)_2\text{C}_2\text{O}_4$ extracts all pectins. The pectins of the cortex and stele have similar constitutions, as evidenced by the furfuraldehyde, uronic anhydride, and OMe-group contents, and both are equally efficient as nutrients for *B. carotovorus*.

P. G. MARSHALL.

Plant gums. F. WEINMANN (Biochem. Z., 1931, 236, 87—98).—The separation of *d*-glycuronic acid from gum-arabic and cherry gum and its purification are described.

P. W. CLUTTERBUCK.

Harmine: preparation from the root *Peganum harmala*, L. A. D. ROZENFELD (Farm. Zhur., 1930, 183—186).—A 3% yield was obtained.

CHEMICAL ABSTRACTS.

Plant chemistry. XVIII. Crystalline protein in the secretions of the Anacardiaceae. H. MOLISCH (Ber. deut. bot. Ges., 1931, 49, 324—327).—A cryst. protein is present in *Manganifera*, *Odina*, *Schinus*, and *Rhus*. P. G. MARSHALL.

Tyramine and hydroxytyramine, precursors of the black pigments of *Sarothamnus scoparius*. Wimm. H. SCHMALFUSS and A. HEIDER (Biochem. Z., 1931, 236, 226—230).—Hydroxytyramine (*tricarbo-methoxy*-compound, m. p. 92—93°; *tribenzoate*, m. p. 141°) and tyramine (*dicarbo-methoxy*-compound, m. p. 99—100°) are the precursors of black pigments in broom pods. P. W. CLUTTERBUCK.

Chemical composition of tobacco. I. Organic bases and acids of fresh leaves. K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1931, 7, 121—132).—An aq. extract is treated with Pb(OAc)₂ and the ppt. discarded. After removal of Pb the filtrate is made alkaline and distilled in steam; nicotine passes over (3 g. per kg.). Phosphotungstic acid ppts. adenine, histidine (with some arginine), and betaine from the residual liquid after acidification with H₂SO₄. If the powdered leaf is extracted with very dil. HCl and Pb(OAc)₂ added, the acids are precipitated. The salts are decomposed by H₂S and the acids esterified and fractionally distilled. Malic (1.3%), citric (0.6%), and oxalic acids (0.09%) are present. P. G. MARSHALL.

[Degradation of nicotine in tobacco.] A. FAITELOWITZ (Biochem. Z., 1931, 237, 90—91).—The contention of Fodor and Reifenberg (this vol., 402) concerning the results of the author (A., 1930, 1484) is refuted. F. O. HOWITT.

Effect of evaporation and radiation on nicotine solutions. J. HIGGINS, P. L. EWING, and H. A. MCGUIGAN (J. Pharm. Exp. Ther., 1931, 42, 213—216).—Nicotine assayed by means of its action on the dog's blood-pressure is not destroyed when heated in a closed vessel at 100°, but is destroyed when irradiated by means of a Hg vapour lamp. The effect of irradiation by a C arc lamp is only small.

W. O. KERMACK.

Leguminous bacteria and plants. X. Activity of leguminous bacteria and the utilisation of fixed nitrogen from nodules of legumes by non-leguminous plants. A. I. VIRTANEN and S. VON HAUSEN (Z. Pflanz. Düng., 1931, 21 A, 57—69).—N compounds formed in root nodules of legumes diffuse into the soil and are utilisable, as such or after ammonification, by other non-leguminous crops. In a mixed crop of peas and oats the latter gained additional N if the ratio of peas : oats was 1 : 1 or 2, but with a smaller ratio the growth of both plants declined. This effect varies with the *p_H* of the medium. Similar results are obtained with other combinations of crops.

A. G. POLLARD.

Constituent of *Euphorbia formosana*, Hay. I. J. SHINODA and C. PING-KUN (J. Pharm. Soc. Japan, 1931, 51, 50—51).—Acidification of a MeOH extract of the roots of *E. formosana*, Hay, and extraction with Et₂O gives an acidic substance, C₁₅H₁₀O₈, m. p. 337—338°, containing 2 OMe and 2 OH groups (*Ac*₂ derivative, m. p. 298—300°), and yielding ellagic acid (tetra-acetate, m. p. 342—343°) on demethylation.

It is, therefore, an *ellagic acid Me₂ ether*, which, because it is not identical with the product previously described (A., 1905, i, 900), and because of its colour reaction with FeCl₃, contains the OH groups in different C₆H₄ rings. R. S. CAHN.

Chemical composition of mulberry leaves. Y. KISHI (Bul. Sci. Fak. Terkultura Kjusu, 1931, 4, 173—190).—The protein in dried leaves and H₂O in fresh leaves decrease from spring to autumn. The *p_H* of the leaf sap increases slightly from spring onwards.

P. G. MARSHALL.

Chemical examination of the roots of *Hygrophylla spinosa*. N. H. GHATAK and S. DUTT (J. Indian Chem. Soc., 1931, 8, 23—28).—Exhaustion of the dried roots of *H. spinosa* with EtOH or other org. solvents yields a phytosterol (cf. J.C.S., 1920, 147, 1624), *hygrosterol*, C₂₈H₄₆O, m. p. 194°, [α]_D²⁵ (in CHCl₃) +27.8° (*Ac* derivative, m. p. 208°; *hydrobromide*, m. p. 59°; *dibromohydrobromide*, m. p. 138—139°; *digitonide*, decomp. 220—230°), together with maltose and an oil. G. DISCOMBE.

Nutmeg oil. E. BUREŠ and H. MLÁDKOVÁ (Časopis Českoslov. Lék., 1930, 10, 317—323; Chem. Zentr., 1931, i, 1987).—The oil of *Nigella sativa* seeds (33.4%) had *d*¹⁵ 0.8960, acid val. 29.42, sap. val. 201.98, ester val., 172.56, I val. 107.40, Reichert-Meissl val. 3.379, Polenske val. 0.535, Hehner val. 89.25, Ac val. 23.89. Myristic and telfairic acids were isolated. A. A. ELDRIDGE.

Paeony seed oil. E. BUREŠ and B. ŠUSTEROVÁ (Časopis Českoslov. Lék., 1930, 10, 293—299, 323—325; Chem. Zentr., 1931, i, 1987).—Characteristic data are recorded. A. A. ELDRIDGE.

Expressed Brazil-nut oil. H. A. SCHUETTE and W. W. F. ENZ (J. Amer. Chem. Soc., 1931, 53, 2756—2758).—The expressed oil (B., 1930, 1162) contains myristin (0.48%), palmitin (13.74%), stearin (5.45%), olein (42.79%), and linolein (26.54%). The olein and myristin contents are lower than those of the residual oil (*loc. cit.*), but the stearin content is higher.

H. BURTON.

Occurrence of calcareous and siliceous substances in plant cells. F. NETOLITZKY (Bull. Fac. Stiinte Cernauti, 1928, 2, 320—325; Chem. Zentr., 1931, i, 2070).—A discussion. A. A. ELDRIDGE.

Preparation of skeletal substances from incrustated cellwalls with the aid of chlorine dioxide. III. The whole-number relation of 3C₆H₁₀O₅ of cellulose to 1C₅H₈O₄ of sparingly soluble xylan to 1CO·CH₂ of acetyl in the skeletal substance of red beechwood (*Fagus sylvatica*). E. SCHMIDT, Y. C. TANG, and W. JANDEBEUR (Cellulosechem., 1931, 12, 201—212; cf. this vol., 606).—Delignification of wood by ClO₂ is carried out in a single stage in presence of aq. pyridine, and the above whole-number ratio in the resulting skeletal substance is confirmed. The total OAc content of the wood is contained in the sparingly sol. xylan portion, which is regarded as a polymeric acetylxylose anhydride. A. A. LEVI.

Chemical composition of red beechwood. R. RUNKEL and G. LANGE (Cellulosechem., 1931, 12, 185—200).—A method for delignification involving the min. destruction of the natural fibrous structure of the

wood is described, and the whole-number ratio between sparingly sol. xylan and cellulose in the skeletal substance (this vol., 606) is confirmed. The distribution of the OMe and OAc groups, and of the substances yielding furfuraldehyde among the constituents of the wood is discussed, and the "genuine lignin" content estimated.
A. A. LEVI.

Determination of the base content of wood. K. BEAUCOURT (Biochem. Z., 1931, 235, 79—85).—The electrolytic determination of Ca, Mg, and Fe separately and in mixtures in terms of g. OH (B., 1928, 346) is trustworthy and has a max. error of 2%. The method is applied to the determination of base content of salt-rich samples of wood, the results being reproducible with an error of less than 5%.

P. W. CLUTTERBUCK.

Chemical aspect of the drying of timber.
II. **The drying of a softwood.** W. G. CAMPBELL and J. BOOTH (Biochem. J., 1931, 25, 756—762).—Air-drying reduces the pentosans and H₂O-sol. material in the wood of silver fir. Lignin is enhanced at the expense of the furfuraldehyde-yielding complexes, and cellulose at that of the H₂O-sol. material of the green wood. Kiln-drying precludes the addition to cellulose and part of the additions to lignin. Oven-drying of green wood induces hydrolysis of the wood substance which is responsible for a slight error in moisture determination.
S. S. ZILVA.

Sugar beet and molasses (nitrogen and raffinose). E. SAILLARD (Compt. rend., 1931, 192, 1748—1750).—The amounts of sugar, protein-N, NH₃-N, and NH₂-N in sugar beet and the rainfall for the periods 1904—1913, 1920—1929, 1930 are recorded; also the dry wt., polarisation after precipitation with basic Pb acetate, dextrose after inversion, and N-content of molasses for the years 1925—1931. In wet seasons the largest amount of sugar and the lowest amount of N are elaborated. In molasses the difference between the direct polarimetric reading and the amount of sugar following inversion increases as the amount of N decreases; this difference was traced in 1931 to the accumulation of raffinose in the roots in the last stages of cultivation.
C. C. N. VASS.

Potassium in sugar beet. H. COLIN and P. BILLON (Compt. rend., 1931, 192, 1746—1748).—Selective cultivation of sugar beet has reduced the mineral content. Formerly the ash contained 50% K₂O and the combined MgO and CaO reached 20%; at the present time sugar beet contains approx. 3% of ash with 20% K₂O, but the greater part of the K is present as K salts of organic acids.
C. C. N. VASS.

Potassium deficiency of fruit trees. T. WALLACE (J. Pomology, 1931, 9, 111—121).—Fruit trees on K-deficient soils are distinguished by the appearance of leaf scorch and chlorosis and by the decreased K content of leaves, shoots, main stem, and pulp (but not stones) of the fruit. There is a corresponding increase in the dry matter content of the fresh material. The response to applications of dung and K-manures is reflected in the composition of the treated trees.
A. G. POLLARD.

Plant tissue fluids. I. Effects of age and environment on the tissue fluids of French beans (*Phaseolus vulgaris*). C. N. ACHARYA and B. N. SASTRI (J. Indian Inst. Sci., 1931, 14, A, 1—9).—Specimens of fluids from various tissues were taken at various stages of growth and examined for sp. gr., n , osmotic pressure, reaction, total solids, mineral ash, total N, sugar content, and diastatic activity. The changes observed are correlated with the translocation incident on flowering and with the changes in metabolism following differences in rate of growth, photosynthesis, or respiration.
F. O. HOWITT.

Hydrogen-ion concentration of potato tubers. J. M. ROBERTSON and A. M. SMITH (Biochem. J., 1931, 25, 763—769).—In the early stages of development the underground stem and the heel end of the tuber are most acid and the average acidity of the tuber increases with maturity. In the dormant state the acidity does not vary much in different parts of the tuber, but when sprouting begins the active eyes are most acid. The acidity of the tuber is independent of environment and is not influenced by large variations in soil acidity. The differences in acidity due to variety and storage are not significant. Comparatively large changes in acidity are associated with certain diseases.
S. S. ZILVA.

Blackening of potatoes after cooking. C. K. TINKLER (Biochem. J., 1931, 25, 773—776).—Potatoes contain a substance in greatly varying amounts which on treatment with HNO₂ and an alkali gives a red colour. The amount of the red substance varies exactly with the amount of blackening which takes place on cooking. Fe may have a pronounced influence on the degree of blackening.
S. S. ZILVA.

Changes in chlorosis-infected leaves of *Abutilon*. H. VON EULER, W. HERTZSCH, S. MYRBÄCK, D. RUNEHJELM, and A. FORSSBERG (Arkiv Kemi, Min., Geol., 1931, 10, B, no. 13, 6 pp.).—The catalase content of chlorosis-infected leaves of *A. striatum* is directly proportional to the degree of green colour. The NH₂:total-N ratio is higher for the white parts for which spectrophotometric observations indicate a low content of all the chlorophyll pigments, and for which the tryptophan content is below normal.
F. O. HOWITT.

Determination of small quantities of mixed reducing sugars and its application to the determination of the products of hydrolysis of starch by taka-diastrase. E. M. WIDDOWSON (Biochem. J., 1931, 25, 863—879).—The method combines the principle of Hanes' modification of Hagedorn and Jensen's method and the iodometric method. It can be applied to the determination of small quantities of mixtures of dextrose, laevulose, and of dextrose and maltose and to the dextrose and maltose obtained by the hydrolysis of starch by taka-diastrase. In the latter case the experimental error was within 1%. There is no loss of sugar when dextrose-maltose solutions are cleared with basic Pb acetate and Na phosphate. Clear solutions from EtOH extracts of apples should be decolorised with charcoal before analysis.
S. S. ZILVA.